MODIFICATION OF NATURAL RUBBER BY GRAFT COPOLYMERISATION OF NON-IONOGENIC HYDROPHILIC MONOMERS IN LATEX

by

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ABSTRACT

Modification of Natural Rubber by Graft Copolymerisation of Non-ionogenic Hydrophilic Monomers in Latex

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This work is an investigation of the modification of natural rubber (NR) by graft copolymerisation of hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA), hydroxyethyl methacrylate (HEMA) and hydroxypropyl methacrylate (HPMA) in NR latex.

Initial studies showed that, at low monomer concentrations, the latex stability increased substantially. This was attributed to the rapid adsorption of the monomers on to the surface of particles in NR latex. However, at high monomer concentrations, the latex stability decreased substantially. This is thought to be brought about by a dehydration process and interaction between the monomers and indigenous soaps. In the presence of the monomers, the stability of the latex decreased rapidly during maturation as a consequence of the hydrolysis of the monomers, dehydration processes, and interaction between the monomers and indigenous soaps. Dilution of the latex, together with subsequent polymerisation of the added monomers, improved the stability of the latex.

The kinetics of the polymerisation of the monomers in the latex was studied. The rates of polymerisation were found to be in the following order: HEA > HPA > HPMA > HEMA. Kinetically the reactions for the four monomers were found to be first-order with respect to initial monomer concentration. However, the orders were found to be zero-order for HEA and HPA, first-order for HEMA, and second-order for HPMA when fitting the various order curves to data for individual polymerisations. No satisfactory explanation was offered to explain the apparent contradictions in the orders of reaction. However, it might be attributed to the locus of polymerisation being both at the surface of rubber particles and in the aqueous phase as a consequence of the heterogeneous nature of NR latex. Generally, the reactions were found to be half-order with respect to initiator concentration, with the exception of HEMA, for which the order was found to be 0.20. The orders of reactions were found to be first-order with respect to dry rubber content (DRC) indicating that the presence of rubber in the latex would accelerate rather than retard the polymerisations.

In a subsequent detailed investigation, crosslinking was shown not to take place during polymerisation in the latex, despite the monomers containing diester impurities. The efficiency of grafting was determined by separation of the homopolymers. However, the degree of grafting could not be determined, as it was not possible to separate the free NR from the mixture. The mechanism of grafting is believed to be dominated by transfer reactions between the growing polymer radicals and NR. However, the grafting reactions might be also via addition reactions between growing radicals and the double bonds of rubber molecules leading to very high grafting efficiency. It is believed that the grafting reactions are temperature-dependent. It was found that the grafting efficiency was much higher when using a dissociative initiator which does not attack NR directly (4-4'-azobis(4-cyanovaleric acid) at ca. 63^{o}C than when using a redox initiator (potassium persulphate-sodium metabisulphite) at 30^{o}C.

The crude graft copolymer latices were found to produce cream. Generally, the vulcanised films from the crude graft copolymer latices were found have reduced water and oil resistance. It was also observed that the latices examined proved unsuitable for dipping application because the deposits ran down the formers.

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Contents

ERRATA

page	line	
2	24	1,4 2-methyl should be 1,4-poly 2-methyl
4	5	dicholorocyclo should be dichlorocyclo
48	16	disproportion should be disproportionation
57	26	
57	30	
57	17	
57	21	
58	17	homologues should be homologous
61	14	maker should be rubber
90	27	Travelling microscope should be Cathetometer
91	17	-,,- -,,- -,,-
91	18	hight should be height
139	16	VFA should be volatile fatty acid number (VFA)
145	4	of rubber particles should be of the electrical double layer surrounding
147	37	presence PHPA should be presence of PHPA
172	31	prolong should be prolonged
214	26	add should be addition
262	4	initiator should be initiator at 30°C
262	26	cc stands for completely coagulated
262	33	

Chapter 1

Introduction

1.1 Natural rubber latex

A latex, as defined by Blackley (1), is a stable dispersion of a polymeric substance in an essentially aqueous medium. Based on this definition, he stated that a latex is essentially a two-phase system, consisting of a disperse phase and a dispersion medium.

Natural rubber (NR) latex is such a dispersion, consisting of a rubber phase dispersed in an aqueous medium. However, NR latex contains a wide range of constituents, as well as rubber and water. These constituents are distributed throughout the rubber phase, the aqueous phase and the inter-phase boundaries. Freshly-tapped NR latex is a whitish fluid having a density between 0.975 and 0.980 g. ml^{-1}, a pH in the range 6.5 to 7.0, and a surface free energy ranging 40 to 45 ergs. cm^{-2}. The composition of fresh NR latex can vary considerably. The following figures are typical:

	%
total solids content	32
dry rubber content	30
proteinaceous substances	1-1.5
resinous substances	1-2.5
ash	up to 1
sugars	1
water	remainder

These constituents are distributed throughout the following principal phases:

(i) **The aqueous phase**

The aqueous phase accounts for approximately 55% w/w of the latex. It has a density of about 1.02 $g.ml^{-1}$ and contains many chemical species such as carbohydrates, proteins and amino acids, and also the serum constituents including free nitrogenous bases such as choline and methyl amine, organic acids (other than amino acids), inorganic anions

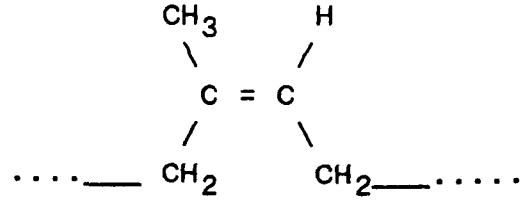
(principally phosphate and carbonate), and metallic ions (including potassium, magnesium, iron, sodium and copper).

(ii) The rubber phase

The rubber phase accounts for approximately 35% w/w of the latex. It is present as particles which have a highly asymmetrical distribution of particle sizes ranging from 200 to 20,000 Å. The particles are sometimes pear-shaped rather than spherical. A typical composition for the rubber phase of NR latex is :

	%
rubber hydrocarbon	86
water	10
proteinaceous substances	1
lipid substances	3

The presence of the proteinaceous substances and lipid substances in the rubber phase plays an important role in keeping the latex stable for a long period of time, as they can act as protective layers (Section 3.1). The rubber hydrocarbon in NR latex is predominantly cis-1,4-polyisoprene (1,4 2-methyl but-2-ene),



The polyisoprene has a carbon-carbon double bond in each repeat unit. The double bond plays an important role in vulcanisation and in the modification of NR by graft copolymerisation of a vinyl monomer in either NR latex or dry NR.

(iii) The lutoid phase

The fresh latex also contains ill-defined aggregates, distinct in character from rubber particles. These can be observed as a yellow fraction when the latex is centrifuged. These

aggregates are called lutoids. The lutoid phase accounts for approximately 10% w/w of the latex,and contains small quantities of soluble proteins (ca. 3%), insoluble proteins (ca. 2%) and phospholipids (ca. 5%).

1.2 Modification of NR in NR latex

Barnard et al. (2) have outlined the principal ways in which NR can be chemically modified. They divided reactions for the chemical modification of NR into three broad types :

(i) Rearrangement reactions involving the isoprene repeat unit. These include cyclisation, cis-trans isomerisation and depolymerisation. They do not involve the addition of new chemical material.

(ii) Addition or substitution reactions to the isoprene unit. These include hydrogenation, chlorination, epoxidation and vulcanisation. These reactions result in the introduction of new chemical atoms or groups into the rubber molecule.

(iii) Graft copolymerisation reactions in which other polymer materials become chemically attached to the backbone of a rubber molecule.

This discussion will be concerned with the grafting reaction in NR latex only as this grafting is the main reaction in the present investigation. According to Campbell et al. (3), the modification of NR by graft copolymerisation using vinyl monomers has been extensively studied. They reported investigations leading to the commercial exploitation of new types of NR polymer, the so-called MG rubber. MG rubber is polymethyl methacrylate grafted onto NR. This rubber was first developed by the British Rubber Producers Research Association in 1958. To date, MG rubber is the only commercially-available modified rubber prepared by a grafting reaction in NR latex.

Investigations (3) have been carried out both to produce new NR grafts and also to improve the existing free-radical graft copolymerisation reaction. In addition, attempts have been made to introduce pre-formed graft segments having terminal groups which can react with NR. In this way,

Campbell et. al. (3) expected that any such new graft copolymer would have side chains uniformly attached to NR, with low homopolymer formation. However, unsolved problems still remain. For example, the polymerisation of dicholorocyclo-propane in NR latex resulted in unsatisfactory polymerisation, and no attempts were made to develop a commercially-useful process. In the case of pre-formed polymer graft segments, attention is still being paid to the synthesis of prepolymers which carry azodicarboxylate and other similar groups. Although the grafting of monomers onto NR appears to be very simple, there are several inherent problems, particularly if grafting is carried out on the polymer in latex form. The important factors which affect the efficiency of a graft copolymerisation reaction are as follows :

(1) Colloid stability of NR latex. The better the stability of latex to coagulation, the greater are the chances of carrying out successful grafting reactions in the latex.

(ii) Nature of the monomer. The monomer plays an important role as this can affect the latex stability, the rate of polymerisation, the efficiency of grafting, as well as the physical and chemical properties of the end-product.

(iii) Nature of the initiator. The reactivity and solubility of the free-radical initiator used can affect the graft-copolymerisation reaction.

1.3 Origin of the present investigation

The modification of NR by the polymerisation of hydrophobic monomers in NR latex has been extensively studied and reported in the patent and scientific literature (7-9, 11, 43, 44, 46-51, 57, 58, 60, 67). Similarly, the polymerisation of hydrophilic monomers in NR latex has also been extensively reported in the literature (4, 5, 43, 45-47, 58, 61-64).

For the purpose of this investigation, hydrophilic monomers may be defined as monomers which have a solubility in water at normal temperature of greater than 2%. In this research programme, the polymerisation of selected non-ionogenic hydrophilic monomers has been investigated. The four non-ionogenic hydrophilic monomers were :

(i) 2-hydroxyethyl acrylate (HEA)
(ii) 2-hydroxyethyl methacrylate (HEMA)
(iii) hydroxypropyl acrylate (HPA)
(iv) hydroxypropyl methacrylate (HPMA)

These monomers are all readily available commercially. Little work has been carried out using these materials in NR latex. They have been chosen because it was expected that, as a group, they would provide interesting information concerning :

(i) the effect of varying monomer reactivity (by comparing HEA with HEMA and HPA and HPMA),

(ii) the effect of varying monomer hydrophilicity (by comparing HEA with HPA and HEMA with HPMA).

It was expected that the grafting of such monomers onto NR would considerably alter the nature of the products and thus provide a range of possible applications for the graft copolymers. The products may have enhanced oil resistance and hence prove suitable in many industrial applications, e.g., seals, hosing and specialist surface coatings.

Previous work in this field is restricted to two publications. These two reports are confined to HEMA only of the monomers selected. Mazam et al. (4) claimed to have successfully polymerised the monomer in NR latex using gamma radiation. However, Erbyl (5) has recently reported the unsuccessful graft copolymerisation of HEMA using both the ammonium persulphate-sodium metabisulphite and the hydroperoxide-polyamine initiator systems. They claimed that the lack of grafting is due to the high solubilities of the initiators in the water phase of NR latex. Preliminary experimental work carried out by the present author as part of an M.Sc project (6) has shown that all four monomers can be polymerised in NR latex at ambient temperature using the potassium persulphate-sodium metabisulphite initiator system. The present programme has continued this investigation in more detail.

1.4 Objectives of the present investigation

In this present research programme, it was intended to investigate in more detail of the preparation of graft copolymers of the four selected monomers grafted onto NR rubber backbone. The following factors were varied:

(i) the monomer type and concentration ;
(ii) the total solids content of the NR latex ;
(iii) the concentration of the initiator employed.

The investigation required a study of the above variables upon the following :

(i) the mechanical stability of the latex ;
(ii) the reaction kinetics of the polymerisation ;
(iii) the efficiency of grafting ;
(iv) selected chemical and physical properties of the products obtained.

It was expected that, being hydrophilic in nature, the monomers would destabilise the latex due to a dehydration effect. It was assumed that this effect is dependent upon the concentration, the hydrophilicity of the monomers and the maturation time. The dehydration effect could coagulate the latex and thus affect the grafting reactions. However, the polymers derived from these monomers might stabilise the latex by a steric mechanism.

The potassium persulphate-sodium metabisulphite initiator system was also expected to destabilise the latex due to compression of the electric double layer surrounding the particles, brought about by the presence of the cations. The acids produced from the initiator could destabilise the latex as well. The initial intention of the project was to carry out a broad survey in order to obtain general information on the effect of added monomer, polymer, initiator, and of mixtures of both monomer and initiator, upon the mechanical stability time (MST) of the latex. It was also intended to investigate the effect of maturation after the addition of monomers, and of the mixture of the initiator and monomer upon the MST of the latex. This information would help to predict the length of time which would elapse before the latex coagulated, and could be compared with the time required for monomer conversion during the graft-copolymerisation reaction.

It was intended to investigate the partition of the monomers between the hydrocarbon n-dodecane as representative of NR, and water, as representative of aqueous phase. The intention was to obtain indications as to the probable locus of initial polymerisation reaction, i.e., whether it is on the surface or in the interior of the rubber particles. It was expected that this information

could assist in the interpretation of relationships, if any, between reaction rates and the surface area of the rubber particles and thus the dry rubber content. It was intended to determine a suitable method for following the conversion of the monomers accurately. In this research programme, only dilatometric and gravimetric methods have been investigated. It was expected that differences in reactivity and in hydrophilicity between the monomers might lead to different orders of reaction and reaction rates. The intention was to obtain general information on the polymerisation characteristics of each monomer, and to obtain kinetic information which might provide evidence concerning the mechanism of the polymerisation reactions. It was also desirable to investigate the reaction using the water-soluble organic initiator 4-4'-azobis(4-cyanovaleric acid) which does not attack NR. It was expected that the use of this initiator system would provide further evidence concerning the grafting reaction via transfer reactions involving NR in NR latex.

To obtain estimates of the efficiency of grafting, accurate methods of determining 1) unreacted monomer, 2) homopolymer, and 3) unreacted NR have been investigated. It was expected the removal of the unreacted monomer from the reaction mixture by a vacuum-drying process at normal drying temperatures (60-100^{o}C) would take a long time because of the high boiling point of the monomers. Furthermore, thermal polymerisation would be likely to occur. It was intended to establish an accurate method which would avoid further thermal polymerisation during the drying process.

After carrying out the graft copolymerisations, the hydrophilic homopolymer and the unreacted NR were separated from the graft copolymers by selective solvent extraction. This required the preparation of linear polymers from the hydrophilic monomers to be used to select suitable solvents for the extraction procedures. These linear polymers were prepared by solution homopolymerisation, in water phase, in the presence of a second phase of petroleum ether containing NR. The efficiency of grafting could be determined by a series of such extractions of the products obtained from the graft-copolymerisation reaction.

The effect of the presence of homopolymers prepared from the hydrophilic monomers upon the stability of NR latex was to be investigated by preparing the polymers independently

and observing their effect, if any, when added to NR latex. A further objective of this investigation was to obtain information concerning selected physical properties of the graft copolymers obtained, in particular, their oil-resistance and water uptake. Solid polymer samples were obtained by dipping, using various coagulants, and by casting films. These films were investigated to determine their tensile properties. Rheometric tests were also carried out in order to determine the vulcanisation behaviour of the rubbers when compounded with various crosslinking systems.

It is desirable to define the terms such as the efficiency of grafting (% EG), the percentage of graft copolymer (% GC), and the degree of grafting (% DG) because they are frequently mentioned in the present investigation. These terms are defined as follows (6, 63):

$$\% \text{ EG} = \frac{\text{mass of polymerised monomer in form of graft copolymer}}{\text{total mass of monomer polymerised}} \times 100$$

$$\% \text{ GC} = \frac{\text{mass of graft copolymer}}{\text{total mass of polymer}} \times 100$$

$$\% \text{ DG} = \frac{\text{mass of polymerised monomer in form of graft copolymer}}{\text{mass of graft copolymer}} \times 100$$

where EG denotes the efficiency of grafting, GC denotes the graft copolymer, and DG denotes the degree of grafting.

Chapter 2

Review of grafting of vinyl monomers to NR in NR latex

2.1 Early work of grafting of vinyl monomers to NR in NR latex

2.1.1 Introduction

According to Bloomfield *et al.* (10), the earliest recorded attempts to modify rubber by polymerisation of monomers dispersed in latex were by Bacon *et al.* (11). These latter workers were sponsored by the Rubber Growers' Association, and reported their findings to the 1938 Rubber Technology Conference.

2.1.2 Early investigations of grafting of vinyl monomers to NR in NR latex

Ceresa (12) has reported considerable patent literature covering the polymerisation of vinyl monomers in NR latex. However, the earliest patent he reports was published in 1945, which is after the work reported by Bloomfield *et. al.* (10). Battaerd and Tregear (13) have also presented a list of patents for the preparation of graft copolymers, including those prepared by the polymerisation of vinyl monomers in NR latex. The present author, however, has found no information on the polymerisation of vinyl monomers in NR latex before in 1928 (7-44).

In 1928, I.G. Farbenindustrie Aktiengesellschaft applied for a patent covering the polymerisation of a diolefin in NR latex (44). The invention is very interesting indeed. Although no ammonia was present in the latex, and no stabiliser had been added to enhance the colloid stability of the latex, very large amounts of monomer were reported to have been polymerised in NR latex. For example, 1 to about 3,636 pphr (parts by weight per hundred parts of rubber) of butadiene was polymerised in NR latex at 60 - 70^{o}C in the presence of hydrogen peroxide (0.3 - 5.5 pphr). The polymerisation proceeded rapidly, and in a short period of time a product resembling NR separated out which could be converted to a useful elastomer by vulcanisation. However, further study of this invention reveals that the results are not as surprising as first appears. The butadiene and hydrogen peroxide were added to the latex such that the final DRC of the latices decreased as the

butadiene and initiator concentration increased (Table 2.1). It is expected that the stability of the latex could be maintained without flocculation occurring in this way.

Table 2.1 Final dry rubber content (DRC) of reaction mixture as related to increasing amount of added butadiene and hydrogen peroxide to NR latex (44)

butadiene (pphr)	hydrogen peroxide (pphr)	butadiene / latex (by weight)	hydrogen peroxide / latex (by weight)	DRC (%)
1.00	0.30	0.03	0.003	21.1
1090.91	2.18	3.00	0.200	6.6
3636.36	5.45	10.00	0.500	2.4

2.1.3 Adverse effect of NR upon polymerisation of vinyl monomers in NR latex

Bacon et al. (11) reported the polymerisation of methyl methacrylate in NR latex. The initiator used was benzoyl peroxide. Polymerisation was carried out at 75°C. They reported that the extent of polymerisation of methyl methacrylate was approximately 20% instead of the expected 80% to 90%. They reported that the reason for the low conversion was inhibition of polymerisation by the ammonia used to preserve the latex. In this case, the ammonia was said to react with benzoyl peroxide, reducing its efficiency as an initiator.

Bacon et al. (43) investigated the polymerisation of a vinyl monomer both in solution and in emulsion, in the presence of NR latex. They concluded that such polymerisations were impracticable because of the presence of the rubber, which greatly retarded the polymerisation reaction. To demonstrate this, they investigated the extent of polymerisation of two monomers, namely, ethyl methacrylate and acrylonitrile. The vinyl monomers were prepared as emulsions (16% w/w in a 1% soap solution). It is not clear whether the monomers were purified prior to use. The benzoyl peroxide was dissolved in the emulsified monomers prior to addition to NR latex. The conditions and conversion of the polymerisation are given in Table 2.2.

As can be seen from this Table, the polymerisations were not very successful in the presence of NR latex. The conversions were 29% compared to 90% with no latex for ethyl methacrylate, and only 6% instead of 70% with no latex for acrylonitrile. Bacon et al. (43) suggested that the low conversions were a consequent not only of the retarding effect of the rubber but also of the inhibitive effects of ammonia and of non-hydrocarbon constituents of the latex.

Table 2.2 Conditions and extent of polymerisation of ethyl methacrylate and acrylonitrile in NR latex (11, 43)

	type of monomer			
	ethyl methacrylate dry parts		acrylonitrile dry parts	
latex	100.00	-	100.00	-
monomer	700.00	700.00	700.00	700.00
soap[x)]	5.80	5.80	5.80	5.80
benzoyl peroxide[xx)]	7.10	7.10	7.10	7.10
temperature, ^{o}C	62	62	62	62
time, hours	22	22	22	22
final DRC, %	1.95	-	1.95	-
monomer, % w/w [xxx)]	14.06	16.14	14.06	16.14
conversion, %	29.0	90.0	6.0	70.0

[x)] e.g., triethanolamine salt of sulphonated lauryl alcohol
[xx)] presumably 100% concentration
[xxx)] aqueous phase

In the opinion of the present author, the unsuccessful polymerisation of the monomers in NR latex might be because of the cage effect. This might be brought about by too high viscosity of the monomer-swollen rubber phase in the early stages of the polymerisation. Such concentrations of rubber in the monomers (12.5%) would reduce the effectiveness of the radicals formed to initiate polymerisation. The inefficiency of the initiator was enhanced by :

(i) **Emulsification of monomers prior to addition to NR latex**

It is assumed that the mixing between the monomers and rubber particles is a diffusion-controlled process. The preliminary monomer emulsification would provide a large surface area of monomer particles. Thus, they could diffuse immediately into the rubber phase. It is expected that the rubber would also swell immediately in the monomer.

(ii) **Addition of the initiator to the emulsified monomers prior to NR latex**

The initiator was pre-dissolved in the monomer emulsions. It is expected that the initiator along with the monomers would diffuse more quickly into the rubber phase than if the initiator was added directly to NR latex. When the emulsified monomers together with the initiator were added to NR latex, the viscosity of the monomers in the latex was low. However, the rubber particles would swell immediately in the monomers and form a monomer-swollen rubber phase. Initially, the swelling was rapid and gradually slowed with time. Consequently, the viscosity of the monomer-swollen rubber phase was much higher than that of the monomers alone during the first stages of the polymerisation. In the initial stages of the emulsion at 60^{o}C, the initiator trapped in the monomer-swollen rubber phase would decompose in pairs and commence initiation of the monomers. However, because of the high viscosity of the monomer-swollen rubber phase, most of the initiator radicals trapped in the monomer-swollen rubber phase recombine rather than initiating the monomers further. As a result, the extent of the polymerisation of the emulsified monomers in NR latex using benzoyl peroxide was low. In the absence of NR latex, however, the radicals derived from oil-soluble initiators were generated in pairs in a monomer phase of a low viscosity. According to Al-Shahib and Dunn (131), a radical from such initiators could escape to the aqueous phase and leave an isolated radical in the oil phase; this is the

essential condition for an emulsion polymerisation. A high conversion of the monomers might be obtained in this way.

2.2 Development of grafting of vinyl monomers to NR in NR latex

2.2.1 Previous attempts to form graft copolymers in NR latex

Because of the apparent retardation effect of NR, the polymerisation of vinyl monomers in NR latex was found to be impracticable, as has been mentioned in Section 2.1.2. However, many inventors have seriously reconsidered this matter. Jacobson (46) applied for a patent to provide a process for the polymerisation of vinyl monomers in NR latex which would overcome the low conversion of monomer to polymer. In his patent, the monomers employed were methyl methacrylate, buthyl methacrylate, 2-nitro-2-methyl propyl methacrylate, dicholoro ethylene, styrene, vinyl acetate and acrylonitrile. For example, monomers were polymerised at concentrations between 20 and 1,900 pphr, in the presence of ammonium persulphate as initiator (1.0 to 20.4 pphr) and of a stabiliser such as sodium cetyl sulphate or the sodium salt of a sulfonated paraffin oil (2.8 to 126.7 pphr). The DRC of the final reaction mixture was between 1.6 and 26.0%. The polymerisation was carried out between 6 and 68^{o}C for 6 to 24 hours. The conversion was quite satisfactory, being of the order of 85 to 98%.

Another attempt to overcome the difficulties reported previously has been proposed by Societe Auxiliaire de L' Institute Francaise du Caoutchouc (47). Here, monomers such as styrene, buthyl methacrylate, and acrylonitrile were polymerised in NR latex. For example, the monomers were polymerised at a concentration of 50 pphr in the presence of a sulphonated fatty alcohol (7.50 pphr), and gelatine (5 pphr) as stabiliser, and hydrogen peroxide (1.5 pphr) as initiator. The polymerisation was carried out at 50-60^{o}C for 24 hours. Though no conversion was reported, a profound modification of the properties of the product using acrylonitrile as monomer was obtained. For instance, the coagulated product was almost completely insoluble in the usual rubber solvents, and the vulcanised product possessed clearly improved resistance solvent.

Jones et al.(48) also made an attempt to provide a process to overcome the difficulties reported previously. In this patent, they firstly stabilised NR latex by adding sodium oleate (9.6 to 135 pphr) followed by sodium hydroxide (0.3 to 3.0 pphr). The rubber was then "oxidised" by ammonium persulphate (1.6 to 15 pphr). To the mixture was added styrene (56 to 960 pphr) and butadiene (24 to 270 pphr). In the case of a styrene/isoprene mixture, the amounts used were 280 pphr for styrene and 120 pphr for isoprene. The DRC of the final reaction mixture was in the range 2 to 20%. The polymerisation was carried out at 40-60^{o}C for 8 hours. The extent of polymerisation was very satisfactory, approaching 100% in all cases. For comparison, a styrene-butadiene copolymer in the proportions of 85/15 in the absence of NR latex was prepared. The yield was only 80% instead of 100% obtained under comparable conditions in the presence of NR latex. In the case of benzoyl peroxide as initiator, Jones et al. (48) successfully polymerised styrene and butadiene in NR latex using the following formulation and conditions (Table 2.3).

Table 2.3 Formulation, conditions and extent of polymerisation of styrene and butadiene in NR latex using benzoyl peroxide as initiator

	dry parts
NR latex (as 50 % DRC)	100.00
sodium oleate	14.44
sodium hydroxide[x)]	0.48
benzoyl peroxide	2.40
water	390.64
styrene	102.04
butadiene	52.05
temperature, ^{o}C	50
time, hours	50
DRC, %	13.91
monomer, % w/w aqueous phase	17.22
conversion, %	ca. 100

x) as 5% aqueous solution

From Table 2.3, it can be concluded that 1) ammonia and non-rubber constituents present in NR latex did not react with benzoyl peroxide, and the rubber hydrocarbon did not act as a retarder. These results are contrary to those reported by Bacon et al. (43) (Section 2.1.3).

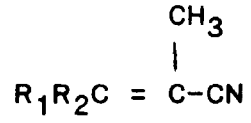
Furthermore, the concentration of the rubber in the monomer was 87.5% w/w in the method of Jones et al.. This was much greater than that for the method of Bacon et al. (12.5%). Thus, one would expect that the cage effect would more likely to occur in the method of Jones et al. than that for the method of Bacon et al., which is not the case. It is not possible to compare in detail the results of the two methods, because too many variables are involved such as the monomer employed, initiator concentrations, temperatures and times of polymerisation.

However, the present author offers some suggestions which might explain the successful polymerisation of Jones et al. The benzoyl peroxide, and the unemulsified monomers were separately added to NR latex. It is expected that most of the monomer and initiator remained as droplets with a small surface area in the aqueous phase. When the polymerisation started at 50^{o}C, the viscosity of the monomers was increased slowly. The rate of increasing the viscosity was due to the formation of the polymers by polymerisation. In these circumstances, the cage effect was unlikely to occur, even though the concentration of rubber in the monomer was theoretically high. As a result, high conversion of the monomers was obtained (Section 2.1.3). Popham et al. (57) polymerised methyl methacrylate in NR latex using benzoyl peroxide at 80-90^{o}C for 4 hours. However, the extent of polymerisation was only 60-70%. They reported that the benzoyl peroxide was dissolved in the monomer, but the monomer was not emulsified prior to addition to NR latex.

Jones et al. (49) patented a method for polymerising of styrene in NR latex with a diene monomer present in an amount equal to or greater than that of styrene. They also stated that, by having NR latex present, the polymerisation reaction proceeded more rapidly and smoothly than it did when NR latex was absent. In this invention, a complicated initiator system was employed consisting of cumene hydroperoxide, ferrous sulphate heptahydrate, sodium thiosulphate pentahydrate and sodium pyrophosphate decahydrate. Conversions of up to 96% of the vinyl monomer mixture to polymer were obtained. The coagulated products

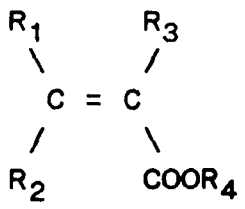
obtained were capable of being masticated on a mill, whereupon they became tacky, as in the case with NR. However, they had greater resistance to thermal degradation than did comparable products made solely of NR. The vulcanised products had good abrasion resistance.

In 1952, Jones et al. (50) patented a further process for polymerising a mixture of a diene monomer and chloroacrylonitrile or a compound of the type :



where R_1, R_2 and R_3 represent hydrogen atoms or alkyl groups. One of the examples described in this patent is as follows: To 50% DRC NR latex was added sodium oleate (21.6 pphr) and potassium persulphate (2.4 pphr). The monomer mixture to be polymerised comprised butadiene (60 pphr) and acrylonitrile (60 pphr). The DRC of the reaction mixture was 13.4%. The polymerisation was carried out at 50°C for 17 hours with constant stirring. Jones et al. (50) also stated that these reactions proceeded more rapidly than if the monomers were polymerised under comparable conditions in the absence of NR latex. The polymerisation was reported to proceed to substantially complete reaction conversion. The polymer produced by this reaction had the advantage over conventional butadiene-acrylonitrile rubber that it could be more easily milled to a smooth sheet on a hot-roll mill. By comparison, the unvulcanised butadiene-acrylonitrile copolymer is difficult to process by the methods customarily employed for NR, such as milling, moulding, etc.

Jones et al. (51) also patented a process for the manufacture of polymeric products prepared by polymerisation of the mixture of 1) a hydrocarbon or chlorohydrocarbon diene, and 2) an ester of the type:



where R_1, R_2, and R_3 represent hydrogen or alkyl groups, and R_4 represents an alkyl group. As in their previous

work, they found that the reaction proceeded more rapidly than when the monomers were polymerised under comparable conditions in the absence of NR latex. The colloid stability of the latex was ensured by maintaining a low DRC. The final reaction mixture was 1.1% DRC. Good conversion of monomer to polymer (ca. 80%) was reported.

2.2.2 Initiation of graft copolymerisation by rubber radicals

NR is a polymer which contains easily-replaceable hydrogen atoms, i.e., labile α-methylenic hydrogen atoms and a labile ethylenic hydrogen atom in each repeat unit. It should therefore be susceptible to attack by an oxidising agent (52, 53, 54), thereby producing unstable polymeric species known as rubber radicals. According to Burlant and Hoffman (55), radicals which are introduced by reaction with initiator radicals along the chain are loci for subsequent reactions with monomers which lead to the formation of graft copolymers. This mechanism of grafting is called "grafting from" (56) to distinguish it from "grafting on", i.e., grafting by way of transfer reactions involving the rubber. Popham et al. (57) stated that it had been previously supposed that the mechanism of grafting of monomers on to rubber took place via such transfer reactions. This "grafting on" mechanism would involve a growing polymer chain being terminated by abstraction of a hydrogen atom from a rubber molecule to produce a rubber radical. The rubber radical could then serve as the point of initiation for subsequent polymerisation and the formation of a grafted polymer chain.

However, further investigation showed that the "grafting on" mechanism in NR latex was extremely unlikely. Azoisobutyronitrile (AZBN) is an initiator which does not attack rubber directly. Popham et al. (57) reported that, AZBN as initiator, the product obtained could be separated into free rubber and free homopolymer when titrated with methanol containing a trace of calcium chloride. Furthermore, Popham et al. (57) stated that the "grafting from" mechanism appears to be operative when oxidising agents such as an organic peroxide or hydroperoxide are used. Such initiators are capable either of producing a rubber radical by abstraction of hydrogen or of activating a rubber molecule through the double bonds. The rubber radical was therefore considered to be responsible for the

polymerisation of monomers in NR latex. Analysis of the products of graft copolymerisations carried out using these peroxide initiators showed that no free rubber was found, but graft copolymers were obtained. Monomers such as methyl methacrylate styrene, ethyl acrylate, and a mixture of methyl methacrylate and divinyl benzene, have been successfully graft-copolymerised in NR latex in this way. Further examples of graft copolymers produced in this way have been patented by Polyplastic (58). According to this disclosure, both hydrophobic and hydrophilic monomers were satisfactorily grafted onto NR in NR latex form.

Bloomfield (129) reported the polymerisation of methyl methacrylate and styrene, the mechanism being presumed to be using the " grafting from". In this report, each of the monomers was polymerised in NR latex in the presence of t-butyl hydroperoxide (0.2 pphr) and tetra-ethylene pentamine (0.1 pphr) at 12^{o}C for methyl methacrylate and 55^{o}C for styrene. The extent of polymerisation was 95% for styrene and 90% for methyl methacrylate.

Nikolov and McLeod (59) claimed that polymeric species in a latex prepared using an oxidising agent are capable of initiating a graft copolymerisation. An interesting aspect of their invention was concerned with finding a method of reducing the amount of homopolymer formed during the polymerisation. They reported that the oxidation of a polymer in latex results not only in the formation of polymeric species capable of initiating graft copolymerisation but also in the simultaneous production of water-soluble peroxidic compounds capable of initiating homopolymerisation. Deactivation of these water-soluble peroxidic compounds before polymerisation is allowed to occur has been found to result in reduction in the amount of homopolymer formed. A good method of destroying these peroxidic compounds is to introduce a water-soluble reducing agent to the aqueous dispersion prior to the polymerisation reaction. Nikolov and McLeod found that, of several reducing agents investigated, a mixture of ferrous sulphate heptahydrate, sodium formaldehyde sulfoxylate, ethylene diamine tetraacetic acid and tri sodium phosphate was the most effective in destroying species which could initiate homopolymerisation. In order to demonstrate the effectiveness of the reducing agents as inhibitors for the homopolymerisation reaction, Nikolov and McLeod investigated the polymerisation of methyl methacrylate in polybutadiene latex. In the absence of a reducing agent,

the amount of homopolymer obtained was almost double that obtained when a reducing agent was present.

Sekhar (60) used the term "hydroperoxidised latex" for a latex which had been aerated by atmospheric oxygen by rotating it on rollers for up to 30 days. To hydroperoxidised latex (20% DRC) was added methyl methacrylate (100 pphr), ferrous sulphate (0.01 pphr) and tetraethylene pentamine (0.10 pphr) at room temperature. The monomer conversion increased with increasing aeration of the latex, being 15% for zero days aeration, 16% for 4 days aeration, 24% for 10 days aeration, and 40% for 30 days aeration. Sekhar also reported that the longer the period for which the latex was aerated, the higher was the efficiency of grafting. For instance, the percentage of graft copolymer was 74.1% for 14 hours of aeration and 80% for 172 hours of aeration. With regard to the efficiency of grafting, Bloomfield et al. (10) stated that polymerisation of methyl methacrylate using persulphate initiator gave low efficiency of grafting, and a correspondingly higher amount of homopolymer was formed. However, no data for homopolymer content were reported.

Bevilacqua and Allendale (9) claimed that the polymerisation of styrene in NR latex using ammonium persulphate at 50^{o}C overnight in the absence of additional surfactant resulted in a high efficiency of grafting (less than 5% homopolymer content). However, in the presence of additional surfactant, the monomer polymerised in the micelles, leading to a larger proportion of homopolymer content in the NR latex (Table 2.4).

Table 2.4 Amount of free polystyrene at different level of surfactant in NR latex

	dry part			
NR latex	100.00	100.00	100.00	100.00
potassium oleate	0.00	0.99	1.97	4.94
ammonium persulphate	0.98	0.98	0.98	0.98
styrene	34.57	34.57	34.57	34.57
free polystyrene, %	3.2	23.1	47.2	80.0

2.2.3 Polymerisation of hydrophilic monomers in NR latex

The polymerisation of a hydrophobic monomer in NR latex was first reported in 1928 (44). However, the polymerisation of hydrophilic monomers in NR latex was not reported until Redfarn and Schidrowitz applied for a patent in 1937 (45). Here, the inventors used maleic anhydride which is a water-soluble monomer. The process involved simultaneously treating the rubber with maleic anhydride and a phenol. The product was especially suitable for use on moulding compositions giving products with improved electrical characteristics. The authors did not report any attempts to separate the components of the product.

In 1939, Bacon et al. (43) published the paper which included reference to the polymerisation of somewhat hydrophilic monomers such as acrylonitrile in NR latex. Burlant and Hoffman (55) stated that, although no difficulties arise when attempts are made to polymerise hydrophobic monomers in NR latex, water-soluble monomers are more difficult to polymerise under similar conditions. Notwithstanding this, many workers have attempted to polymerise hydrophilic monomers in NR latex. For example, it has been reported that mixtures of somewhat hydrophilic monomers and hydrophobic monomers, such as acrylonitrile/ styrene in the ratio of 30/50 pphr (47), and acrylonitrile /butadiene in the ratio of 60/60 pphr (50), have been successfully graft-copolymerised on to NR in NR latex.

An interesting procedure for graft copolymerising hydrophilic monomers in NR latex has been reported (61). Two hydrophilic monomers, i.e., methacrylic acid and acrylonitrile, were partially copolymerised in bulk using benzoyl peroxide as initiator. The product was a milky dispersion and was called a "vinyl resin dispersion". This dispersion was added to NR latex and graft copolymerised at 100^{o}C for two hours to complete the reaction. The polymer obtained was found to be highly resistant to swelling in organic solvents, and to have comparatively high modulus as well as good tensile strength, hardness and abrasion resistance.

Haward et al. (62) have developed polymeric products which are said to be very satisfactory for use in adhesive compositions. The products can be prepared by polymerising vinyl pyridine in conjunction with another monomer in NR latex. The monomers used consisted of various pairs from

methyl methacrylate, styrene, butyl acrylate and acrylonitrile. The product obtained was reported to be remarkable for its adhesive power, and was used to produce improved rubber-to-metal bond. Sekhar (60) also investigated the polymerisation of hydrophilic monomers, i.e., methacrylic acid and acrylonitrile, in hydroperoxidised NR latex. He considered that reactive sites, which were probably hydroperoxidic in nature, were formed along the rubber backbone during aeration of the latex over a period of time. In this case, no hydroperoxide initiator was required for the initiation of polymerisation. Sekhar merely added the hydrophilic monomers to the latex, followed by small amount of reducing agents, i.e., iron (II) ions and polyamine. The polymerisation was carried out at ambient temperature for 18 hours. The percentage conversions for monomers polymerised in aerated latex were 89% for methacrylic acid and 55% for acrylonitrile. Although Sekhar was able to establish a high grafting efficiency for methyl methacrylate, demonstrated by a low free polymer content (less than 10%), he did not report the grafting efficiency for the more hydrophilic monomers.

Burfield and Ng (63) polymerised methacrylamide, a water-soluble hydrophilic monomer, in NR latex. They expected that hydrophilic monomers would show a distinct advantage in self-stabilisating the latex, and that the grafting efficiency could be easily determined. Therefore, they did not add any stabiliser to the latex before polymerisation. Potassium persulphate (1.3 pphr) was used to initiate the polymerisation of methacrylamide (13 pphr). The DRC of the final latex was 19%. The polymerisation was carried out under nitrogen at 60^{o}C and stirred for 24 hours. They found that the rate of polymerisation was first-order with respect to monomer concentration up to at least 70% conversion. They also found that the higher was the monomer concentration, the higher was the efficiency of grafting. Compared to the ungrafted rubber, the methacrylamide-grafted rubber had substantially increased the modulus and hardness, at the expense of tensile strength and elongation at break. The methacrylamide-grafted rubber was superior in resistance to swelling in solvents compared to other modified rubbers such as methyl methacrylate-grafted rubber, methacrylic acid-grafted rubber, acrylonitrile-grafted rubber, and acrylamide-grafted rubber.

Burfield and Ng (64) further investigated the mechanism of grafting of a hydrophilic monomer on to NR in NR latex. They found that the intrinsic viscosity of the free homopolymer isolated from the grafted system was very close to that of polymer obtained from a control polymerisation. Based on this results, they believed that the grafting mechanism via transfer reactions with the rubber is negligible. As mentioned in Section 2.2.2, Popham et al. (57) also claimed that the grafting mechanism via transfer reactions using hydrophobic monomers in NR latex is negligible.

Mazam et al. (4) investigated the polymerisation of other hydrophilic monomers in NR latex using gamma radiation as initiator. The hydrophilic monomers polymerised were glicidyl methacrylate (GMA), hydroxyethyl methacrylate (HEMA), and diethylaminomethyl methacrylate (DE). Up to 15 pphr of the monomer was added to the latex, which had a DRC of 35%. The polymerisation was carried out by exposing the mixture to a ^{60}Co source of nominal field intensity 0.5 MR per hour or more. The conversion obtained was 75 to 95% for lower than 3 MR irradiation dosage, and 100% for higher than 3 MR irradiation dosage. The film-forming properties of both the DE-NR latex and the GMA-NR latex were said to be good. However, Mazam et. al. (4) reported that the HEMA-NR dry films produced distinct patterns. Mazam et al. (4) believed that this was because the monomer HEMA was water-soluble, and for this would favour polymerisation in the aqueous phase and at the surface of the latex particles. As a result, the polymerised monomers were not uniformly distributed throughout the latex particles. Generally, there was enhancement of the tensile strength of NR after polymerisation with these monomers. For DE-NR, however, there was an optimum DE monomer concentration (10 pphr) which gave the highest tensile strength. The decrease of the tensile strength above 10 pphr monomer was attributed to an increase in the incompatibility between the modified NR, homopolymer and DE-NR graft rubber components.

During a research project carried out previously (6), the present author investigated the polymerisation of hydroxyalkyl methacrylates such as hydroxyethyl methacrylate and hydroxypropyl methacrylate, and of hydroxyalkyl acrylates such as hydroxyethyl acrylate and hydroxypropyl acrylate, in NR latex. This investigation showed that all these monomers could be graft-copolymerised

on to NR in NR latex using the potassium persulphate-sodium metabisulphite initiation system at 20°C. The objective of the present work was to investigate these graft copolymerisation reactions and their products in more detail.

Recently, Erbyl (5) attempted to modify NR by graft-copolymerisation of hydrophilic monomers in NR latex for contact lense applications. NR was chosen for the backbone polymer because of its high oxygen permeability (oxygen permeability coefficient =

$$238 \times 10^{-10} \text{ cc (STP), mm, } cm^2, \text{ s}^{-1}, \text{ cm Hg}^{-1}$$

which matches the oxygen consumption rate of the cornea, and because of its appropriate mechanical properties. NR possesses the necessary mechanical properties for resisting the deformation which occurs during blinking. However, NR, being non-polar, has poor wettability. One of the requirements of a contact lense is that it can be wetted by the tear fluid. To improve the wettability of NR, it is necessary to modify it, preferably by using a hydrophilic monomer. The monomers employed in the investigation of Erbyl were 2-hydroxyethyl methacrylate (HEMA), n-vinyl pyrollidine (NVP), and methacrylic acid. The initiators used were polyamine-activated hydroperoxide, and the ammonium persulphate-sodium metabisulphite combination. Analysis showed the products to be a mixture of polymers, no grafting having taken place.

2.2.4.Commercial exploitation of graft copolymers derived from NR latex

As mentioned in Section 2.1.2 (44), I.G. Farbenindustrie Aktiengesellschaft, described the physical properties of NR obtained by polymerisation of vinyl monomers in NR latex. However, the latex used in the invention was free of ammonia. Further attempts were made to polymerise vinyl monomers in NR latex in the presence of ammonia. Bacon et al. (11) failed to polymerise methyl methacrylate in latex using benzoyl peroxide as an initiator. They believed the reason for this was that the ammonia acted as an inhibitor for the polymerisation of the monomer.

Subsequent workers (66) also concluded that ammonia retarded the polymerisation of acrylonitrile, methyl methacrylate and styrene in NR latex using benzoyl peroxide

as initiator. However, successful polymerisations were achieved using persulphate (46, 48, 50, 51) and a polyethylene polyamine-activated hydroperoxide as initiator. Discovery of the later initiators (57) led to the commercial production of Heveaplus MG (67). According to Campbell *et al.* (3), NR grafted with polymethyl methacrylate is the only commercially-available NR graft material. In the United States of America, a similar product is marketed as SM latex (13). The present author is not aware of any other commercially-modified NR prepared using a hydrophilic monomer. This discussion is therefore restricted to the commercial exploitation of methyl methacrylate-grafted rubbers. The process for the commercial preparation of Heveaplus MG is said to be as follows (67): Centrifuged ammoniated NR latex is diluted with an equal amount of water. The required amount of methyl methacrylate, mixed with tertiary butyl hydroperoxide (0.2 pphr), is stirred into the latex. The stirring is continued until a homogeneous dispersion is obtained. Tetraethylene pentamine (10% solution, 0.2 pphr) is then stirred in to the mixture. Polymerisation is allowed to continue at ambient temperature for two hours, without stirring. The product is coagulated by running the modified latex into at least three times its volume of boiling water containing calcium chloride (0.1%). The coagulum is sheeted on a washing mill, and dried in sheet form. If the products contain a high ratio of polymethyl methacrylate to rubber, the crumb obtained is separated, washed by hydro-extraction, and dried in shallow trays at 100°F. After partial drying, the crumb is sufficiently coherent to be sheeted for final drying. BX Plastics Ltd. was the first to produce Heveaplus MG using concentrated NR latex (68). Heveaplus MG can be produced with a range of rubber:methyl methacrylate ratios. The concentration of methyl methacrylate as a weight percent of the total material is indicated by the final figure, e.g., Heveaplus MG 23 is a graft copolymer containing approximately 23% by weight of methyl methacrylate. The most common grade is Heveaplus MG 50 (13). A grade which contains 40% methyl methacrylate is recommended for adhesive applications (69).

Devan and Bloomfield (70) considered that Heveaplus MG should be a promising material for bonding surfaces of different polarity. They described potential uses for Heveaplus MG in several patents. For example, Heveaplus MG could be used for bonding NR or synthetic rubbers to

leather, PVC, textiles, metals and rubber. Heveaplus MG, together with tackifying resins, can produce a single-coating adhesive or pressure-sensitive adhesive tapes based upon various types of backing. Loan (71) investigated the possibility of using Heveaplus MG in tyre-cord adhesives to replace the terpolymer latex. The tyre-cord adhesives were frequently made of rubber latex, resorcinol formaldehyde and vinyl pyridine-styrene-butadiene terpolymer latex. He reported that the strength of adhesion developed by the adhesive based on Heveaplus MG was about 30% higher than that obtained with the terpolymer latex under comparable conditions. Furthermore, he reported that the Heveaplus Mg adhesive was far less sensitive to curing temperature than was the terpolymer latex adhesive. He also reported that the penetration of the Heveaplus MG adhesive into the tyre cord was much lower than that of terpolymer adhesive. He believed that the dynamic properties of the Heveaplus MG adhesive are better suited to this application than are those of the terpolymer latex adhesive.

Bloomfield (72) reported that a process for the production of Heveaplus MG 50 from field latex has been developed by the Rubber Research Institute of Malaysia. The product is said to be somewhat different in appearance from that prepared from the concentrated latex. The product obtained from the concentrated latex is a coarse crumb; the product obtained using the fresh field latex is a thin crepe, and is more compatible with added rubber. The process for the preparation of Heveaplus MG using fresh latex is said to be as follows (68): To fresh ammoniated latex is added methyl methacrylate (100 pphr) monomer containing cumene hydroperoxide (0.36 pphr), with constant stirring for 25 minutes. The aim of the stirring is to facilitate the penetration of the monomer in to the rubber particles and to prevent the reaction starting prematurely under the influence of amines naturally present in the latex. The amines can initiate the reaction before monomer penetration has occurred to the desired extent. To initiate the reaction, tetraethylene pentamine (0.3 pphr) as a 10% v/v solution in water is added to the mixture and mixed thoroughly for 2 to 3 minutes. The batch is left to stand overnight. The following day, a dispersion of antioxidant (Nonox EXN) is added to the reacted latex. The Heveaplus MG is coagulated with formic acid at 100^{o}C, whereas MG 30 is cold coagulated with 10% sulphuric acid. The coagulum is milled into crepe and dried at room temperature. According to Muthurajah (68), consumers prefer the product prepared

from the fresh latex, as it is more soluble and requires less milling than does that prepared from concentrated latex.

2.2.5 Summary

The following conclusions can be drawn from this review of graft copolymerisation reactions occurring in rubber latices, principally in NR latex:

(i) The use of peroxidic water-soluble compounds such as persulphates, and hydrogen peroxide (1-20 pphr) proved successful in polymerising various monomers in NR latex to greater than 80% conversion. The polymerisation was enhanced by using a stabiliser (2-127 pphr), employing low DRCs (e.g. achieving a final DRC of 6-26%) and carrying out the polymerisation at elevated temperatures (50 - 80^{o}C). At low (room) temperature , however, using redox initiators, e.g. tertiary butyl hydroperoxide (0.2 pphr) and tetraethylene pentamine (0.1 pphr), methyl methacrylate could be successfully polymerised in NR latex to ca. 90% conversion.

(ii) The conditions which are necessary for a high efficiency of grafting when a hydrophobic monomer is polymerised in NR latex are :

a. No additional surfactant should be present. The surfactant provides micelles for emulsion polymerisation of the monomer leading to a high proportion of homopolymer content. Addition of surfactant to an extent of 1% w/w on the total solids content increases about 7 times the amount of homopolymer formed as compared to a similar polymerisation in the absence of added surfactant.

b. NR latex can be activated by passing atmospheric oxygen through the latex for a long period of time (ca.172 hours). In this way, the grafting efficiency can be increased from 74% to 80%.

c. AZDN as initiator produces no grafting when monomers are polymerised in NR latex.

d. Only about half the expected yield of homopolymer may be formed when a reducing agent is employed. A particular system which has been examined is a mixture of ferrous sulphate, ethylene-diamine tetra-acetic acid, sodium formaldehyde sulphonate, and trisodium phosphate.

(iii) The early attempts to polymerise vinyl monomers (ethyl methacrylate and acrylonitrile) using benzoyl peroxide at elevated temperature (62^{o}C) for 22 hours were unsuccessful (ca. 20% conversion) compared with the same monomers polymerised in aqueous solution (ca. 90% conversion). This might have been due to a cage effect brought about by the high viscosity of the monomer-swollen rubber phase in NR latex during the early stages of the polymerisation. The increase in the viscosity may have been enhanced by 1) emulsification of the monomer prior to addition to NR latex leading to an increase in diffusion and the rate of swelling of the rubber in the monomers, and 2) dissolving the initiator in the monomers leading to initiation occurring in the viscous monomer-swollen rubber phase instead of in monomers of low viscosity.

(iv) The changes which led to successful polymerisation are as follows: the monomers were not emulsified prior to addition to NR latex. Preferably, the benzoyl peroxide initiator was added directly to NR latex instead of dissolving it in the monomers. These treatments may have avoided the cage effect, even though the concentration of rubber in the monomer was theoretically high. A high conversion of monomers polymerised in NR latex using benzoyl peroxide was obtained in this way.

Chapter 3

Colloid Stability of NR latex

3.1 Introduction

Cockbain (73) has stated that, although NR latex is a very complex physical and chemical system, its colloidal behaviour is very similar to that of a large number of other hydrophobic colloidal systems. Cockbain and Philpott (74) defined a stable latex as one in which no aggregation or coalescence of the rubber particles occurs under the conditions studied.

Blackley (1) stated that, in general, the subject of latex stability has two quite distinct aspects :

(i) the tendency for an individual particle of rubber to undergo changes by interaction with the aqueous phase, for example, the hydrolysis of non-rubber constituents which are associated with the surface of the particle,

(ii) the interactions between rubber particles.

Furthermore, Blackley (1) stated that at least three important and interrelated factors are responsible for the colloid stability of latex :

(i) the reduction of the free energy associated with the interfacial films surrounding the rubber particles,

(ii) the presence of similar electric charges on the rubber particles giving rise to repulsions between particles,

(iii) the presence of a layer of tightly-bound water molecules around the particles acting as a mechanical barrier preventing the coalescence of two particles.

Cockbain (73) states that the stability of a latex depends ultimately upon the electric charges associated with the interfacial films surrounding the rubber particles, and also upon the degree of hydration of the particle surfaces. The rubber particles in ammoniated latex possess an inner

core consisting of rubber hydrocarbon, surrounded by a layer of lipids. An outer film, which is adsorbed on to the lipid layer contains proteins and fatty-acid soaps. The arrangement of the interfacial region of a rubber particle is shown schematically in Figure 3.1.

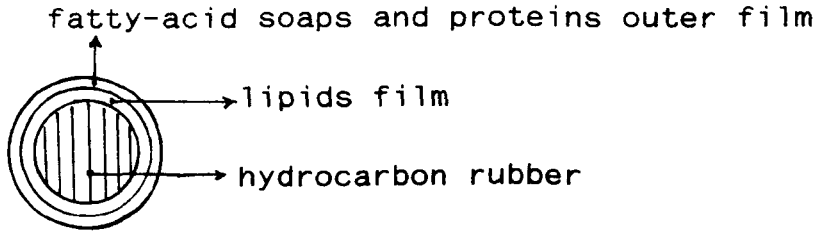


Figure 3.1 Schematic arrangement of interfacial region surrounding a rubber particle

Due to the nature of fatty-acid soaps, proteins and lipids, the film layers have the properties of a hydrophilic colloid. Consequently, the adsorbed films will have a so-called hydration layer consisting of water molecules bound to the soaps, proteins and lipids. The composition of both lipids and soap-protein layers, and the degree of hydration of the so called protective layers, will determine the stability of a latex. For example, the coagulation of latex by solvents such as acetone or alcohol is attributed to the dehydration of the interfacial films.

Flocculation, coagulation, thickening, gel formation, coalescence and creaming are common indications of colloidal instability. Blackley (1) outlined two ways in which a latex can be colloidally destabilised:

(i) By reducing the height of the potential-energy barrier between pairs of particles. This reduction can be brought about by a) the insolubilisation of the adsorbed stabiliser by addition of a coacervant, b) compression of the double layer by ions of opposite polarity to that of the particle side of the double layer, and c) indirect interaction between the precipitated coacervant and the surface phase. Here, the added coacervant precipitates and competes with the polymer particles for the colloidal stabilisers adsorbed on the rubber particles,

(ii) By increasing the average kinetic energy of the particles by physical destabilising agencies such as mechanical stirring.

According to Van Dalfsen (75), if a latex is subjected to mechanical agitation, the rubber particles should increase in average kinetic energy sufficiently to overcome the repulsive forces between charged particles in the latex. Once this repulsive barrier has been overcome, the particles enter into each other's spheres of attraction. Under the same speed of motion, the greater the surface charge on the particles, the lower is the rate of collision, and thus the more stable is the latex. The ability of the latex to resist mechanical agitation is called the mechanical stability of the latex.

Pendle and Gorton (76) stated that Dawson (77) established the basis of the modern test for the mechanical stability time of latex (MST). In the MST test, latex is diluted with aqueous ammonia solution (1.6% for HA latex) to 55.0 $\pm$ 0.2% TS, and is then stirred at high speed (14,000 $\pm$ 200 r.p.m.) at 35 $\pm$ 1^{o}C. The MST is defined as the time in seconds from the start of stirring to the end point. The end point is determined by dipping a clean glass road into the latex at 15 s intervals and drawing it gently over the palm of hand. The end point should be taken as the first appearance of flocculum in the film so deposited (78).

3.2 Previous investigations of the factors which affect the mechanical stability time (MST) of NR latex

3.2.1 Total solids content of latex

Dawson (77) investigated the factors which affect the MST of NR latex. He found that the total solids content significantly affected the MST of the latex. Generally, the higher the solids content, the lower the MST of the latex. Dawson reported that the MST varied from about 300 to 500 seconds for approximately 60% total solids content and from about 650 to 1,500 seconds for approximately 40% total solids content. Using an extrapolation method, he determined an approximate maximum total solids content of the latex which would give a zero MST. This maximum was 69%. He stated that the significant increase in the MST of the latices with decreasing total solids content was not only due to the particles being farther apart, but also due to increased solvation of the particles in highly diluted

latices. Belmas (79) studied the effect of dilution on the distribution of alkali-metal cations and alkaline-earth cations between the two phases of latex preserved with ammonia. The latices were diluted with 0.5, 1, 2, 4, 6, 8 and 10 parts by weight of pure water per one part of latex. With a dilution of 0.5, the metals were desorped from the surface of the rubber particles such that 21% of the potassium was deabsorbed, 18% sodium and 14% of calcium. Furthermore, the greater the dilution was, the greater the extent of desorption was. The desorption of calcium was less than the desorption of the alkali metals. To some extent, this desorption would increase the surface potential on the rubber particles and hence the stability of latex. The dilution would also enhance dissociation of the carboxyl groups of the protein layer of the particles and adsorbed fatty acids. These factors would also contribute to the increase in the stability of latex.

Madge et al. (80) reported that the total solids content of latex greatly influences the MST of two latices with different total solids content. The MST of an NR latex having 51.5% total solids content was 50% greater than that having 58% total solids content.

Minoura (81) studied the effects of total solids content upon the MST of unmodified latices, i.e., clonal latex GT-1 and PR 107, and of modified PR-107 latex containing small and different amounts of ammonium hydroxide, calcium hydroxide, potassium hydroxide, and n-propyl alcohol. The latices were diluted with distilled water to 55, 50, 45, 40 and 35% total solids content. In all cases, the MST of the latex increased progressively with decreasing total solids content and the additions did not affect MST. Furthermore, he showed that there is a linear relationship between the inverse of the total solids content and the MST. He argued that the process of particle collision during high-speed stirring, leading to curdiness, is a second-order process. By assuming that the total solids content is the concentration of reactants, he derived the following equation, which is consistent with his observations :

$$\frac{C}{C_o(C_o-C)} = K.t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

where K is the reaction rate coefficient, C is the concentration of rubber particles after time t, t is the

time, and C_o is the concentration of rubber particles when t=0. Within the scale of his dilution experiments, and based on his derivation, he suggested that the variation in MST with total solids content is mainly influenced by the concentration of the latex, the influence of any solvation change being small. However, if the scale of dilution is large, he stated that the change of solvation has to be taken into account.

Tan (82) also studied the effect of total solids content upon the MST. For practical reasons, the total solids contents selected were in the range 50 to about 61%. He found that a plot of the inverse total solids content against the MST deviated slightly from linearity. According to Tan, the rate coefficient, K, in Equation (3.1), does not remain constant because the nature of the reactant is constantly changing during the test. Furthermore, K also depends upon the total solids content of latex.

3.2.2 Addition of alkalis and electrolytes

Dawson (77) investigated the effect of ammonia concentration upon the MST of latex. He found that ammonia concentrations greater than 0.4% on the aqueous phase have little effect upon the MST of the latex. At ammonia concentrations below this figure, however, a rapid fall in MST was observed. The rate of decrease was much greater for latices having high initial stability than for those having lower initial stability.

Minoura (83) also investigated the effects of ammonium hydroxide, potassium hydroxide and calcium hydroxide upon the MST of NR latex from different clonal sources, such as AVROS 50 [KOH Number 790 mg/100 g total solids (TS)], GT-1 [KOH Number 1,175 mg/100 g TS] and PR-107 [KOH Number 1,352 mg/100 g TS]. The present author has attempted to interpret results which Minoura tabulated, rather than merely his published curves, because the tabulated results cover a range of ammonia concentrations up to 5.4%, whereas the curves cover a range up to only 2.6% ammonia concentration. The results of Minoura show that the MST of latex having a relatively low KOH Number [<790 mg/100 g TS] can be expected to increase rapidly with increasing ammonium hydroxide concentration up to 4.5%. For latex having a relatively high KOH Number (1,175 mg/100 g TS), the MST increases progressively with increasing ammonium hydroxide concentration until the concentration reaches

3.6%, after which further addition of ammonia has little effect. In the case of latex having a high KOH Number (1,352 mg/100 g TS), ammonia concentrations greater than 1.6% have no effect upon the MST of latex. Thus the higher the KOH Number, the less ammonia is required to stabilise the latex. Minoura (83) further suggested that ammonia not only increases the extent of hydration of the latex particles but also reacts with fatty acids to form soaps, thereby enhancing the MST of the latex. Furthermore, ammonium hydroxide is a weak base and not ionised completely at high concentration; thus it does not decrease the MST of the latex.

In the cases of the addition of sodium hydroxide and potassium hydroxide addition, Minoura (83) found that the MST of latex increases progressively with increasing amount of either base, and that it reaches a limiting level which corresponds approximately to the KOH Number of the latex. This limiting level is higher for potassium hydroxide than for sodium hydroxide. Further additions of either of these bases beyond this amount causes a rapid decrease in MST of latex due to a decrease in the ion dissociation of the soaps as a consequence of a common-ion effect and also, presumably, because of the increase in the ionic strength of the aqueous phase of the latex.

These results were confirmed by Pendle and Gorton (76). In their view, an increase in MST by potassium and sodium hydroxide was, at least in part, due to a replacement of ammonium soaps by potassium soaps as well as being due to a suppression of the ionisation of ammonium salts which brings about a reduction in the ammonium ion concentration.

At higher levels of alkali addition, a sharp reduction in the MST of the latex occurs as a consequence of the high ionic strength of the aqueous phase at these levels. However, Loha (84) has suggested that the reduction in MST of latex brought about by the addition of excess potassium hydroxide is a consequence not only of the high ionic strength of the aqueous phase but also, in part at least, of a reduction in the degree of hydration of the ionic charges on the surface of the rubber particles.

When calcium hydroxide was added, Minoura (83) found that the MST of the latex decreased progressively with increasing calcium hydroxide concentration. He suggested that calcium hydroxide reacts with fatty-acid soap anions

to form insoluble calcium soaps, thereby causing a reduction in the charge on the rubber particles and thus reducing the MST of latex.

As mentioned above, the addition of certain levels of alkalis such as potassium hydroxide, ammonium hydroxide, and sodium hydroxide, increases the MST of latex. However, the addition of an electrolyte to NR latex increases the ionic strength of the aqueous phase. This increase in ionic strength will compress the double layers surrounding the particles which provide at least part of the stability of the latex. As a result, the electric repulsions between the particles are insufficient to overcome the attractive force which tend to cause flocculation or coagulation of the latex (85).

Belmas (79) studied the effect of added electrolytes upon the extent of adsorption of the corresponding metal cations at the surface of the rubber particles. He showed that addition of electrolytes increases the adsorption of the cations at the surface of rubber particles. Undoubtedly a reduction in surface charge of rubber particles would occur. Cockbain and Philpott (74) reported that potassium chloride salts at levels of 0 to 25×10^{-3} moles/100 g latex solids decreased significantly the MST of latex due to a reduction in the surface potential, and in the thickness of double layer. Tan (82) also studied the effects of added electrolytes upon the MST of NR latex. He reported that potassium chloride and potassium sulphate decreased progressively the MST of the latex with increasing amounts of the salts. He suggested that the reduction in MST is most probably a consequence of the effect of increasing ionic strength. The effects of other electrolytes, such as magnesium chloride, upon the MST of latex was far more dramatic than the effects of the other two salts studied. He suggested that the drastic fall in MST with increasing magnesium chloride concentration is a consequence not only of increased ionic strength, but also of interaction between the magnesium ions and the adsorbed anions of higher fatty acids to form insoluble magnesium soaps.

3.2.3 Addition of alcohols

According to Madge (86), one of the factors which affects the stability of NR latex is the degree of hydration of the soap-protein layer at the surface of the rubber particles. Under certain conditions, alcohols act as

dehydrating agents, and are able to coagulate the latex entirely as a consequence of the dehydrating effect on the interfacial film. Based on the above argument, Madge developed an alcohol-titration method to study the relationship between the MST of latex and the amount of alcohol required to coagulate the same latex. He called the volume of alcohol required completely to coagulate a fixed volume of latex the "alcohol coagulation volume" (ACV). However, there is little correlation between ACV and MST. Madge further considered that the MST of a latex is very dependent upon other characteristics of the protective layer besides the amount of bound water present at the surface of the rubber particles.

Minoura (87) studied the effect of varying the length of the alkyl group of an alcohol upon the MST of latex. He used methanol, ethanol and n-propanol. The amount of alcohol added to the latex ranged from 0 to 11 pphr for methanol, 0 to 10.5 pphr for ethanol and 0 to 5.8 pphr for n-propanol. In all cases, the MST of the latex increased progressively with increasing amount of added alcohol. Minoura suggested that, at low level alcohol concentrations, the alcohols are absorbed on to the surface of the rubber particles, thereby increasing the thickness of the adsorption layer and hence the MST of the latex. At the same levels (mol/l latex) of alcohols, the effectiveness of the various alcohols in enhancing the MST of the latex was in the following order: n-propanol > ethanol > methanol. He further suggested that, the longer the alkyl chain length of alcohol added, the thicker was the adsorption layer, and thus the higher the MST of latex. At certain levels of added alcohol, however, dehydration of the surface layers occurs, and the alcohols are no longer able to increase the MST of the latex. Minoura suggested that the cause of the dehydration of the hydration layer is interaction between the added alcohols and the adsorbed proteins and fatty acid soap anions. It was observed that the order of effectiveness of the alcohols in effecting dehydration is n-propyl > ethyl > methyl. Unfortunately, Minoura did not investigate the effects of maturation in the presence of alcohols on the MST of latex, as the dehydration of the dehydration layer in the presence of the alcohols may well depend upon the time.

Pendle and Gorton (76) also investigated the effects of a wide range of alcohols upon the MST of NR latex. They confirm that, at low levels of addition of alcohol such as methanol, ethanol and propanol, there is an increase the MST of the latex. They also confirm that alcohols with a higher alkyl chain lengths confer higher MST upon the latex. An interesting aspect of their investigation is that the number of hydroxyl groups appears to play little part in stabilising latex, since glycerol tends to reduce the MST of latex. Pendle and Gorton stated that it is the reduction in dielectric constant brought about by the addition of the alcohol which affects the MST of latex, rather than the hydroxyl groups of the alcohol. To clarify this matter, they compared the effect of ethanol with that of tetrahydrofuran (THF), a non-alcohol, water-miscible solvent, with a low dielectric constant. They found that THF increases the MST significantly, although it is less effective than is ethanol. They argued that the water-miscible materials of low dielectric constant are capable of reducing the ionisation of the salts in the aqueous phases, thus reducing the ionic strength of aqueous phase. Consequently, the MST of the latex increases.

3.2.4 Addition of surfactants

3.2.4.1 Introduction

Blackley (1) has stated that surfactants are substances which are capable of modifying the surface properties of aqueous media, even though they are present only in very small amounts. The principal effect of the majority of the surfactants is that they lower the surface free energy of the aqueous phase-air interface and also the interfacial energy of the interface between aqueous phases and immiscible organic liquids. Surfactants can be divided into four main groups, namely, anionic, non-ionogenic, amphoteric and cationic types, according to whether the surface-active entity of the substances is an anion, a neutral molecule, an amphoteric ion or a cation. In the present study, only anionic and non-ionogenic surfactants will be reviewed, as the others are not relevant the work described in this thesis.

3.2.4.2 Effect of added anionic surfactants

There are three classes of surfactant which are of interest, namely, carboxylates, sulphates and sulphonates. Only carboxylates and sulphates will be reviewed in this thesis, as the other type is not relevant.

3.2.4.2.1 Carboxylates

This group has the surface-active anion RCO_2^-, where R is a long chain aliphatic hydrocarbon group, and is the non-polar hydrophobic component. The ionised group, $-CO_2$, is a polar hydrophilic component. Many workers have investigated the effects of this type surfactant upon the MST of latex. Madge *et al.* (80) reported that the addition of as little as 0.3% potassium laurate increased the MST of NR latex approximately 12-fold. Cockbain and Philpott (74) published results concerning the joint effects of both the level of fatty-acid soaps (0.1 to 0.6 millimoles/100 g total solids) and the alkyl chain-length of the soaps (C_7 to C_{17}) upon the MST of NR latex. They showed that the addition of 0.1 millimole of potassium decanoate per 100 g of latex solids, which would cover less than 5% of the surface area of the particles, doubles the MST. The order of the effectiveness of the alkyl chain in increasing in the MST is $C_9 > C_{11} > C_{13} > C_{15} > C_7 > C_{17}$.

Blackley *et al.* (88) have offered an explanation of the enhancement of MST that is brought about by small additions of soaps, such as potassium laurate, which are of intermediate chain length. They suggested that the size of the alkyl chains is long enough for the soap anion to be adsorbed at the rubber-water interface, but short enough to disrupt the coherence of clusters of the adsorbed soap anions having long alkyl chains which are naturally present in the latex. Blackley *et al.* (88) have also published results showing that the enhancement of MST depends upon both the alkyl chain-length of the carboxylate and its level. They observed maximum enhancement at $C_{11}H_{25}CO_2K$. Jurado and Mayhan (89) showed that more than 95% of the indigenous soaps are present in the rubber phase, and also that about 90% of the soaps have long alkyl chains, such as a substituted furanoic acid, C_{18} and C_{16}. According to Blackley *et al.* (88), the disrupted indigenous soaps tend to disperse around the rubber particles and rearrange themselves in such a way that they are more evenly distributed at the surface of the rubber

particles thereby increasing the mechanical stability. In the case of either short- or long-chain soaps, Blackley et al. (88) suggest that the short-chain soaps are not strongly adsorbed, whereas the long-chain soap anions can do little to disrupt the coherence of the clusters of adsorbed soap anions.

Blackley and Azas (90) investigated the effect of soaps having the same alkyl chain length but different chemical structures, in particular, the C_{18} carboxylate soaps, upon the MST of NR latex. They found that the enhancement of the MST is dependent not only upon the alkyl chain length of the soap but also to some extent upon the nature of the hydrophobic chain of the soap. It was suggested that soaps whose hydrophobic chain contains one or more carbon-carbon double bonds are of a different nature to the indigenous soaps. Therefore, the soaps would encourage the disturbance of the regularity in the packing of an indigenous adsorption layer, and hence enhance the MST. They expected that the more carbon-carbon double bonds, the more effective disturbance of the adsorbed molecular clusters, and also that a cis configuration would be a more disruptive influence than a trans configuration. The order of effectiveness in enhancing the MST was observed to be linoleate > 9,10-dihydroxy stearate > ricinoleate > 12-hydroxy stearate > oleate > linoleate & elaidate > stearate.

Blackley and Haynes (91) have reported the effects of laurate soaps of various counterions upon the MST of NR latex. They found that, to some extent, the counterion of the soaps affects the MST of latex to which the soap is added. For a given molar addition, the order of increasing effectiveness of the laurates of various counterions was found to be potassium > sodium > lithium > ammonium > morpholinium. Morpholinium laurate was found to be significantly less effective in enhancing the MST. This was attributed to partial adsorption of the counterions into the Stern layer at the particle surfaces.

3.2.4.2.2 Sulphates

Sulphate surfactants have the typical chemical structure $R.SO_4$ (or $RO.SO_3$), where R may be a long-chain aliphatic or an aromatic hydrocarbon group. The sulphates are much less sensitive to acids and heavy metal ions than are the carboxylates (1). Blackley and Emengo (92) have studied

the behaviour of sulphates in rubber latices. They also investigated the effect of impurities in sulphates upon the MST. They removed some of the inorganic-electrolyte impurities by twice crystallisating from aqueous methanol followed by continuous extraction with petroleum ether.

They found that purified sodium dodecyl sulphate at a level of 0.07% w/w on latex solids increased the MST by a factor of about 1.3. Blackley and Emengo (94) also reported the behaviour of various sulphate surfactants upon the MST of NR latex. The sodium n-alkyl sulphates used were the homologous series C_6, C_8, C_{10}, C_{12}, C_{14}, and C_{16} compounds. They found that the effects of sodium n-alkyl sulphates are broadly similar to those of added potassium n-alkanoates. The mechanism of enhancement of MST in the presence of the sulphates was thought to be similar to that for enhancement by added potassium n-alkanoates (Section 3.2.4.2.1). Blackley and Emengo found that, at any given level of addition, the MST increases progressively with increasing alkyl chain length of the sulphate, until it reaches a maximum at C_{10} (decyl sulphate), and then falls progressively with further increase in alkyl chain length. The order of effectiveness of hydrophobe moiety in increasing the MST was found to be $C_{10} > C_8 > C_6 > C_{12} > C_{14} > C_{16}$.

The effect of n-dodecyl sulphates having various counterions such as lithium, sodium, potassium, ammonium, morpholinium, calcium, and magnesium upon the MST was also investigated by Blackley and Emengo (92). They concluded that the counterions have only a minor effect upon the ability of a sulphate surfactant to enhance the MST of NR latex. The order of the effectiveness of the sulphates of the various counterions in enhancing MST was found to be ammonium > potassium > sodium, lithium > morpholinium > calcium > magnesium.

3.2.4.3 Effect of added non-ionic surfactants

According to Blackley (1), non-ionic surfactants are surface-active substances which do not give rise to ions in normal circumstances. Typical examples of such surfactants are the adducts of ethylene oxide and fatty acids, fatty alcohols or alkyl phenols. The general formula is $R\{(CH_2.CH_2.O)_n\ H\}m$, where R is a hydrophobic group derived from the fatty acid base alcohol or phenol; m is the number of separate polyethenoxy chains, determined by the

nature of the acid, alcohol, or phenol with which the ethylene oxide has been reacted; and n is the average number of ethylene oxide units which have reacted with one molecule of the hydrophobe base. For a simple fatty acid, $R.CO_2H$, or fatty alcohol ROH, m is equal to unity. For a trihydric alcohol, m is 3. The hydrophilic component is provided by the polyoxyethylene chains. The properties of the adduct are greatly dependent upon the ratio of the hydrophilic and hydrophobic chain lengths. Because of wide variations in the chain length, these adducts are frequently characterised by the molar ratio of ethylene oxide to the hydrophobic starting material.

Cockbain and Philpott (74) made an initial study of the influence of non-ionic surface-active agents in ammonia-preserved NR latex concentrate. The surface-active agent used was Vulcastab LW, an ethylene oxide-fatty alcohol adduct. The Vulcastab LW was used at levels of 0 to 0.4% by weight on the latex solids. The MST was found to decrease progressively with increasing amount of the soap until it reached a minimum value at about 0.05 to 0.09% addition. Then the MST increased slightly as the amount of the surfactant was increased. Cockbain and Philpott suggested that the initial decrease in the stability is a consequence of displacement of some of the anionic proteins or soaps from the particle interface, causing a significant

Table 3.1 Details of fatty-alcohol ethoxylates used by Blackley et al. (95)

commercial designation	mole ratio-ethylene oxide to hydrophobic moiety	HLB value	appearance of 10 % aqueous solution at room temperature
Texofor A2	2	5.3	OPS[x)]
Texofor A16	6	10.4	thick white paste
Texofor A10	10	12.9	SCS[xx]
Texofor A14	14	14.4	clear viscous solution
Texofor A1	24	16.3	clear viscous solution
Texofor A30	30	16.9	clear viscous solution
Texofor A45	45	17.8	clear viscous solution
Texofor A60	60	18.3	clear viscous solution

x) only partially soluble
xx) slightly cloudy solution

reduction in the surface potential. Apparently, the reduction in surface potential cannot be compensated for by an increase in the degree of hydration of the surface film.

Blackley et al. (95) published the results of a more detailed investigation of the effects the structure of ethylene oxide adducts upon the effect of those adducts upon the MST of NR latex. They used a series of ethoxylates containing the same hydrophobe moiety, C_{16}-C_{18}, but different molar ratios of ethylene oxide to hydrophobe base, the range being from 2 to 60 as given in Table 3.1. The quantity of ethoxylates employed was in the range 0 to 1.5 pphr. The results showed that the addition of small amounts of the ethoxylates decreased the MST until it reached a minimum. This minimum is different for each of the ethoxylates used. The initial reduction in stability was attributed to the following factors:

(i) In the case of ethoxylates having short polyethylene oxide chains, insoluble phases are formed which have high specific surface onto which stabilisers from the rubber particles are absorbed, thereby reducing the stability of the latex,

(ii) In the case of ethoxylates having intermediate polyethylene oxide chains of intermediate length, the degree of hydration is enhanced and they tend to adsorb at the rubber-aqueous phase and displace the natural protective layers containing protein and fatty-acid soaps. Because the level of the ethoxylate is low, one would expect that an increase in the degree of hydration brought about by the ethoxylates would not overcome the reduction in surface charge and potential of the rubber particles caused by the loss of proteins, lipids and fatty acid-soaps.

Further additions of ethoxylates having average ethylene oxide chain lengths above 45 caused the MST to increase progressively with increasing amount of the ethoxylate. This is attributed to the fact that such ethoxylates are hydrophilic in nature, and will cause increase in the degree of hydration that is able to overcome the loss of surface charge and potential caused by the displacement of the proteins and fatty-acid soaps. In the case of ethoxylates having a molar ratio of ethylene oxide to

hydrophobe base of less than 30, the extent of the increase in the hydration layer appears to be only slight, and the MST, though increasing with further addition of the ethoxylates, did not rise above that of original latex. Another interesting aspect of the findings of Blackley et al. (95) is that the addition of ethoxylate together with an electrolyte such as potassium chloride, or with a reduction in the ammonium content, increased the MST. This peculiar behaviour was attributed to salting out of the ethoxylate from solution, and thus becoming capable of being more readily adsorbed on to the surfaces of the rubber particles.

Blackley and Chua (96) further investigated the effects of various ethoxylates upon the MST of latex in which the mole ratio of ethylene oxide to hydrophobe base was kept constant, approximately 30, but the nature of the hydrophobe base was varied. The details of the ethoxylate used are given in Table 3.2.

Table 3.2 Details of fatty-alcohol ethoxylates used by Blackley and Chua (96)

commercial designation	hydrophobe base	HLB value	appearance of 20% solution at room temperature
Texofor A30	mixture of cetyl and alkyl alcohol	16.9	clear viscous solution
Texofor B30	lauryl alcohol	17.5	clear viscous solution
Texofor FP300	p-octyl phenol	17.1	clear viscous solution
Texofor D30	castor oil	11.6	clear viscous solution

The addition of the ethoxylates (up to 1.5% by weight on the latex solids content) caused an initial marked decrease in MST. Further addition of the surfactant caused the MST of the latex to increase slightly, but not to the original stability of the latex. However, the MST increases remarkably with further addition of the ethoxylates above 0.75% for Texofor B30 and above 1.00% for Texofor FP300. In the case of Texofor FP300, the MST increased 10-fold compared to the original latex by adding only 1.5% ethoxylate. Again, the addition of the ethoxylates to latex

destabilised by adding electrolytes such as potassium chloride, ammonium acetate, or by reduction of ammonia, was found to confer higher MST.

3.2.5 Effect of added creaming agents

Being hydrophilic in nature, it may be expected that the hydrophilic homopolymers obtained from the polymerisation of the non-ionogenic hydrophilic monomers in NR latex would act as creaming agents. Thus it is desirable to review the effect of added creaming agents upon the stability of NR latex. As mentioned in Section 2.1, creaming is one of the indications of colloidal instability of latex, in the sense that the latex is not macroscopically homogeneously stable. According to Cockbain and Philpott (74), when a creaming agent is added to latex, the Brownian movement of the particles is slowed down, and aggregation of the particles into clusters occurs. At low levels of creaming agents, aggregation is limited to the larger rubber particles, but at higher levels of creaming agent, the smaller rubber particles become incorporated in the aggregates. However, the efficiency of creaming decreases if the concentration of creaming agents is too high. This is attributed to too high configurational stability of the aggregates, in which the individual particles are now less able to arrange themselves readily into a close-packed configuration. The creaming process is reversible, because the aggregated particles can be easily broken down by stirring or dilution. Therefore it seems probable that creaming is a consequence of a secondary minimum in the potential energy-separation curve for pairs of latex particles. According to Twiss and Carpenter (97), the depth of the secondary minimum is controlled by the strength of the polar forces of the creaming agent. Furthermore, one would expect that hydrophilic polymers having multiple polar groups such as -OH or -COOH would be the most effective creaming agents.

Blackley (1) has stated that the precise way in which creaming agents accelerate the process is still obscure. However, he has outlined three possible theories of creaming:

(i) The creaming agent enhances the effective size of rubber particles brought about by the adsorption of the heavily-hydrated agent, and the viscous drag on this hydration layer effectively suppresses the Brownian movement. This theory is

rejected for two reasons:

a. the particles are required to be hydrated to an improbable extent,

b. the extensive hydration would reduce the effective difference in densities between particle and serum, thereby discouraging the aggregates to rise to the surface and produce cream.

(ii) The creaming agent reduces the effective charge on the rubber particles, and consequently the rubber particles approach one another more closely than hitherto. The creaming agent also causes formation of a heavily-hydrated layer, thereby preventing coalescence. This theory is also rejected because there is no observed reduction of charge as determined by measurements of electrophoretic mobility.

(iii) The creaming agent adsorbed on the surfaces of particles forms a loose network which entangles with the creaming agent dissolved in the aqueous phase. The Brownian movement is restricted by the "anchoring" effect of such a network. The formation of clusters occurs because the particles undergo Brownian motion until they became entrapped in localised networks that are sufficiently strong to hold them. The clusters keep growing by entrapping particles until the buoyancy of the clusters is sufficient to break them free from the networks and carry them upwards. Because of the compressing effect from below, they become more compact, thereby causing expulsion of the aqueous phase. This theory provides the most probable mechanism of the creaming process.

Tan (82) investigated the effect of creaming agents, particularly methyl cellulose, upon the MST of latex. Two grades of a creaming agent were employed, namely, Celacol M450 and Celacol M2000. A 2% aqueous solution of each had viscosity of 450 cP and 2,000 cP respectively at 20^{o}C. The amount of methyl cellulose used was 0 to 0.04% w/w on the total latex for Celacol M450, and 0 to 0.07% for Celacol M2000. The MST was found to increase progressively with

increasing amount of the creaming agents. This effect was attributed to the formation of an additional hydration layer brought about by hydrogen bonding of water molecules to the adsorbed methyl cellulose. As a consequence, the hydration (solvation) stabilisation of the latex increased.

Chapter 4

Reaction kinetics of free-radical polymerisation with special reference to graft copolymerisation in NR latex

4.1 Introduction

The earliest reported (98) attempt to quantify and interpret the rates of a chemical reaction is believed to have been by Ludwig Ferdinand Wilhelmy in Germany in 1850. Wilhelmy used a differential equation, and also attempted to quantify the temperature-dependence of rates of chemical reactions. Since then, many workers have increasingly developed the kinetic approach to provide essential evidence concerning the mechanism of chemical processes, although valuable evidence provided by non-kinetics investigations, such as characterisation of the product, often provides additional evidence for the mechanism of reaction.

Reaction kinetics is concerned with the study of the rate of conversion of reactants into the products. The rate of conversion of a particular substance is very dependent upon the concentration and nature of the reactants, and also upon the reaction conditions. In this work, the kinetics of polymerisation has been investigated, i.e., the kinetics of the conversion of non-ionogenic hydrophilic monomers into polymers. The reaction medium being NR latex will undoubtedly influence the results obtained.

4.2 Kinetics of free-radical polymerisation

An initiator is a substance which is capable of initiating the polymerisation of a vinyl monomer. According to Odian (99), the initiation of a free-radical polymerisation commences with the decomposition of an unstable initiator, I, into two free radicals (R.). This is followed by the addition of a radical to the first monomer molecule to produce the chain-initiating species, M_1. , as follows:

Initiation :

$$I \underset{}{\overset{k_d}{\rightleftharpoons}} 2\,R. \qquad \text{.....4.1}$$

$$R. + M \xrightarrow{k_i} M_1. \qquad \text{.....4.2}$$

where I is an initiator molecule, R. is an initiator radical, k_d is the rate coefficient for the decomposition of the initiator (usually in the range 10^{-4} - 10^{-9} s^{-1}), M

is the monomer, and k_i is the rate coefficient for the initiation step. The rate of initiator disappearance, or decomposition of initiator, should follow first-order kinetics as follows:

$$\frac{-d[I]}{dt} = k_d [I] \quad \text{.....4.3}$$

Integration of this equation yields,

$$[I] = [I_o]\, e^{-k_d t} \quad \text{.....4.4}$$

where $[I]_o$ is the initial concentration of initiator and [I] is the concentration of initiator at time t.

These considerations suggest that the kinetics of the initiation step should be straightforward. However, O'Driscoll and Ghosh [100] believe that the decomposition of the initiator can be complex and dependent upon the nature and concentration of the initiator, reactant and medium or solvent.

In the present work, the decomposition of initiator and the initial reaction of the initiator radical are expected to be more complex as NR latex is the reaction medium. It is expected that the long-chain hydrocarbon, polyisoprene, having a carbon-carbon double bond in each repeating unit will react with the radicals and perhaps also with the non-rubber constituents. Furthermore, the initiator free radicals may be produced in a solvent "cage". Therefore, the effectiveness of the initiator radicals in attacking the monomer will be reduced, as they may recombine before diffusing out of the cage, or they may diffuse out of the cage but not combine with a monomer molecule. Odian (99), however, stated that, once a radical has diffused out of the solvent cage, reaction with the monomer occurs in preference to other possible reactions.

The rate of initiation is determined not only k_d and [I] but also by the efficiency of the initiator (f). This initiator efficiency is defined as the ratio between the concentration of effective initiator radicals capable of initiating polymerisation and the total concentration of initiator radicals formed from the initiator in the primary step. The rate of initiation is then given by :

$$R_i = f\, k_d\, [I] \quad \text{.....4.5}$$

Initiation is followed by the subsequent reaction of the monomer radicals with further monomer molecules, thereby producing growing chain radicals. This is the propagation stage.

$$\text{Propagation :} \quad M_1\cdot + M \xrightarrow{k_p} M_2\cdot \quad \text{.....4.6 a}$$

$$M_2\cdot + M \xrightarrow{k_p} M_3\cdot \quad \text{.....4.6 b}$$

The general propagation step is

$$\text{-- } M_n\cdot + M \xrightarrow{k_p} \text{-- } [M]\cdot_{n+1} \quad \text{.....4.6 c}$$

where k_p is the rate coefficient for propagation.

The propagating radicals can stop growing either by combination of two radicals to form a terminated polymer [Equation 4.7 a], or by a disproportion reaction in which a hydrogen radical is transferred to another radical producing two polymer molecules, one having a saturated end-group and the other having an unsaturated end-group [Equation 4.7 b]. These two reactions represent the termination stage of the polymerisation.

Termination :

(i) by combination :

$$\text{---}M_n\cdot + \text{---}M_m\cdot \xrightarrow{k_{tc}} M_{n+m} \quad \text{.....4.7 a}$$

(ii) by disproportion :

$$\text{---}M_n\cdot + \text{---}M_m\cdot \xrightarrow{k_{td}} M_n + M_m \quad \text{.....4.7 b}$$

where k_{tc} and k_{td} are the rate coefficients for termination by combination and disproportion respectively. If the particular mode of termination is not specified, one can assume that the rate coefficient for termination, k_t, is the sum of the rate coefficients for combination and termination :

$$k_t = k_{tc} + k_{td} \quad \text{.....4.8}$$

The rate of termination is then

$$R_t = \frac{-d[M.]}{dt} = k_t [M.]^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots 4.9$$

The rate of disappearance of monomer, -d[M]/dt, is essentially the rate of polymerisation, and is the sum of the rates of reactions 4.5 and 4.6 c, i.e.,

$$-d[M]/dt = R_p + R_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.10$$

The number of monomer molecules which react in the initiation reaction is far less than the number which react in the propagating step. Therefore one can assume that R_i is negligible relative to R_p. The rate of monomer disappearance is then given by:

$$-d[M]/dt = R_p \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.11$$

It is assumed that the reactivity of a chain radical is independent of chain length, and hence that the rate coefficients for all the propagation steps are equal. The polymerisation rate is then given by:

$$R_p = k_p [M.] [M] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.12$$

where $[M.] = \sum [M_n.]$.

It is also assumed that, in the initial stages of a polymerisation, the concentration of radicals increases rapidly, but soon reaches a steady value (the steady-state assumption). At this stage, the rate of change of concentration of radicals becomes zero. Therefore, the rates of initiation (R_i) and termination (R_t) of radicals must be equal. Hence this steady-state assumption can be represented by the equation,

$$R_t = R_i = k_t [M.]^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.13a$$

or

$$[M.] = \sqrt{\frac{R_i}{k_t}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.13b$$

Substituting Equation 4.13 b into Equation 4.12 yields,

$$R_p = k_p [M] \sqrt{\frac{R_i}{k_t}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.14$$

Substituting Equation 4.5 into Equation 4.14, gives the rate of polymerisation as

$$R_p = k_p [M] \sqrt{\frac{f\, k_d [I]}{k_t}} \quad \ldots\ldots\ldots\ldots\ldots\ldots 4.15$$

Hence the rate of polymerisation is predicted to be first-order with respect to monomer concentration and half-order with respect to initiator concentration.

4.3 Inhibition and retardation

Odian (99) distinguishes an inhibitor from a retarder. An inhibitor inactivates every radical, and polymerisation is completely halted until the inhibitor is consumed. A retarder also reacts readily with radicals, but the difference is that the product of this reaction is radicals that react slowly with monomer to initiate further polymerisation. Hence the rate of polymerisation is greatly reduced.

Goldfinger *et al.* (102) and Odian (94) have outlined the reaction kinetics of inhibition and retardation as follows: they assume that the inhibitor or retarder, Z , competes for the propagating radicals to form an inactive product as follows:

$$M_n. + Z \xrightarrow{k_{pz}} Z. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.16$$

where $Z.$ is an inhibitor radical which has low reactivity and terminates without regeneration of the original inhibitor molecule. The rate of reaction 4.16 is given by

$$\frac{-d[M.]}{dt} = \frac{-d[Z]}{dt} = k_{pz} [M_n.] [Z.] \quad \ldots\ldots\ldots\ldots 17$$

If this reaction predominates, polymerisation will cease. The relative values of k_p [M] and k_{pz} [Z] determine whether inhibition $\{k_{pz}$ [Z] >> k_p [M]$\}$ or retardation $\{k_p$ [M] ~k_{pz}[Z] is the predominant reaction. Therefore, attempts to stop completely a polymerisation reaction depend not only upon the ratio of inhibitor to monomer but also upon the ratio of the propagation rate coefficient to the inhibition rate coefficient.

4.4 Determination of order of reaction

The method commonly used to determine the order of a reaction is to investigate the change of concentration of a substance with time during a chemical reaction using the integration method pioneered by Wilhelmy as mentioned in Section 4.1. Because of the difficulties of direct measurement of a reaction rate, one has to assume that a reaction is of a given order n with respect to a particular reactant. At the beginning of the reaction (t = 0), the concentration of reactant A is A_o. The amount of A which has been consumed per unit volume at time t is x. Then, the remaining concentration of A at time t is $(a_o - x)$. Therefore, the rate of disappearance of A is given by (103)

$$\frac{dx}{dt} = k\,(a_o - x)^n \qquad \text{.....4.18}$$

Integration of the above subject to the initial condition x = 0 when t = 0 gives a result which depends upon whether n is or is not unity.

(i) If n is unity, the rate coefficient, k , is given by

$$k = \frac{1}{t} \ln \frac{a_o}{a_o - x} \qquad \text{.....4.19}$$

(ii) If n is other than unity, the rate coefficient, k , is given by

$$k = \frac{1}{t(n-1)} \left[\frac{1}{(a_o - x)^{n-1}} - \frac{1}{a_o^{n-1}} \right] \qquad \text{.....4.20}$$

The integrated equations for rate coefficient, k , for various order of reactions are given in Table 4.1. By selecting suitable ordinates for the y-axis and then plotting the data against time, one can determine whether a particular reaction is first, second, or third order with respect to the concentration of a particular reactant. This graph can also be used to determine the rate coefficient for the reaction. As can be seen from Table 4.1, this method works well if n is an integer and hence if the reaction is very simple reaction. However, if n is other than these, this method becomes complicated.

Table 4.1 Equations for reactions of various orders

order (n)	$\frac{dx}{dt}$	kt	common units for the rate coefficient
0	k	x	$mol\ dm^{-3}\ s^{-1}$
1	$k(a_o-x)$	$\ln(\frac{a_o}{a_o-x})$	s^{-1}
2	$k(a_o-x)^2$	$\frac{2}{a_o(a_o-x)}$	$dm^3\ mol^{-1}\ s^{-1}$
3	$k(a_o-x)^3$	$\frac{2\ a_o - x^2}{2\ a_o/(a_o - x)^2}$	$dm^3\ mol^{-1/2}\ s^{-1}$

4.5 Methods of determining rates of chemical reactions

4.5.1 Dilatometry

4.5.1.1 Introduction

Dilatometer was originally used to measure the thermal expansion or contraction of liquids and solids (104). Polymers are more dense than their corresponding monomers due to reduction in the distance between the monomer units brought about by polymerisation. Therefore polymerisation is usually accompanied by a reduction in volume. Thus, it is possible to use dilatometry to determine the conversion

of monomer to polymer. Starkweather and Taylor (105) were the first to report the use of dilatometry to determine the rates of polymerisation. They investigated the polymerisation of vinyl acetate. Many workers have since used dilatometers to follow the polymerisation of vinyl monomers in bulk, solution, aqueous phase or other media such as NR latex (63, 64, 106, 107, 108).

4.5.1.2 Measurement of volume change during conversion of monomer to polymer

Complete polymerisation of a vinyl monomer can cause a reduction of 20 - 30% of the original volume of the monomer. Tobolsky *et al.* (109) suggested that polymerisation of a vinyl monomer would result in a 15-20% shrinkage, brought about by the exchange of a double bond and van der Waals forces for two single bonds. Nichols and Flowers (110) calculated theoretical values for shrinkage of 26 different vinyl and alkyl monomers by measuring the equivalent volume of monomer molecules using revolving molecular models from Fisher-Hirschfelder-Taylor atom models. They found that there is a hyperbolic relationship between the percent shrinkage and the equivalent volume of revolution. These results were then compared with those obtained experimentally. These observed shrinkages were calculated from the difference between the specific gravity of the monomer and that of polymer:

$$\% \text{ shrinkage} = \frac{\rho_p - \rho_m}{\rho_p} \qquad \text{.....4.21}$$

where ρ_p is the specific gravity of polymer and ρ_m is the specific gravity of the monomer. They found good agreement between the theoretical and observed shrinkages values. It was also shown that the total shrinkage ranged from 3 to 34% when the monomers were polymerised to complete conversion. In any case, one would expect the volume change of a vinyl monomer during a polymerisation reaction to be directly proportional to the total number of monomer molecules that have polymerised.

In order to obtain accurate results, the choice and type of dilatometer for a particular polymerisation reaction is very important. For bulk and solution polymerisations, a simple dilatometer can be used without stirring. For polymerisation of a vinyl monomer in NR latex, particularly

hydrophilic monomers, a special design is necessary to ensure that macroscopic homogeneity between the dispersed particles and the added monomers is maintained during the course of the polymerisation. Further practical aspects of using a dilatometer that must be considered include:

a) precise temperature control,

b) sufficient heat transfer from the reactants but without excess exotherm, so that a constant temperature is maintained in the sample,

c) the necessity of having a measuring capillary of uniform bore.

A temperature fluctuation in the surrounding water bath of $\pm$ 0.1^{o}C is considered to be too large, and will cause significant total volume change. The usual internal diameter of the capillary is 1 to 2 mm.

4.5.2 Gravimetric method

This method is commonly used to follow conversion during polymerisation, particularly for the more volatile monomers which evaporate easily during drying without further polymerisation occurring. The conversion is followed by stopping the polymerisation after a known time and determining the yield. Polymerisation is stopped by the addition of an inhibitor to a weighed sample of the reaction mixture. At zero time, the inhibitor is expected to deactivate the radicals which result from the decomposition of the initiator. Subsequently, the inhibitor is expected to stop the polymerisation by deactivating the growing polymer radicals. The unreacted monomer in the reaction mixture is then removed by drying the mixture to a constant weight. For a monomer having a low boiling point, the drying time required to remove the monomer is short. In this way, no further polymerisation of the monomer occurs and the conversion can be determined accurately. The accuracy of this method is very dependent upon the effectiveness of the inhibitor, both to stop the polymerisation and to ensure that no further polymerisation occurs during the drying stage. According to Flory (101), the inhibitors most commonly used are those molecules which one way or another react with active chain radicals to yield product radicals of low reactivity, or non-radical products. Such an inhibitor is benzoquinone. Using as

little as 0.01% benzoquinone causes total suppression of the polymerisation of styrene and other monomers. Bartlett and Kwart (111) have studied the behaviour of some inhibitors and retarders in the peroxide-initiated polymerisation of liquid vinyl acetate. The inhibitors used were duroquinone, p-, o- and m-dinitrobenzenes, dinitrodurene, 2,2-diphenyl-1-picrylhydrazyl, nitrobenzene, and iodine. They found that duroquinone and 2,2-diphenyl-1-picrylhydrazyl stop one chain per molecule of inhibitor, whereas iodine and nitrobenzene, which are very efficient inhibitors, can stop two chains per molecule. Kice (112) studied the inhibition of the polymerisation of methyl methacrylate and methyl acrylate. The inhibitors used were 2,2-diphenyl-1-picryl hydrazyl, benzoquinone, furfurylidene malononitrile, benzhydriline malononitrile, trinitrotoluene, m-dinitrobenzene, p-nitrotoluene, diphenylamine and sulphur. It was found that benzoquinone was the most efficient in inhibiting the polymerisation of methyl methacrylate initiated by 2,2'-azo-bis-isobutyronitrile polymerisation of methyl methacrylate. The rate coefficients for the aromatic nitro compounds used as inhibitors for vinyl acetate were 10^5 smaller in methyl methacrylate. In this case, the effectiveness of the inhibitors was dependent upon the concentration and nature of the monomer, catalyst, inhibitor, etc.

4.6 Possible mechanisms of free-radical graft copolymerisation

4.6.1 Introduction

A graft copolymer is a polymer which has one or more block-like side-chains bound to the backbone polymer chain by covalent bonds. This is illustrated in Figure 4.6.1, in which A is the repeat unit of the backbone and B is the repeat unit of the graft. The side-chains have a structure which is quite different from that of the main-chain.

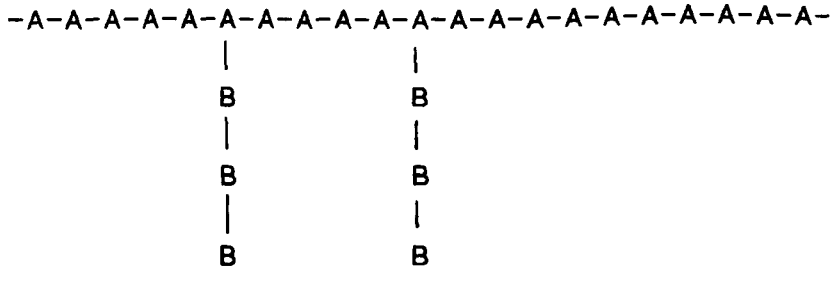


Figure 4.1 Structure of a typical graft copolymer

Therefore a graft copolymer may well form a multiphase material possessing both main-chain and side-chains which could have either polar groups or non-polar groups in their structures. Knowing the structure of both the main chain and side chains, one may predict the physical properties of the material and whether the backbone and branches are thermodynamically compatible or incompatible. The graft copolymerisation of a vinyl monomer on to another polymer is an attractive method for modifying polymer properties. These multiphase polymers could offer unusual combinations of chemical and physical properties, and thus broaden the range of applications of polymers. Because of the randomness of reactions during polymerisation, free-radical graft copolymerisation can also produce homopolymer during the course of the reaction. Therefore the end-product obtained from a graft-copolymerisation reaction can contain both homopolymer and unreacted monomer, as well as the graft copolymer. To obtain high efficiency of grafting (Section 1.4) it is necessary to have a deeper understanding of the possible mechanisms of the reaction, so that one can take steps to minimise the formation of such homopolymers if they are undesirable.

4.6.2 Mechanisms

Quirck (113) has reviewed recent studies on the mechanism of free-radical graft copolymerisation. Let the backbone polymer be represented by P, initiator by I, monomer by M, and any chain-transfer agent by SH. Radicals present in the polymerisation are represented by HX., these include polymer radicals, P. or $P\text{-}(M)_n$. , and growing chain radicals, $\text{-}(M)_n$. In the initiation stage, radicals can be either transferred to the backbone polymer, P , or transferred from an initiator radical, R. , to the monomer, giving the following two possible initiation reactions:

$$R. + P \longrightarrow RP. \quad \text{.....4.22}$$

$$R. + M \longrightarrow RM. \quad \text{.....4.23}$$

In these reactions, R. could be generated according to the reaction 4.1. In the presence of added monomers, both these radical species can react with monomer molecule to produce a growing radical by addition giving the following two possible types of propagation reaction:

$$RP. + n\,M \longrightarrow RP\text{-}(M)_n. \quad \text{.....4.24}$$

$$RM. + n\,M \longrightarrow R\text{-}(M)_{n+1}. \quad \text{.....4.25}$$

In the presence of a reactive backbone polymer such as NR, the growing radicals can attack the backbone polymer by addition through the double bond of the repeat unit as follows:

$$RP\text{-}(M)_n. + P \longrightarrow RP\text{-}(M)_n\text{-}P. \quad \text{.....4.26}$$

$$R\text{-}(M)_n. + P \longrightarrow R\text{-}(M)_n\text{-}P. \quad \text{.....4.27}$$

However, in the presence of a chain-transfer agent, SH , the growing radicals can terminate by the following reactions:

$$RP\text{-}(M)_n. + SH \longrightarrow RP\text{-}(M)_n\text{-}H + S. \quad \text{.....4.28}$$

$$R\text{-}(M)_n. + SH \longrightarrow R\text{-}(M)_n\text{-}H + S. \quad \text{.....4.29}$$

At least some of the following termination reactions will also take place :

$$RP\text{-}(M)_n. + HX. \xrightarrow{\text{combination}} RP\text{-}(M)_n\text{-}XH \quad \text{.....4.30a}$$

$$RP\text{-}(M)_n. + HX. \xrightarrow{\text{disproportion}} RP\text{-}(M)_n\text{-}H + X \quad 4.30b$$

$$R\text{-}(M)_n. + HX. \xrightarrow{\text{combination}} R\text{-}(M)_n\text{-}XH \quad \text{.....4.31a}$$

$$R\text{-}(M)_n. + HX. \xrightarrow{\text{disproportion}} R\text{-}(M)_n\text{-}H + X \quad \text{..4.31b}$$

The sequence of reactions leading to the production of graft copolymer is shown in Equations 4.22 and 4.24, in which $RP\text{-}(M)_n.$ reacts either by addition Equation 4.26), by transfer (Equation 4.28), or by termination (Equations 4.30a and 4.30b). It should be noted that that Equation 4.26 represents a potential crosslinking reaction. In the case when homopolymerisation is the initial process (Equation 4.23), grafting may still occur by addition to the backbone polymer (Equation 4.27) or via termination by combination with a backbone polymer radical (Equation

4.31a), in which X. = P. or P-$(M)_n$. . The reactions which lead to the formation of homopolymer are shown in Equations 4.23, 4.25, 4.29, 4.31a where [X. = R-$(M)_n$.], and 4.31b. The presence of homopolymer would cause heterogeneity in the final product which in turn may lead to undesirable phase separation. Quirck suggests that effective grafting could be obtained by carrying out the graft reaction such that chain transfer to the polymer (Equations 4.28 and 4.29 with SH = PH) is a termination mode.

4.7 Previous investigation of the kinetics of graft copolymerisation of vinyl monomers in NR latex

4.7.1 Using dilatometric methods

At least five reports (63, 64, 106, 107, 108) have been published concerning the use of dilatometry as a technique for determining the conversion of vinyl monomers in NR latex. Allen et al. (104) polymerised hydrophobic monomers such as styrene, methyl methacrylate, and homologues methacrylic esters in NR latex. The polymerisations were carried out at room temperature and above (50-70^{o}C) using either AZBN or persulphate as initiator. Allen et al. started with a latex having a dry rubber content of 5%, used ammonium persulphate (1.6 pphr), and found that the polymerisation rate increased progressively with increasing monomer conversion until it reached a maximum at about 9% conversion, and then decreased rapidly with further monomer conversion. They also observed that, at low monomer concentration, order of the maximum polymerisation rate with respect to initiator concentration was one at low initiator concentration, and became half at higher initiator concentration. They attributed this to a reduction in the relative importance of monomolecular termination brought about by chain- transfer reactions which occurs at low initiator concentrations, which they believed to be unlikely at higher rates of initiation when bimolecular termination predominates.

Allen et al. (104) found ammonium persulphate to be a far more efficient initiator than AZBN. Quantitatively, $f((NH_4)_2S_2O_8)$ / f(AZBN) = 7.5. They claimed the reduced efficiency of AZBN may be a consequence of the high viscosity of the latex producing a cage effect which reduces the effective decomposition rate of AZBN. To some extent, the present author agrees with this explanation.

However, the recombination of the AZBN radicals is believed to be the dominant process as a consequence of the high viscosity of the monomer-swollen rubber phase (Section 2.1.3) rather than decomposition rate of AZBN. As a result, the effective of the initiator radicals capable of initiating monomer became low.

The results of Allen et al. show, that at low conversion of the monomers, the maximum polymerisation rate is higher with low initiator concentrations than with high initiator concentrations. As conversion proceeds, this reverses, and the rate passes through a maximum at about 9% conversion. The decrease in polymerisation rate is probably a consequence of a decrease in monomer concentration, the extent of the decrease being much greater at low levels of initiators.

Cooper and Vaughan (107) investigated the graft copolymerisation of methyl methacrylate in NR latex using dilatometry for low monomer concentration. Based on kinetic considerations, they criticised the mechanism of grafting of methyl methacrylate to NR proposed earlier by Kobryner and Banderet (114). Based on the characterisation of the products, Kobryner and Banderet (114) had proposed the following mechanism, according to which grafting occurs only by a termination reaction between a rubber macro radical, P. , and a growing polymethyl methacrylate chain, $R-(M)_n$. :

Initiation:

$$I \longrightarrow R. \quad \text{.....} \quad 4.32$$

$$R. + PH \longrightarrow RH + P. \quad \text{.....} \quad 4.33$$

Propagation:

$$R. + M \longrightarrow RM. + n\,M \longrightarrow R-(M)_n. \quad 4.34$$

Termination:

$$R-(M)_n. + R-(M)_m. \begin{cases} \xrightarrow{\text{combination}} R-(M)_{n+m}R & \text{.....} \quad 4.35 \\ \xrightarrow{\text{disproportion}} R-(M)_n + R-(M)_n & \quad 4.36 \end{cases}$$

$$R\text{-}(M)_n\cdot + P\cdot \longrightarrow R\text{-}(M)_n\text{-}P \quad \ldots\ldots\ldots\ldots 4.37$$

$$P\cdot + P\cdot \longrightarrow P\text{-}P \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.38$$

Cooper and Vaughan (107), however, suggested that graft copolymers are obtained, not only from the reaction between rubber radicals (P.) and growing polymer radicals $R\text{-}(M)_n\cdot$ (Equation 4.37), but also from polymerisation which commences from rubber radicals (Equation 4.24), and the reaction of growing polymer chains with rubber molecules as follows:

$$RM\cdot + P \longrightarrow RMP\cdot \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.39$$

Burfield and Ng (63) have carried out graft copolymerisations of a hydrophilic monomer, methacrylamide, in NR latex. The rates of polymerisation were measured dilatometrically. They found that, up to 70% conversions, the rate of polymerisation was first-order with respect to monomer concentration, i.e.,

$$RP = k\,[M]_o \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.40$$

where k was the gradient of the first-order plot and $[M_o]$ was the initial monomer concentration (mol/l). Burfield and Ng (63) did not specify whether the unit was expressed interms of the volume of aqueous phase or the whole latex. The other interesting aspect of their results is that the rate of polymerisation increased markedly with increasing concentration of rubber particles in the reaction system. They suggested the following possible explanations for this:

(i) non-rubber constituents, such as cations or anions, catalyse the decomposition of the initiator used, i.e., potassium persulphate,

(ii) reactive groups in rubber, such as hydroperoxides, which can act as additional sources of free radicals, are present in the rubber;

(iii) in some respects, the rubber particles act as inert filler, and hence effectively increase the monomer and initiator concentration in the aqueous phase of the reaction system;

(iv) physical effects, such as the high viscosity of the polymer contained in the latex.

Burfield and Ng (64) further investigated the influence of both the rubber and the non-rubber components on the rate of polymerisation of methacrylamide in NR latex. They reported that the rate of polymerisation was directly proportional to the rubber concentrations up to 37%, i.e., that

$$R_p = k\,[RH][M] \quad \text{.....4.41}$$

where RH is the rubber hydrocarbon concentration, g/l latex. The first-order dependence of polymerisation rate on rubber hydrocarbon concentration is not easily explained by the above considerations. Hydroperoxide groups, ROOH, present on the maker molecules might act as an initiator. This would be expected to give rise to half-order dependence of rate of polymerisation on hydroperoxide concentration, and thus upon rubber hydrocarbon concentration. Burfield and Ng reported the presence of a reducing agent , Fe^{2+}, in the latex which could form a redox system with the hydroperoxide as follows :

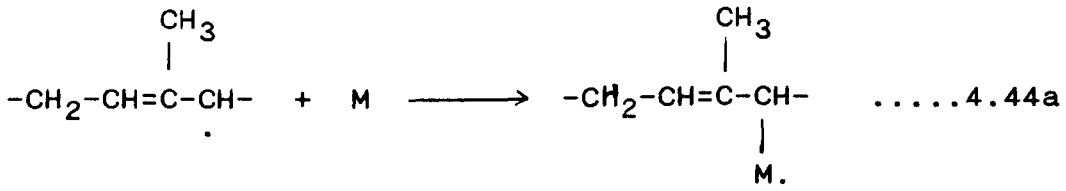
$$Fe^{2+} + ROOH \xrightarrow{k_d} Fe^{3+} + RO. + OH^- \quad \text{..4.42}$$

Since increasing the latex concentration will increase the concentration of both metal ion and rubber hydrocarbon, the rate of initiation would be second-order with respect to rubber hydrocarbon concentration. Therefore, the overall rate of polymerisation would be first-order with respect to rubber hydrocarbon concentration. Another explanation suggested by them is that the presence of non-rubber components, such as amines, might bring about termination reactions that are first-order with respect to radical concentration

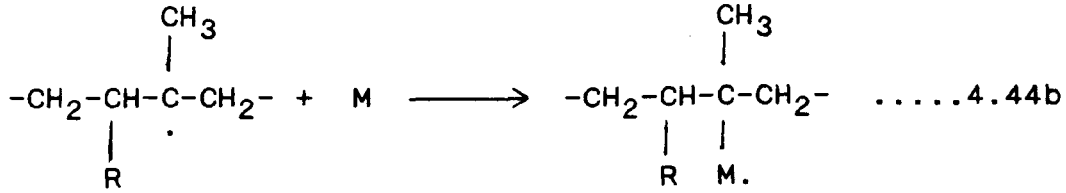
$$M_n. + N \longrightarrow MH + S \quad \text{.....4.43}$$

where N is the non-rubber constituent, such as an amine, and S is a species which is incapable of re-initiating polymerisation. As a consequence, the overall rate of polymerisation would be first-order with respect to rubber hydrocarbon concentration.

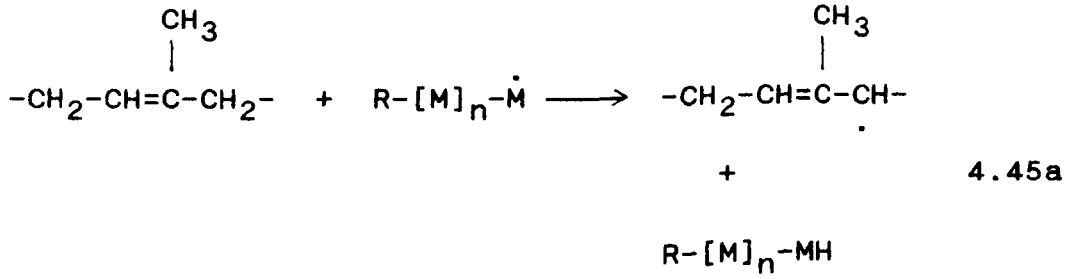
Burfield and Ng (64) further suggest that the grafting mechanism involves the addition of monomer molecules to a rubber radical (reactions 4.44 a and 4.44 b) rather than the addition of a polymeric radical to the rubber molecule 4.45 a and 4.45 b,



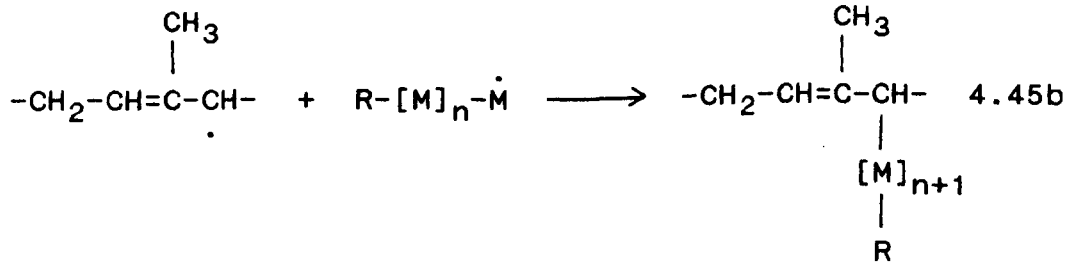
.....4.44a



.....4.44b



4.45a



4.45b

where R is the initiator radical attached to the polymer backbone. They also reported that adding sodium dodecyl sulphate (SDS) to the reaction system decreased slightly the overall polymerisation rate as in accordance with the equation

$$RP = k\,[K_2S_2O_8]^{0.5}\,[MAA]\,[SDS]^{-0.07} \quad \ldots\ldots\ldots\ldots 4.46$$

They stated that, for hydrophilic monomers, particularly acrylamide, the locus of polymerisation is the aqueous phase rather than interior of the rubber particles; in other words, no polymerisation is brought about by an emulsion reaction, although soap is present.

Karnika de Silva et al. (108) also used dilatometry to measure the rate of polymerisations of methyl methacrylate in deproteinized NR latex using an organic redox initiator system. They reported that, during polymerisation, a substantial increase in the temperature of the polymerisation mixture occurred. For example, using the reaction system for both MG 49 and MG 23 latices, the temperature increased about 50°C within approximately 30 minutes of the start of the polymerisation. They used the volume changes to determine conversion of monomer to polymer, and hence rates of polymerisation. However, in the view of the present author, the polymerisation rates that they presented are questionable because the dilatometric technique is not suitable if the temperature of the reaction system fluctuates to any appreciable extent, as discussed in section 4.5.1.2.

4.7.2 Using gravimetric methods

A gravimetric method has frequently been used to determine the final conversion of vinyl monomers polymerising in NR latex. Cockbain et al. (115) determined the conversion of methyl methacrylate polymerised in NR latex, initiated by γ-irradiation and by a redox system. In the case of initiation by the redox system, the reaction mixture was allowed to stand for a minimum of 6 hours in order to obtain > 92% conversion. The conversion was calculated by comparing the total solids content of the latex before and after polymerisation. The total solids content was determined by drying samples of the latex at 60°C and finally heating to a constant weight at 100°C. Cockbain et al. did not mention if an inhibitor was added to the samples prior to the determination. Mazam et al. (4) used the gravimetric method to determine the conversion of three hydrophilic monomers when polymerised in NR latex, as described in Section 2.2.3. The method used was similar to that of Cockbain et al. (115).

In the early investigation of the polymerisation of four hydrophilic monomers in NR latex by the present author (6), a gravimetric method was used to follow the course of the

reactions. The reaction rates were determined by measuring the total solids content of the latex before, during and after polymerisation. The total solids contents were determined by heating the samples at 70°C for 10-12 minutes. An inhibitor (hydroquinone) was added prior to this heating. Finally, the samples were vacuum dried at 80°C for 3-3.5 hours. The conversion at time t is given by the following equation:

$$\% \text{ conversion at time } t = \frac{[\text{TSC at } t=t] - [\text{TSC at } t=0]}{[\text{TSC}^{x)}] - [\text{TSC at } t=0]} \times 100 \quad \ldots\ldots 4.46$$

where $\text{TSC}^{x)}$ is the theoretical total solids content at 100% coversion. No investigation was made of the effectiveness of the inhibition procedure. However, unexpectedly high initial conversions were obtained (80% for hydroxyalkyl acrylates and about 35-45% for hydroxyalkyl methacrylates, in less than ten minutes reaction. These conversions were much higher than expected, particularly as the monomers used were not purified and still contained inhibitor. The presence of an inhibitor should result in an initial induction period in the conversion-time curves, particularly at low polymerisation temperatures, e.g., 20°C, even though the initiator used was a powerful inorganic redox system. Therefore questions arise as to whether the inhibitor used was really capable of inactivating initiator radicals and growing polymer radicals completely, or whether further polymerisation had taken place during the drying process.

Chapter 5

Characterisation of graft copolymers

5.1 Introduction

The characterisation of a polymer is very important, as it provides useful information concerning the fundamental properties of the polymer, such as molecular structure and physical properties. The molecular structure can be characterised by several methods such as relative molecular mass, elemental analysis, spectroscopy, gas chromatograpy, x-ray diffraction and optical methods. The physical properties can be characterised by several methods such as solubility, crystallinity, melting point, glass-transition temperature, density, ageing test and mechanical properties (116). These methods for characterisation of molecular structure and physical properties are interrelated to each other. Therefore the scope of characterisation can be relatively narrow or extremely broad, depending upon the objective of the characterisation and the properties of the polymer in question.

5.2 Product of graft-copolymerisation reactions

Inagaki and Tanaka (117) claim that it is unavoidable that the products of graft copolymerisations contain polymeric impurities, presumably due to random polymerisation reactions. As mentioned in Section 4.6.1, the product of a graft copolymerisation may contain not only a true graft copolymer but also an unreacted monomer, homopolymer, and unreacted backbone polymer. Inagaki and Tanaka (117) further state that the isolation of a true graft copolymer from the crude graft product is the most important task to be performed in advance of the molecular characterisation. This separation may be very difficult, so that the percentage of grafting may well be an apparent value because of imperfect isolation. If isolation is imperfect, this may nullify any conclusions which have been drawn concerning the reaction mechanism. The proportions of the components of a crude graft copolymer depend upon the original grafting system, such as the nature of the monomer, initiator, and backbone polymer. An appropriate method for isolating the true graft copolymer has to be devised for each different grafting system employed. However, there are several general types of procedure which can be used, singularly or collectively, to separate the

graft copolymer from the crude product. A successful isolation of unreacted monomer, true graft copolymer, homopolymer and unreacted backbone polymer from a crude product would enable one to determine the efficiency of grafting, the percentage of graft copolymer and the degree of grafting.

5.3 Removal of impurities from crude graft copolymer

To determine the efficiency of grafting, the percentage of graft copolymer, and the degree of grafting, one should isolate unreacted monomer from the crude product. Ceresa (12), Inagaki and Tanaka (117), Ikada(118) and Ceresa (119), have outlined the characterisation of graft copolymers from the crude product. However, none of them has mentioned a method of removing unreacted monomer from the crude product. Presumably, they assume that the monomer has been completely converted to polymer. If not, then their characterisations are confined to determining the percentage of graft copolymer, and to studying the possible mechanism of reaction only, and do not include the determination of the efficiency and degree of grafting.

5.3.1 Separation of unreacted monomer

There are many methods that can be used to determine the unreacted monomer in the crude product such as the dilatometric and gravimetric methods described in Section 4.5.1.2. The dilatometric method, however, is best used for determining the conversion during a polymerisation reaction. It is not practical to measure the unreacted monomer at the end of the reaction by using the dilatometric method because of difficulties of maintaining the temperature constant to within $0.1^{o}C$ for a long period of polymerisation. The gravimetric method, however, is more convenient to use, particularly for those monomers which have low boiling points, and for which further polymerisation during the drying process can be avoided. However, for monomers which have high boiling points, which usually include hydrophilic monomers, special attention must be given to avoiding polymerisation during a prolonged drying. Further polymerisation can be avoided by adding an effective inhibitor/antioxidant to the crude product, and by using a good vacuum drying system to evaporate the unreacted monomer as rapidly as possible.

5.3.2 Isolation of graft copolymer

Ikada (118) has outlined two methods for separating the graft copolymer from the crude product, namely, selective precipitation and solvent extraction.

5.3.2.1 Selective precipitation

Basically, this technique involves precipitating only one homopolymer from a solution of the crude product by adding an appropriate precipitant. This method is straightforward in principle. However, some problems may occur if the grafted homopolymer molecules collapse to form the core of micelle into which homopolymer may be trapped, as illustrated in Figure 5.1. If this occurs, this method cannot give a true separation of the polymer.

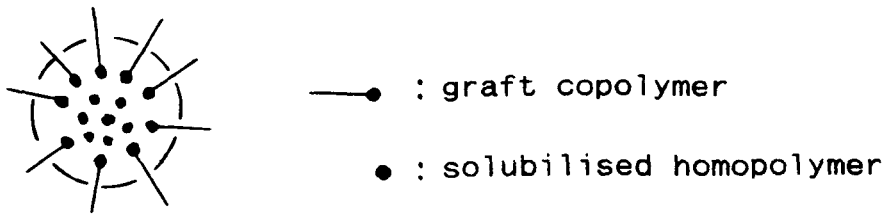


Figure 5.1 Schematic representation of emulsification of homopolymer by graft copolymer (118)

Using a co-precipitation technique, however, Ikada (118) has been able to separate homopolymer from the crude product. Here, the homopolymer (poly-A) and the graft copolymer (poly-A-B graft) are first coprecipitated together keeping the unreacted poly-B in the solution. For this purpose, the solubility of the poly A-B graft should differ sufficiently from that of poly-B. Poly-B may then be removed from the solution. The poly-A is then removed by precipitating it with an appropriate non-solvent which keeps the poly-A-B graft copolymer in the solution. Using this technique, Ikada was able to separate homopolymers of polystyrene (PS) and polyvinyl acetate (PVAc) from a polystyrene-polyvinyl acetate graft copolymer (poly-PS-PVAc graft copolymer).

5.3.2.2 Selective extraction methods

Selective solvent extraction has been used to separate the components of the mixtures obtained from graft-copolymerisation reactions. This method is simple but time-consuming if separation is to be efficient. It is the most

widely-used method. To obtain a pure graft copolymer free of homopolymer, two extractions are required. However, sometimes the graft copolymer may be co-dissolved with one of the homopolymers in a "micelle" type system. If this is the case, then an extraction procedure cannot be used.

Ikada (118) studied the separation of the components of the mixture obtained from the graft copolymerisation of polyvinyl acetate and styrene. The separation is dependent upon the dispersability of the graft copolymer in the solvent used. If the graft copolymer became finely dispersed, separation was not possible. Therefore a solvent had to be found in which the graft copolymer did not form a fine dispersion. The results with acetone and methanol are shown in Table 5.1. Acetone is a solvent for PVAc and swells PS, whereas the pure graft copolymer is completely dispersed. Methanol, however, is a solvent for PVAc but a non-solvent for PS, whereas the pure graft copolymer is not dispersed and therefore not dissolved away. Thus, if

Table 5.1 Dispersability of pure PVAc-Styrene graft copolymer at room temperature

solvent	PVAc[a)]	PS[b)]	graft copolymer
acetone	soluble	swollen	dispersed
methanol	soluble	insoluble	not dispersed

a) = $\bar{M}_n = 1.14 \times 10^5$

b) = $\bar{M}_n = 1.11 \times 10^5$

the solubility of one component of the crude graft copolymer differs significantly from that of the other component, the extraction method can be used to separate the components of the crude graft copolymer. Ceresa (12, 119) divides extraction methods into three techniques, namely,

a) selective solution,

b) fractional elution,

c) combinations of elution and precipitation.

(a) Selective elution

This method involves selecting solvents which are capable of dissolving only one of the polymer species, being a non-solvent for the others. Under these conditions, selective elution offers good separation into two, if not three, fractions. The rate of extraction is dependent upon the extractability of the homopolymer in a particular solvent.

(b) Fractional extraction

The components of crude graft copolymer are extracted using successive mixtures of non-solvent and solvent, either cold or at an elevated temperature. The successive mixtures progressively contain greater proportions of the solvent for the polymeric species. This technique has been successfully used to separate the respective homopolymers of a block copolymer of ethylene and vinyl acetate.

(c) Combined extraction and precipitation

Ceresa (12) claimes this to be the most efficient method of separation. This method is useful, particularly if a solvent can dissolve free homopolymer present in the crude product, but cannot dissolve either of the other two fractions. Extraction is followed by fractional precipitation to separate the remaining homopolymers from the product. For example, isolation of free rubber and free polystyrene from a crude graft can be achieved by first extracting the free rubber with petroleum ether (60-80^{o}C), followed by fractional precipitation of the residue in benzene solution with methanol as precipitant.

5.4 Previous characterisations of crude graft copolymers of NR

5.4.1 Introduction

Many graft copolymers of NR have been prepared and their characterisations attempted. Hence there are many reported

studies of the separation of crude NR graft copolymers. These characterisations have been either simple or complex, depending upon the nature of the second monomer used. NR would be difficult to separate from non-polar polymers with similar solubilities. Therefore special techniques are employed to separate such homopolymer from the product. A crude NR graft copolymer prepared by polymerisation of hydrophilic monomers in NR, on the contrary, might be easier to separate from the reaction mixture, because its solubility would differ significantly from that of NR. However, there are other factors which have to be taken into considerations, particularly the linearity of the homopolymers. If the homopolymers crosslink during the polymerisation reaction, it is highly unlikely to be possible to separate any of the components of the mixture.

5.4.2 Characterisation of graft copolymers prepared by grafting hydrophobic monomers to NR

Merret (120) used a fractional precipitation technique to characterise graft copolymers prepared by polymerising either methyl methacrylate or styrene in NR in benzene solution using benzoyl peroxide initiator at 25-70^{o}C. The crude graft copolymer product was first diluted with benzene to 1% total polymer concentration. The free NR, graft copolymer and free polymethyl methacrylate (PMMA) were separated by incremental addition of methanol. The free NR flocculated initially, followed by the graft copolymer, and finally the free PMMA. There was a reasonable interval between the precipitation of the free NR and that of the graft copolymer, and also between the precipitation of the graft copolymer and that of the free PMMA (121). In the case of the NR/PMMA graft copolymer system, the free NR was flocculated completely by adding up to 23% of methanol. The graft copolymer and the free PMMA remained in solution. The precipitated free NR was separated by centrifuging. Further addition of 100-120% methanol to the solution resulted in an opaque and stable sol. This sol was not affected by the presence of an ionic compound such as calcium chloride. Addition of further methanol to 183%, however, destabilised the sol. This metastable sol was easily flocculated by adding a minute amount of calcium chloride. The flocculated sol was deduced to be an NR/PMMA graft copolymer. Further addition of methanol, up to 500% of the original solution, flocculated the free PMMA, which was collected by centrifuging. The

amounts of methanol required to separate each of the polymer fractions are summarised in Table 5.3. The above method failed to work satisfactorily for the NR/polystyrene (PS) graft copolymer system, because the free PS collapsed earlier than did the graft copolymer, and no sol of the NR/PS graft copolymer was formed unlike in the case of NR/PMMA graft copolymer. To delay the collapse of the free PS, methyl ethyl ketone (MEK) was added to the NR/PS graft solution in the ratio of 2:1 by volume. In fact, MEK also enhances the insolubility of the free NR,

Table 5.3 Amounts of methanol required to precipitate each of the polymer fractions from 10 ml of a 1% benzene solution of crude NR/PMMA graft copolymer

methanol (ml)	fraction of polymer precipitated
0 - 2.3	free rubber
2.3 - 2.4	no precipitate
2.5 -18.3	NR/PMMA graft
18.3-18.9	no precipitate
19.0-50.0	free PMMA

and so only a little methanol is required to precipitate it. Under those conditions, the free NR fraction was precipitated by adding 2% methanol. The graft copolymer was isolated by further addition of 2-5% methanol without calcium chloride.

Allen (123) believes that this fractionation method does not effectively separate the components of the mixture produced by a graft copolymerisation reaction. The fractionation method also appears to separate the polymer into fractions of different relative molecular mass (RMM). The RMM of the NR (75-330 x 10^3) and the PMMA (11-100 x 10^3) obtained were lower than would be expected for those polymers. Apparently the graft copolymer can solubilise the free PS. Further investigation showed that a mixture of petroleum ether and benzene can extract the free NR from the crude graft copolymer. Allen and Merret (124) therefore used a combination of extraction and fractional precipitation methods to separate the graft copolymer. The procedure was first to extract the free NR using a 50/50

mixture of benzene and petroleum ether (80/100°C) overnight, followed by heating at 40°C for half an hour. The insoluble materials were then dissolved in benzene, and separated into graft copolymer and free homopolymer by a methanol precipitation method.

Angier and Watson (125) used selective solvent extraction to separate the free NR and PMMA from the graft copolymer prepared by masticating NR in the presence of vinyl monomers. The free NR was extracted using petroleum ether (60-80°C) for 4-14 days. The free PMMA was extracted using acetone. In the case of the free PS, the masticated rubber was first moulded at 140°C for 60 minutes with 1.5% di-tert-butyl peroxide. The free PS was then extracted using carbon tetrachloride, dried down and redissolved in chloroform. Angier and Turner (126) employed shock precipitation of the solution into methanol to separate a NR/PMMA graft copolymer. This was followed by the separation of polymer fractions by first cold extracting for 5 days with petroleum ether (60-80°C) to separate the free NR, and then cold extracting for 5 days with acetone to separate the PMMA. Ghosh and Sengupta (127) also used this technique with slight modification to separate the free NR, NR/PMMA graft copolymer, and free PMMA fractions from the crude graft copolymers prepared from NR and methyl methacrylate in benzene solution. Turner (128), however, extracted the free NR using benzene only for 7 days at 25°C. He believed that this method achieved almost complete separation of the free NR.

5.4.3 Characterisation of graft copolymers prepared by grafting hydrophilic monomers to NR

Burfield and Ng (63) attempted to characterise the crude graft copolymer prepared by polymerising methacrylamide (MAA) in NR latex. The diluted grafted latex was coagulated using formic acid solution until flocculation became visible, and then centrifuged at 3,000 r.p.m. for 5 minutes to separate the clear serum containing polymethacrylamide (PMAA) from the flocs containing grafted and ungrafted NR. The free PMAA in the serum was recovered by precipitation with acetone, followed by drying at room temperature. The free NR, however, could not be isolated from the crude graft copolymer, as it proved difficult to dissolve.

Mazam et al. (4) characterised the graft copolymer prepared by polymerisation of hydrophilic monomers in NR latex initiated by gamma radiation (Section 2.2.3). Films of the grafted latex were prepared by drying on a glass plate at 25°C and then by vacuum-drying for 2 hours, followed by heat treatment at 80°C. The gel fraction of the films and the free homopolymers, were isolated by a selective extraction technique. In the case of the separation of the gel fraction, the dried films were extracted using boiling toluene for 20 hours. The free homopolymers, such as polyhydroxyethyl methacrylate (PHEMA) and polydiethylaminomethyl methacrylate, were extracted with boiling methanol for 5 days.

Dalimunthe (6) has attempted to characterise graft copolymers prepared by polymerisation of hydrophilic monomers in NR latex (Section 2.2.3). Preliminary investigation showed that undried polymers such as PHEMA and polyhydroxypropyl methacrylate (PHPMA) dissolve in a 1:1 mixture of acetic acid and IMS, whereas polyhydroxyethyl acrylate (PHEA) and poyhydroxypropyl acrylate (PHPA) dissolve in but-1-ol. These results were based on observations in which the homopolymers were prepared by homopolymerisation of the appropriate monomers in aqueous solution. It would be expected that the presence of divinyl impurities in the monomer (e.g., ethylene glycol dimethacrylate) would produce an insoluble crosslinked gel. Further studies on the polymerisation of the individual monomers are necessary to establish whether or not such crosslinking takes place.

Chapter 6

Materials, Apparatus and Experimental Procedures

6.1 Mechanical stability of NR latex

6.1.1 Materials

6.1.1.1 NR latex

A high-ammonia substage NR latex concentrate supplied by LRC Products Ltd., London, was used without modification. The substage latex was used because it contains less non-rubber materials than normal high-ammonia latex. It was expected that grafting would be more effective in the presence of low non-rubber materials than in the presence of high non-rubber materials. The properties of the latex were determined in duplicate. The average values are recorded in Table 6.1. The total solids content (TSC), dry rubber content (DRC), alkalinity, potassium hydroxide number (KOH No.), volatile fatty acids number (VFA No.), and mechanical stability time (MST) were determined using procedures described in B.S 1672:1972.

Table 6.1 Properties of the substage NR latex

property	batch				
	A	B	C	D	E
pH	11.23	11.25	10.56	10.60	10.39
total solids content,%	60.75	60.23	60.62	60.85	60.87
dry rubber content,%	59.87	59.39	59.97	59.99	60.02
volatile fatty acid number (VFA No.)	0.02	0.02	0.01	0.03	0.03
alkalinity, g ammonia per 100 g water	1.85	1.88	1.90	1.69	1.77
potassium hydroxide number (KOH No.)	0.47	0.49	0.51	0.47	0.47
mechanical stability time, seconds	1140	1020	983	1360	1370
odour	N	N	N	N	N
colour	W	W	W	W	W

N) = normal; W) = white

6.1.1.2 Non-ionogenic hydrophilic monomers

The monomers were used as received without purification, as previous work had showed this to be impractical (Section 9.11.1). The purities reported here are quoted from the data sheets (139-142) and from information supplied directly by B.P.

6.1.1.2.1 Bisomer HEA (2-hydroxyethyl acrylate)

Bisomer HEA was supplied by B.P. Chemicals. Bisomer HEA is a technical grade having the following composition:

2-hydroxyethyl acrylate	94%	(minimum)
acrylic acid	0.3%	
diester (as ethyleneglycol diacrylate)	0.5%	(maximum)
water content	0.5%	(maximum)
inhibitor (p-methoxy phenol)	0.02%	(minimum)
di & higher oxides of di- or tri-ethyleneglycol acrylate	remainder	

In this work, Bisomer HEA is referred to as HEA. The monomer has a relative density at 20°C of 1.1076, and a boiling point at 5.00 mm Hg of 82°C.

6.1.1.2.2 Bisomer HPA (2-hydroxypropyl acrylate)

Bisomer HPA was supplied by B.P. Chemicals. Bisomer HPA is a technical grade having the following composition:

hydroxypropyl acrylate	94%, being 80% as 2-hydroxypropyl acrylate and 20% as 2-hydroxy-1-methyl-ethyl acrylate
acrylic acid	0.3%
diester (as propyleneglycol diacrylate)	1.0% (maximum)
water content	1.0% (maximum)
inhibitor (p-methoxy phenol)	0.02%
di & higher oxides of ethylene glycol acrylate	remainder

In this work, Bisomer HPA is referred to as HPA. The monomer has a relative density at 20°C of 1.054, and a boiling point at 3.75 mm Hg of 85°C.

6.1.1.2.3 Bisomer HEMA (2-hydroxyethyl methacrylate)

Bisomer HEMA was supplied by B.P. Chemicals. Bisomer HEMA is a technical grade having the following composition:

2-hydroxyethyl methacrylate.....	96%	
methacrylic acid (MAA).....	0.3%	
diester (as ethyleneglycol di-methacrylate).....	0.5%	(maximum)
water content.....	1.0%	(maximum)
inhibitor (p-methoxy phenol).....	0.02%	
di & higher oxides of ethyleneglycol methacrylate.....	remainder	

In this work, Bisomer HEMA is referred to as HEMA. The monomer has a relative density at 20°C of 1.0700, and a boiling point at 2.27 mm Hg of 82°C.

6.1.1.2.4 Bisomer HPMA (2-hydroxypropyl methacrylate)

Bisomer HPMA was supplied by B.P. Chemicals. Bisomer HPMA is a technical grade having the following composition:

hydroxypropyl methacrylate.....	96%, being 80% as 2-hydroxypropyl methacrylate and 20% as 2-hydroxy-1-methyl ethyl methacrylate.
methacrylic acid (MAA).....	0.3%
diester (as propyleneglycol di-methacrylate).....	0.4%
water content.....	1.0% (maximum)
inhibitor (p-methoxy phenol).....	0.02%
di & higher oxides of ethyleneglycol methacrylate.....	remainder

In this work, Bisomer HPMA is referred to as HPMA. The monomer has a relative density at 25°C of 1.0660, a boiling point at 7.99 mm Hg of 92°C, and a solubility in aqueous solution at 25°C of 130 g/kg water (11.5% w/w). The other three monomers are miscible with water in all proportions. At higher concentrations, a two-phase mixture is formed. The monomer was frequently added to NR latex as such mixture. High concentrations were frequently used in order to maintain a constant initial total solids content throughout much of this work.

6.1.1.3 Other materials

Other materials used throughout this work, including that described in Sections 6.2, 6.3, 6.4 and 6.5, are given in Table 6.2.

6.1.2 Apparatus

6.1.2.1 Klaxon stirrer

The Klaxon stirrer is usually used for determination of the mechanical stability time (MST) of NR latex in accordance with B.S. 1672: 1972. A diagram of the apparatus is shown in Figure 6.1. The apparatus consists of a polymethyl methacrylate cup and a stainless steel stirrer. The stirrer was driven by a high-speed Klaxon motor, Type HM 5 uB2, made by Klaxon Ltd. The speed of the stirrer is indicated by three reeds which vibrate violently at 13,800; 14,000 and 14,200 r.p.m. respectively. The stirrer speed is adjusted using the motor speed control (Figure 6.1) so that it rotates at 14,000 $\pm$ 200 r.p.m.

The distance between the base of the stirrer disc and the base of the cup is fixed at 13$\pm$1 mm. Adjustment is made by means of a cylindrical slip gauge and the locking rings. The method use for determination of MST was a slight modification of that specified in B.S.1672:1972, and was as follows:

(i) The B.S. method requires that the latex should be diluted to 55.0 $\pm$ 0.2% TSC. If the alkalinity is above 1.0% NH_3, a 1.6% aqueous ammonia solution should be used. In this experiment, however, to keep the TSC constant at about 55.0 $\pm$ 0.2% and to avoid variation of the ammonia content of the samples when different levels of each of the monomers were added, distilled water was used instead of ammonia solution.

(ii) The diluted latex was warmed with gentle stirring to about 36 - 37^{o}C. The empty cup was warmed by placing in a 40^{o}C air oven in order to maintain the temperature of the samples at 35 $\pm$ 1^{o}C, and to avoid heat loss during weighing and transfer of the samples into the test cup.

Table 6.1 Other materials used thoroughout this work, including that described in Sections 6.2, 6.3, 6.4 and 6.5.

material		purity (%)	supplier	form in which supplied	abbreviation	how used
trade name	chemical name					
Texofor FP-300	x)	ND	ABM Chemicals Ltd.	solid	-	as received
Texofor A-60	xx)	ND	ABM Chemicals Ltd.	solid	-	as received
-	potassium persulphate	99.5	Fluka	solid	-	as received
-	sodium metabisulphite	97	Aldrich Chemical Ltd.	solid	-	as received
-	sodium lauryl sulphate	99.5	BDH Chemicals Ltd.	solid	SLS	as received
-	n-dodecane	99	Aldrich Chemical Ltd.	liquid	-	as received
-	potassium oleat	ND	Fisons Scientific Apparatus	paste	-	as received
-	hydroquinone	98.5	Aldrich Chemical Ltd.	solid	-	as received
-	2,2-diphenyl-1-picryl-hydrazyl hydrate	98	Aldrich Chemical Ltd.	solid	DPPH	as received
-	4-tert-butylcatechol	98	BDH Chemical Ltd.	solid	-	as received
Galvinoxyl	2,6-di-tert-butyl-[3,5-di-tert-butyl-4-oxo-2,5-cyclohexa-diene)-p-tolyloxy]	99	Aldrich Chemical Ltd.	solid	-	as received
Flectol H	2,2,4-trimethyl-1,2 dihydroquinoline	ND	Monsanto Chemicals Ltd.	solid	-	as received
Nonox DPPD	N,N'-diphenyl-p-phenylene diamine	ND	ICI Ltd.	solid	-	as received
Nonox B	an acetone-diphenyl-amine condensation product	ND	ICI Ltd.	solid	-	as received
Nonox AN	phenyl-alpha-napthyl-amine	ND	ICI Ltd.	solid	-	as received

Nonox DN	ND	ND	ICI Ltd.	solid	-	as received
Flexzone 3-C	N-isopropyl-N'-phenyl-p-phenylene diamine	ND	UniRoyal	solid	-	as received
Nonox EXN	ND	ND	ICI Ltd.	solid	-	as received
Antioxi-dant 2246	2,2'-methylene bis(4-methyl) 6-tert-butyl phenol	ND	Anchor Chemicals Ltd.	solid	-	as received
Santoflex AW	6-ethoxy-2,2,4-trimethyl-1,2-dihydro-quinoline	ND	Monsanto Chemicals ltd.	solid	-	as received
Nonox WSL	ND	ND	ICI Ltd.	solid	-	as received
silicone high-vacuum grease	ND	ND	Dow corning	paste	-	as received
industrial methylated spirit (IMS)	a mixture of ethanol (90%), methanol (9%) and water (1%)	99	Charles Tennant & Co.	liquid	IMS	as received
-	acetic acid	99.8	Aldrich Chemical Ltd.	liquid	-	as received
-	tetrahydrofuran	99	Aldrich chemical Ltd.	liquid	THF	as received
petroleum ether	ND	ND	Aldrich chemical Ltd.	liquid	PE	as received
-	toluene	99.9	BDH Ltd.	liquid	-	as received
-	allyl alcohol	99	Aldrich chemical Ltd.	liquid	-	as received
-	sodium hydroxide	96	Fisons Scientific apparatus	pearl	-	as received
-	4,4'-azobis(4-cyanovaleric acid)	75	Aldrich chemical Ltd.	solid	-	as received
-	sulphur	98.8	Anchor chemical Ltd.	solid	-	as received
-	dicumyl peroxide	99	Hercules Ltd.	solid	-	as received
-	tetramethyl thiuram disulphide	99	Bayer Ltd.	solid	TMTD	as received

-	n-cyclohexyl-2 benz-thiazole sulphenamide	99	Bayer Ltd.	solid	CBS	as received
Pristerene 4901	a mixture of stearic acid (48%), palmitic acid (48%) and linoleic acid (2%)	-	Ellis & Everard Chemicals Ltd.	solid	-	as received
-	zinc oxide	99	BDH Ltd.	solid	-	as received
-	isooctane	99	BDH Ltd.	liquid	-	as received
-	calcium nitrate	99	Fisons Scientific Equipment	solid	-	as received
-	ammonium acetate	98	BDH Chemicals Ltd.	solid	-	as received
-	ferric chloride hexa-hydrate	98	BDH Chemicals Ltd.	solid	-	as received
-	magnesium chloride hexahydrate	98	Hopkin & Williams Ltd.	solid	-	as received
-	zinc chloride	95	BDH Chemicals Ltd.	solid	-	as received
-	calcium chloride hexa-hydrate	98	BDH Chemicals Ltd.	solid	-	as received
-	lithium chloride	98	Hopkin & Williams ltd.	solid	-	as received
-	potassium chloride	99	BDH Chemicals Ltd.	solid	-	as received
-	barium chloride di-hydrate	99	BDH Chemicals Ltd.	solid	-	as received
-	cethyltrimethylammo-nium bromide	98	BDH Chemicals Ltd.	solid	-	as received
-	hydrochloride acid	37	Aldrich Chemicals Ltd.	liquid	-	as received
-	polyvinyl methyl ether	50	Basf Ltd.	liquid	PVME	as received
Dow corning releasel 66 emulsion	ND	ND	Hopkin & Williams Ltd.	paste	-	as received

-	a mixture of equal volumes of IMS with aqueous acetic acid (10% v/v).	-	-	liquid	IMSA	-

x) : a fatty-alcohol ethoxylate containing *p*-octyl alcohol as hydrophobe base, and HLB value: 17.1

xx): a fatty-alcohol ethoxylate containing a mixture of cetyl and oleyl alcohols as hydrophobe base, and HLB value: 18.3

ND : not disclosed

1. Vibrating reeds
2. Electric motor
3. Stirrer shaft
4. Stirrer disk
5. Test cup
6. Platform
7. Locking nots
8. Speed control
9. Switch on/off

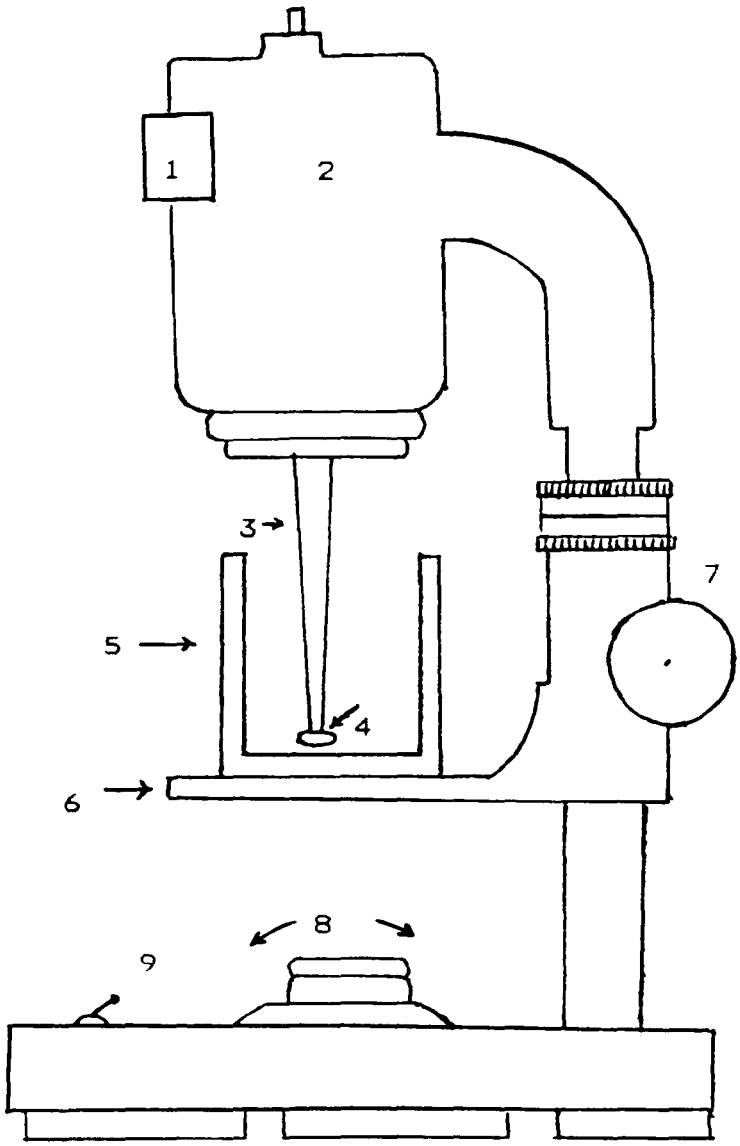


Figure 6.1 Klaxon stirrer for mechanical stability time (MST) tests

(iii) The warmed and diluted latex should be filtered through a stainless steel 180-μ mesh wire cloth. In this work, however, a muslin cloth was used to filter the latex and remove any coagulum present. The latex was immediately weighed (80.0 $\pm$ 0.1 g) into the test cup. The temperature of the latex was 35 $\pm$ 1^{o}C prior to weighing. The speed of stirring was maintained at 14,000 $\pm$ 200 r.p.m. throughout the test.

(iv) The end-point was determined by dipping a clean glass rod into the latex and drawing it gently over the palm of the hand. The end-point is normally taken as the first appearance of flocculum in the film so deposited. The end-point is confirmed by the presence of an increased amount of flocculum in the film after an additional 15 seconds. The end-point was also observed as the first appearance of minute flocs when a drop of latex was introduced on to a large surface of distilled water in a watch glass. The end-point was confirmed by no redispersion of the flocs occurring after the flocs had been blown on the surface of water. In all cases, the end-point obtained using both methods coincided within a reasonable margin.

(v) The MST of the latex should be expressed as the number of seconds between the commencing of stirring and the end-point.

(vi) The difference between duplicate measurements of the sample should be less than 5%. This criterion was met in this work. The above method has been used throughout this work.

6.1.3 Experimental procedures

6.1.3.1 Preliminary investigation of the effect of non-ionogenic hydrophilic monomers upon the stability of NR latex in the presence of stabilisers

Stabilisers [Texofor A-60 (0 to 4 pphr), Texofor FP-300 (0 to 8 pphr), and SLS (0 to 8 pphr)] were added to separate portions of NR latex (Batch A). The mixtures were stirred thoroughly using a clean glass rod, and then matured at 20 $\pm$ 2^{o}C for up to 7 days. The monomers [HEA (0 to 2 pphr),

HPA (0 to 2 pphr), HEMA (0 to 4 pphr), and HPMA (0 to 4 pphr)] were then added to separate portions of the stabilised latices. Each portion of the latices was diluted with distilled water to 55% TSC. Each of the latices was stirred thoroughly using a clean glass rod and matured at 20 $\pm$ 2^{o}C for up to 7 days. The stability of the latices was determined by visual observation such as fluidity, viscosity and coagulation of the samples. Details of the additions of stabilisers and monomers to NR latex are given in Appendix 1A. Details of the preparation of stabiliser solutions of high concentration are given in Appendix 1B.

6.1.3.2 Partition of non-ionogenic hydrophilic monomers between hydrocarbon and aqueous phases

One of the aims of this experiment was to determine whether the hydrophobicity of the monomers would affect their tendency to be absorbed into the hydrocarbon/rubber phase of NR latex. The extent of absorption could affect both the stability of the latex and also the mechanism and kinetics of the subsequent polymerisation. To determine the extent of any such absorption, the partition coefficient between n-dodecane and water was determined. Distilled water (4.00 ml) was placed in a clean 10-ml measuring cylinder. n-Dodecane (1.40 ml) was then added into separate portion of the water. Into separate portions of the mixture was added drop by drop 0.60 ml of each of the monomers. The distribution of each of the monomers throughout the two phases was carefully observed by noting any changes in the volumes of the aqueous and hydrocarbon phases. Each of the mixtures was stirred thoroughly and left for at least half an hour in order to reach equilibrium. The change in volume of each phase in the mixture was recorded. The temperature was maintained at 25^{o}C throughout. The partition coefficient (K) for the monomers was calculated as follows (Equation 6.1):

$$K\ (25^{o}C) = \frac{C_W}{C_D} \qquad \text{.....6.1}$$

where C_W is the concentration of monomer in the water (mol/l), and C_D is the concentration of monomer in the hydrocarbon (mol/l).

6.1.3.3 Effect of non-ionogenic hydrophilic monomers upon mechanical stability time (MST) of NR latex before maturation

The different monomers were mixed with NR latex in varying proportions. It was found that there was a maximum quantity of each monomer that could be added, above which flocculation occurred. The maximum amount of each monomer which could be added to the latex was

HEA ca. 14 pphr
HPA ca. 11 pphr
HEMA ca. 12 pphr
HPMA ca. 8 pphr

Each of the samples was stirred thoroughly using a clean glass rod prior to the MST test. The details of the monomer additions to the latex, together with the monomer concentrations, are given in Appendix 2.

6.1.3.4 Effect of maturation time upon mechanical stability time (MST) of NR latex containing non-ionogenic hydrophilic monomers

It was found that the optimum concentration of added monomers that could give maximum values of MST were: ca.9 pphr for HEA, ca. 3 pphr for HPA, ca. 2 pphr for HEMA and ca. 2 pphr for HPMA (Section 7.4). The effect of maturation time upon the maximum MST values was then investigated. Mixtures of the monomers and NR latex in proportions that had given the maximum MST in the previous work were prepared. These mixtures were matured at 20 $\pm$ 2^{o}C for up to 5 days. The details of the amounts of monomers added to the latex are given in Appendix 3.

6.1.3.5 Effect maturation time upon mechanical stability time (MST) of NR latex containing low levels of non-ionogenic hydrophilic monomers

NR latices containing each of the monomers (ca. 1 pphr) were treated and tested as described in the previous section. However, the maturation time was extended to 12 days. The details of the monomer additions are given in Appendix 4.

6.1.3.6 Effect of redox initiator upon mechanical stability time (MST) of NR latex without maturation

Potassium persulphate ($K_2S_2O_8$) (0 to 0.6 pphr) and sodium metabisulphite ($Na_2S_2O_5$) (0 to 0.6 pphr) were added to NR latex (Batch B). It was found that, if the level of the initiators was increased beyond these levels, the latex flocculated or coagulated. The solutions of potassium persulphate and sodium metabisulphite were prepared such that, when they were added into the latex, the ratio of potassium persulphate to that of sodium metabisulphite was 1:1 by weight, and the final TSC of the mixtures was 55.0%. The details of the initiator additions are given in Appendix 5.

6.1.3.7 Effect of both initiator and monomers upon mechanical stability time (MST) of NR latex before and after maturation

6.1.3.7.1 Preparation of control latex containing initiator

A control latex was prepared containing potassium persulphate (0.4 pphr) and sodium metabisulphite (0.4 pphr) using latex Batch B. The final TSC of the mixture was 55.0%. The mixture was stirred thoroughly using a clean glass rod prior to the MST test. The details of the addition of the redox initiator to the latex are given in Appendix 6(i).

6.1.3.7.2 Preparation of control latices containing monomers

Control latices were prepared containing ca. 2 pphr of each of the four monomers, using latex Batch B. Each of the mixtures was stirred thoroughly using a clean glass rod prior to the MST test. The details of the monomer additions are given in Appendix 6(ii).

6.1.3.7.3 Effect of mixtures of initiator and monomers upon mechanical stability time (MST) of NR latex

Latices were prepared containing the redox initiator system together with each of the monomers under study (2.0 pphr). Each of these mixtures was stirred thoroughly using a clean glass rod prior to the MST test. To study the effect of maturation of the mixtures, each of the mixtures was kept in a 2-l plastic cup. MST tests were carried out after

maturation for 4, 24, 116 and 330 hours. The details of the initiator and monomers additions are given in Appendix 6(iii).

6.1.3.8 Effect of dilution upon mechanical stability time (MST) of NR latex containing non-ionogenic hydrophilic monomers and initiator before maturation

The standard procedure for determining the MST of the latex is to use a TSC of 55.0 $\pm$ 0.2%. However, it was observed that the addition of large quantities of the monomers to the latex at 55.0% TSC caused the latex immediately to coagulate. Therefore it was necessary to investigate the MST of NR latex at lower TSC in the presence of the monomers and initiators.

The MST of latices (Batch C) having TSC values 55.0%, 50.0% and 45.0% were determined. The amount of initiator and monomers added to the latex was the same for each of the TSCs, i.e., 0.4 pphr of potassium persulphate, 0.4 pphr of sodium metabisulphite, and 2.0 pphr of each of the monomers. In the case of latex containing 55.0% TSC, the initiator and monomer solutions were prepared such that the final TSC of the latices after they had been added to the latex was 55.0%. In the case of latex having 50.0% TSC, the initiator and monomer solutions were prepared more dilute than those which were added to the latex having 55.0% TSC. A further addition of distilled water to the mixtures was necessary to reduce the TSC to 50.0%. In the case of latex having 45.0% TSC, the procedure was the same as for the preparation of the latex having 50.0% TSC. However, a further addition of water was necessary to reduce the TSC to 45.0%. The details of the initiator and monomer additions and the amounts of water added to the latices are given in Appendix 7.

6.1.3.9 Effect of homopolymers of non-ionogenic hydrophilic monomers upon mechanical stability time (MST) of NR latex

The preparation of the polymers is described in Section 6.3.3.1(iv). Polyhydroxyethyl acrylate (PHEA) and polyhydroxypropyl acrylate (PHPA), prepared in IMS solution, are soluble in water. However, polyhydroxyethyl methacrylate (PHEMA) and polyhydroxypropyl methacrylate (PHPMA), prepared in IMS solution, are insoluble in water (Section 9.11.1).

(i) **Effect of added polyhydroxyethyl acrylate (PHEA) and polyhydroxypropyl acrylate (PHPA) upon mechanical stability time (MST) of NR latex**

The PHEA and PHPA were prepared as 7% w/w solutions by dissolving them in water at 20°C for 2-3 days. The polymers [PHEA (0.1 pphr), PHEA (0.2 pphr), PHPA (0.1 pphr), PHPA (0.2 pphr)] were added to separate portions of NR latex (Batch B). A latex containing no homopolymers was used as control. The mixtures were stirred thoroughly using a clean glass rod, and matured at 20 ± 2°C. The MST test was carried out after maturing the mixtures for more than 3 weeks. maturation.

(ii) **Effect of added polyhydroxyethyl methacrylate (PHEMA) and polyhydroxypropyl methacrylate (PHPMA) upon mechanical stability time (MST) of NR latex**

The PHEMA and PHPMA were dissolved in IMS (10% w/w) at 20°C overnight. It was observed that the addition of a small quantity of the polymer solutions into the latex (0.1 pphr) caused flocculation. The solutions were therefore to be diluted with water to a concentration of 3.3% w/w to avoid flocculation occurring. The final mixture contained IMS (30% w/w) in the polymer solution. NR latices (Batch B) containing the following were prepared:

a. PHEMA (0.1 pphr) plus IMS (0.9 pphr)
b. PHEMA (0.2 pphr) plus IMS (1.8 pphr)
c. PHPMA (0.1 pphr) plus IMS (0.9 pphr)
d. PHPMA (0.2 pphr) plus IMS (1.8 pphr)

To investigate the effect of the presence of the IMS upon the MST, the following experiments were carried out. Into separate portions of NR latex (Batch B) were added 0.9 pphr, 1.8 pphr of IMS. A control latex containing no IMS and no polymer was also prepared and tested. The mixtures were thoroughly stirred using a clean glass rod and matured at 20 ± 2°C. The MST test was carried out after maturing the mixtures for more than 3 weeks at room temperature (20 ± 2°C). It was assumed that any effect of

the IMS upon the MST of the latices containing IMS and polymers was additive, and could be inferred from the effect of the same amount of IMS upon the MST of the control latex. On this basis, the MST of the latex containing polymer only (if such could be prepared) was estimated as follows:

$$MST(P) = MST(P+IMS) + \{MST(C) - MST(IMS)\} \quad \text{.....6.2}$$

where MST(C) is the MST of the control latex, MST(IMS) is the MST of the latex containing only IMS, MST(P+IMS) is the MST of the latex containing polymer and IMS, and MST(P) is the estimated MST of the latex containing only polymer. This equation assumes that the effect of the IMS upon MST is independent of the presence of the polymer, since it can be re-written as

$$MST(P) - MST(P + IMS) = MST(C) - MST(IMS) \quad \text{.....6.3}$$

6.2 Investigation of kinetics of polymerisation of non-ionogenic hydrophilic monomers in NR latex

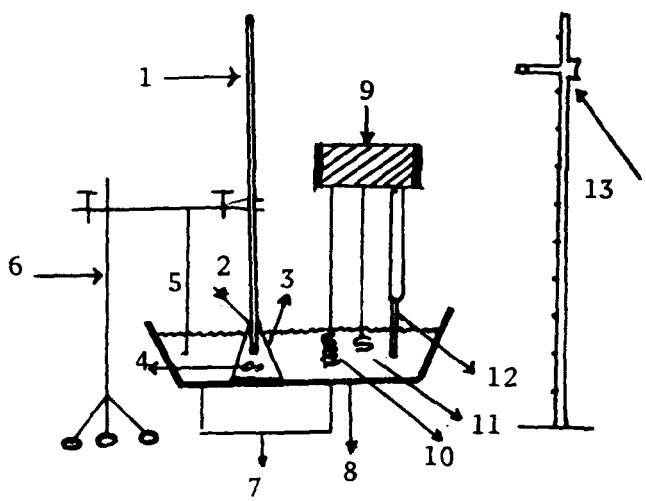
6.2.1 Apparatus

6.2.1.1 Apparatus used for gravimetric method

A thermostated vacuum oven, the pressure in which could be reduced to 0.16 mm Hg, was used.

6.2.1.2 Apparatus used for dilatometric method

The dilatometer used in this work was specially designed and prepared by the present author. The dilatometer was designed so that the water-soluble initiator and monomers mixed well with the rubber phase of NR latex. A diagram of the apparatus used to follow the polymerisations by dilatometry is shown in Figure 6.2.



1. Veridia capillary
2. Silicone grease
3. Conical flask
4. Agitator
5. Precision thermometer
6. Clamp
7. Magnetic stirrer
8. Plastic container
9. Circotherm
10. Heater
11. Stirrer
12. Automatic temperature regulator
13. Travelling microscope

Figure 6.2 Diagram of apparatus, including dilatometer, used to follow polymerisation of non-ionogenic hydrophilic monomers in aqueous solution and in NR latex

The apparatus for following polymerisations by dilatometry consisted of a Veridia capillary tube of constant bore, a magnetic stirrer, a Circotherm, a precision thermometer, a travelling microscope and a 50-ml conical flask. The Veridia capillary had a bore diameter of 3.0 mm and a length of 40 cm length. The tip of the capillary was carefully joined to a B-19/26 cone joint. The magnetic stirrer was necessary to ensure proper mixing between water-soluble monomers, initiator and the rubber phase of the latex. The Circotherm comprised a circulating pump, a heater and an automatic temperature regulator. The Circotherm maintained a constant temperature in the water bath for a long period of time [Section 6.2.2.2 (ii)]. The precision thermometer measured up to 30.00^{o}C with 0.02^{o}C divisions. The same thermometer was used to measure the temperature of the water-bath throughout this work. The travelling microscope was used to measure the decrease in hight of the meniscus of the liquid in the capillary. The volume of the polymerisation reaction system was restricted to about 50 ml in order to ensure that the temperature inside the flask was the same as that in the water bath.

In addition to the above equipment, silicone grease was used to seal the capillary to the flask and avoid leaks through the joint. A rubber band was used to 1) reinforce the joint between the capillary and the conical flask, and 2) avoid a possible movement of the capillary due to vibration caused by the agitator in the conical flask and by the circotherm placed in the water bath.

Various matters relevant to the accuracy of measurements made using the dilatometer were investigated. These matters were as follows:

(i) **Leakage from dilatometer**

To ensure that the joint between the flask and the capillary was leak-free, the following experiment was carried out: A 50-ml conical flask was filled with distilled water and heated in a water-bath to 29^{o}C. The joint of the capillary was then coated with silicone grease. The capillary was inserted gently into the flask. The joint between the capillary and the flask was reinforced by means of a rubber band. The dilatometer was placed in water-bath having a

constant temperature (29 ±0.03°C). The water was then stirred using the magnetic stirrer. The height of water in the capillary was immediately recorded using the travelling microscope. The initial height of the sample was taken when the temperature of the sample in the capillary had reached equilibrium after a few minutes. It was observed that there was no drop in height of water in the capillary over a period of more than four hours. Most of the polymerisations in this work were of less than 4 hours duration.

(ii) **Fluctuation of temperature of water-bath**

The temperature of the water bath not containing the dilatometer was set at 27.70°C. The temperature of the water bath was recorded continuously for up to 79 minutes, noting whether the light of the automatic temperature regulator was on or off. The results of the measurements are given in Table 6.3.

Table 6.3 Temperature variation of water bath

time	temperature, °C	
	light on	light off
0	-	27.70
8	27.64	-
17	-	27.70
26	27.68	-
34	-	27.71
44	27.62	-
52	-	27.71
60	27.66	-
70	-	27.70
79	27.68	-

The highest temperature when the light was off was 27.71°C, and the lowest temperature when the light was on was 27.62°C. The average temperature between the highest and the lowest was 27.67°C. The temperature variation of the water-bath was within 0.04°C. In this work, however, the

temperature of the water bath was maintained at 30 ± 0.03°C.

(iii) **Effect of temperature variation of water-bath upon dilatometer reading for NR latex plus added monomer**

The formulation shown in Table 6.4 was used to investigate the effect of temperature variation upon the dilatometer reading of NR latex plus the monomer. The dilatometer was placed in the water-bath as described in Section 6.2.2.2.(i). The temperature of the water-bath, was 30 ± 0.03°C. It was observed that there was no increase in height of the latex plus monomer in the capillary when the temperature of the water bath was increased by 0.40°C, or when the temperature was lowered by 0.15°C. A temperature variation of ± 0.10°C was therefore considered not to affect significantly the dilatometer reading for the NR latex plus added monomer.

Table 6.4 Formulation for investigation of effect of temperature variation upon dilatometer reading of NR latex containing HEMA

material	mass (g)	dry parts by weight
NR latex (as 59.99% DRC)	25.00	100.00
distilled water	20.00	133.00
HEMA	16.00	10.67
total, g	61.00	-
DRC, %	24.59	-

(iv) **Effect of redox initiator upon volume of NR latex**

The effect of initiator upon the volume of NR latex was studied using the formulation shown in in Table 6.5. The sample was placed in the dilatometer as described previously. The temperature of the water bath was 25 ± 0.03°C.

The changes in volume over 23 hours are given in Table 6.6. As can be seen, there was no significant change in the volume of NR latex in the presence of the redox initiator over the period of 23 hours.

Table 6.5 Formulation for investigating effect of redox initiator upon volume of NR latex

material	mass (g)	dry parts by weight
NR latex (as 59.97% DRC)	15.53	100.00
$K_2S_2O_8$ (as 2% w/w)	4.90	1.04
$Na_2S_2O_5$ (as 2% w/w)	4.90	1.04
distilled water	35.67	543.38
total, (g)	61.00	-
DRC, %	15.27	-

Table 6.6 Effect of redox initiator upon volume change of NR latex at 25 $\pm$ 0.03^{o}C

time (hours)	initial height of sample (cm)	decrease in height (cm)	decrease in volume (cm)
1	24.861	0.000	0.000
2	24.861	0.000	0.000
3	24.861	0.000	0.000
4	24.861	0.000	0.000
5	24.859	0.002	0.001
6	24.859	0.002	0.001
7	24.859	0.002	0.001
23	24.838	0.023	0.016

(v) Effect of mixing upon volume of monomers and NR latex

Portions (7.0-7.5 cm^3) of 18.99% TSC NR latex were added to a 10-ml calibrated measuring cylinder. The exact volume of the latices was measured using the travelling microscope. Portions (ca. 8.0 g) of each of the monomers were added into separate portions of the latices. Each of the latices was then stirred thoroughly using a small stainless steel wire. The temperature of the latices was maintained at 25°C. The theoretical volume of each of the monomers was the sum of the volumes of the latex plus each of the monomers. The volume of each the monomer was calculated using its mass and density. The density of each monomer at 25°C is given in Section 6.1.1.2. The actual volume of each of the monomer/latex mixtures in the measuring cylinders was recorded using the travelling microscope. The measurements of the volumes were carried out in duplicate, and the average values are given in Table 6.7. In the case of HEA, HEMA and HPMA, small volume changes due to mixing of monomers and latex were observed. In the case of HPA, a small volume increase was also observed. In all cases, however, the volume changes upon mixing the monomers and NR latex were negligible, being less than 1 % v/v.

Table 6.7 Volume changes upon mixing monomers and NR latex

	monomer			
	HEA	HPA	HEMA	HPMA
volume of latex ($x10^{-1}cm^3$)	72.82	74.80	73.73	70.82
volume of monomer ($x10^{-1}cm^{-3}$)	7.64	7.46	6.68	9.04
expected volume of latex + monomer ($x10^{-1}cm^{-3}$)	80.46	82.36	80.41	79.86
observed volume of latex + monomer ($x10^{-1}cm^{-3}$)	80.05	81.62	80.07	79.53
% v/v change	0.51	0.89	0.42	0.41

(vi) Effect of initial temperature upon apparent onset of polymerisation of non-ionogenic hydrophilic monomers in NR latex

Three samples were prepared to the formulation shown in Table 6.8. Those components of each of

Table 6.8. Formulation used for investigation of apparent onset of reaction

material	concent-ration (% w/w)	mass (g)	level (pphr)
NR latex (59.99% DRC)	-	25.00	-
water	-	16.70	111.41
$K_2S_2O_8$	4.00	1.50	0.40
$Na_2S_2O_5$	4.00	1.50	0.40
HEMA	10.00	16.00	10.07
total, g	-	60.70	-
DRC, %	-	24.96	-

the samples were separately heated to different temperatures (28.8°C, 30.0°C, and 31.5°C) respectively prior to placing them in the dilatometer. The dilatometer was then placed in the water-bath at 30 ± 0.03°C. The capillary height was determined at various times. To compare the effect of the different initial mixture temperatures, the appropriate initial height was subtracted from all the subsequent readings, so that the initial height became zero. The result of changing the temperatures upon the height change of the samples in the capillary is shown in Figure 6.3. In the case where the initial mixture temperature was lower than the bath temperature, the volume increased slowly until it reached an apparent equilibrium and then decreased. In the case where the initial mixture

temperature was the same as that of the water-bath, the volume increased slightly until it reached an apparent equilibrium and then decreased. In the case where the initial mixture temperature was higher than the bath temperature, the volume decreased initially until it reached an apparent equilibrium for a short period before decreasing further. The onset of the polymerisation reaction was therefore taken as the point where the volume of the sample decreased after an equilibrium stage was reached. The initial height (h_o) of the sample was taken as the height of the meniscus at the equilibrium stage.

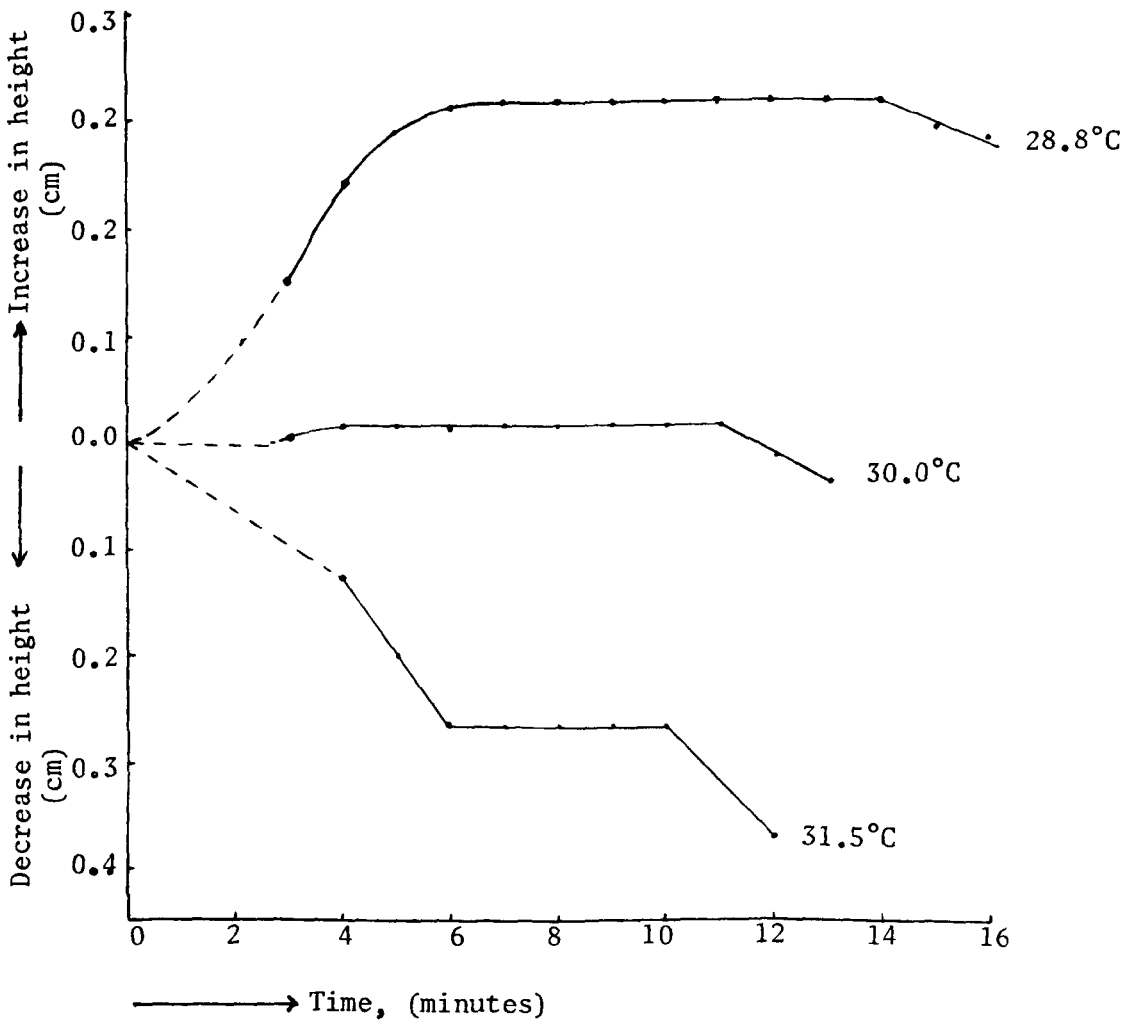


Figure 6.3 Effect of mixing temperature upon apparent onset of polymerisation of HEMA

(vii) Effect of polymerisation of non-ionogenic hydrophilic monomers upon temperature of NR latex

Polymerisations are normally exothermic. Experiments were therefore carried out to determine if the exotherm affected the temperature during polymerisation. To study this effect, the formulation given in Appendix 14 was used. Potassium persulphate and sodium metabisulphite (at 30°C) were added together to separate portions of NR latex. Each of the monomers (at 30°C) was added to separate portions of the latex containing the redox initiator. The reaction mixtures were then put into the water bath at 30°C. The mixtures were stirred thoroughly using a clean glass rod. No rise in temperature above 30°C during the polymerisation was observed. Therefore any exotherm which occurred had no effect upon the polymerisation temperature of the system.

(viii) Reproducibility of dilatometric technique

The general procedure for this experiment is described in Section 6.2.3.2.1. The formulation used to investigate the reproducibility of the dilatometer is shown in Table 6.9. The polymerisation was carried out in duplicate at 30 $\pm$ 0.03°C for up to 1.5 hours. The disappearance of monomer during polymerisation (as inferred from the contraction) was plotted against time according to the first-order rate equation. This equation was used because the polymerisation of HEMA in NR latex follows the first-order kinetic equation (Sections 8.3.6 and 8.3.7).

$$\ln \frac{[M]_o}{[M]} = k.t \quad \text{.....6.4}$$

where $[M]_o$ is the initial monomer concentration (mol/l latex), [M] is the monomer concentration at time t (mol/l latex), t is the time of polymerisation, and k is the rate coefficient (s^{-1}). The values of [M] at time t were calculated as follows:

$$[M] = [M]_o - \left[\frac{\Delta h}{\Delta h_{100}} \times [M]_o\right] \quad \text{.....6.5}$$

where Δh is the fall in height of the meniscus in dilatometer (cm), Δh_{100} is the fall in height of monomer at 100% conversion (cm), calculated using Equation A.9.4 (Appendix 10). The fall in height of meniscus in dilatometer is given by:

$$\Delta h = (h_o - h_t) \quad \text{.....6.6}$$

where h_o is the initial height of the meniscus in dilatometer (cm), and h_t is the height of the meniscus at time t (cm). The relationship between Δh and time, t, for duplicate measurements is given in Figures 6.4A and 6.4B. The rate coefficients (k) from the duplicate measurements were calculated to be 17.6×10^{-5} s^{-1} and 17.9×10^{-5} s^{-1} respectively (Figures 6.4C and 6.4D). The reproducibility of the measurements of the rate coefficient was satisfactory, the difference between the two duplicate measurements being less than 1 % of the mean value.

Table 6.9 Formulation used to study reproducibility of dilatometric technique

material	concent-ration (% w/w)	mass (g)	dry parts by weight
NR latex (Batch C)	-	23.40	100.00
NH_4OH	1.50	11.50	1.23
$K_2S_2O_8$	4.00	0.80	0.22
$Na_2S_2O_5$	4.00	0.80	0.21
HEMA	10.00	20.00	14.26
total, g	-	56.40	-
DRC, %	-	24.84	

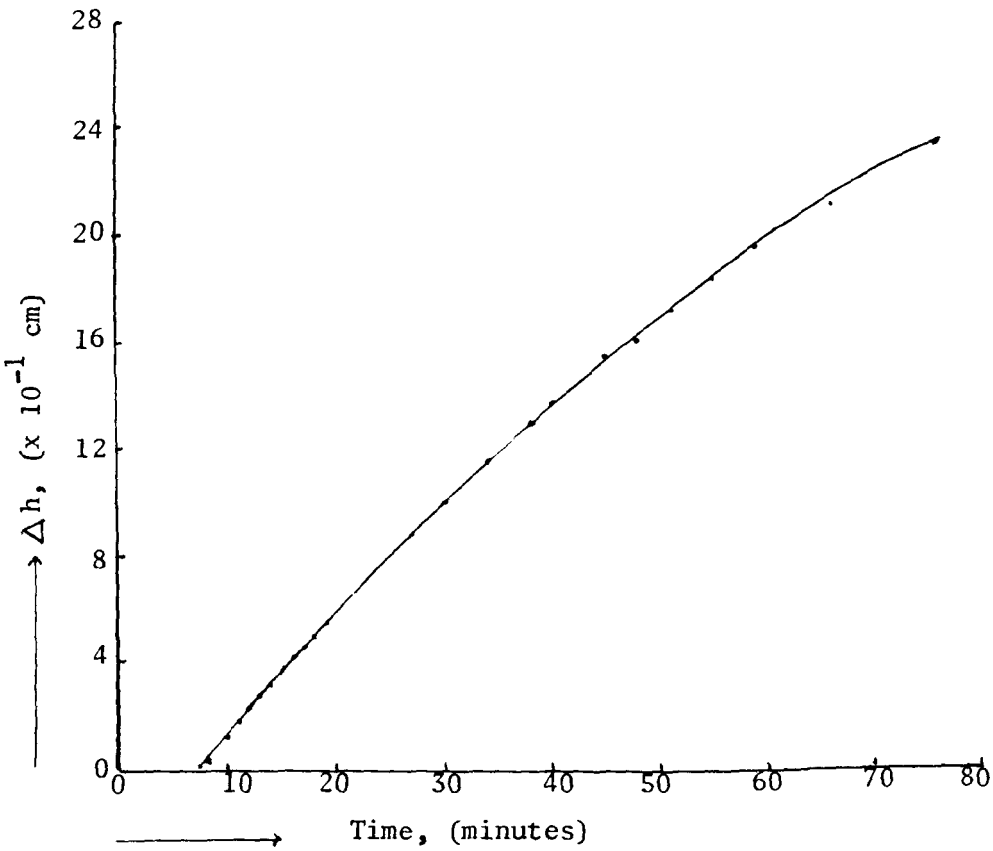


Figure 6.4A Plots of fall in height of meniscus in dilatometer, Δh, versus time of polymerisation of HEMA at 30.00 ± 0.03°C for the investigation of the reproducibility of the dilatometer technique

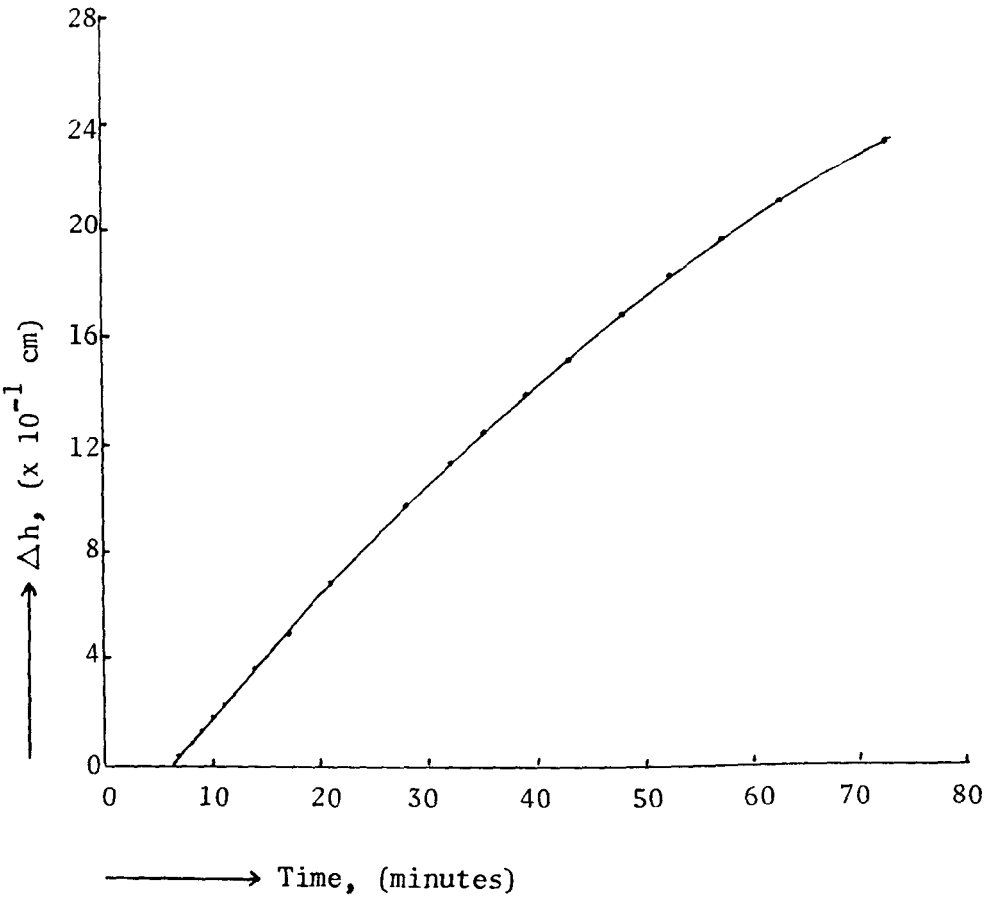


Figure 6.4B Plots of fall in height of meniscus in dilatometer, Δh, against time of polymerisation of HEMA at 30.00 ± 0.03°C for the investigation of the reproducibility of the dilatometer technique

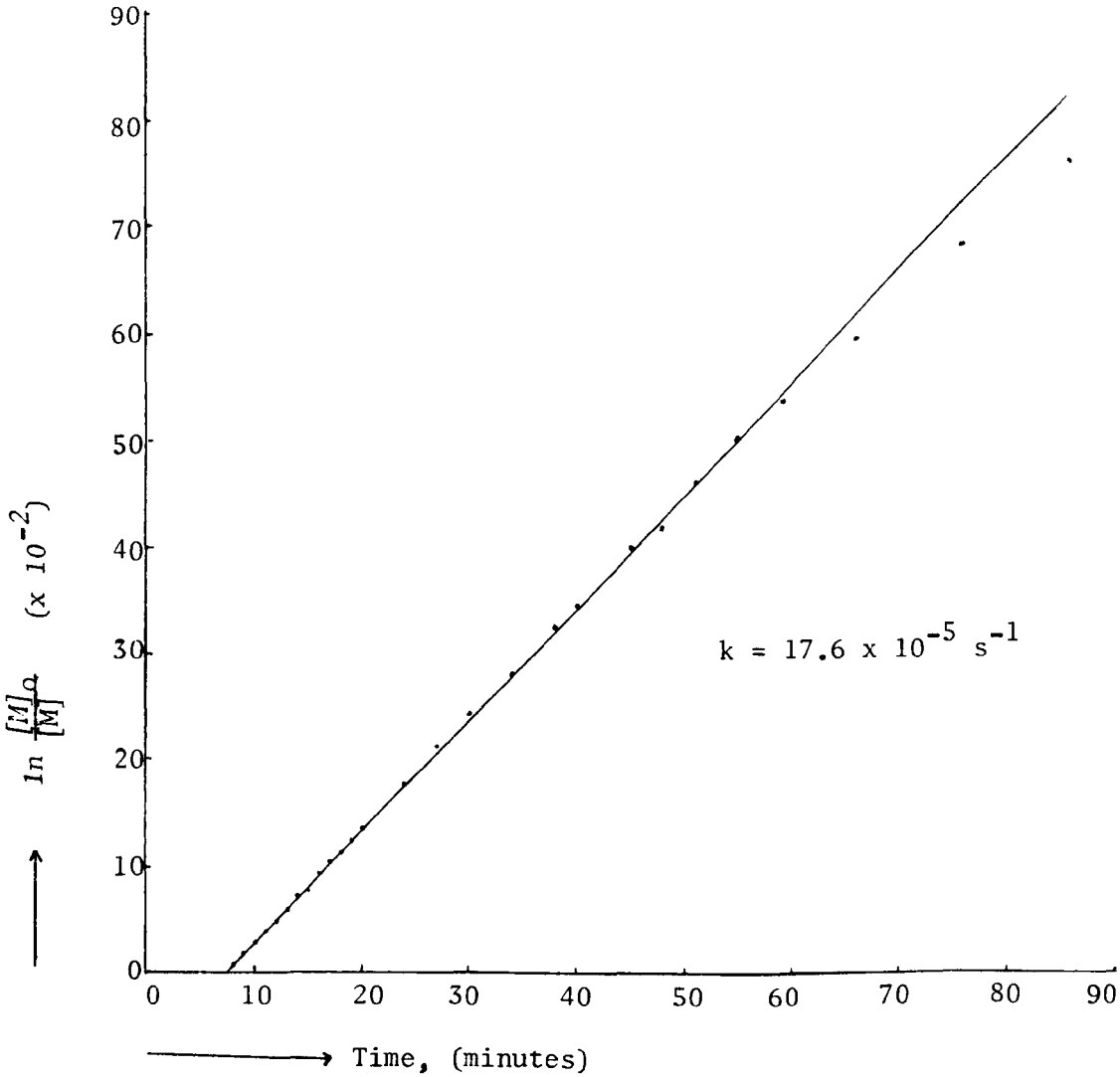


Figure 6.4C Relationship between natural logarithm of disappearance of HEMA in NR latex and time for the investigation of the reproducibility of the dilatometric technique

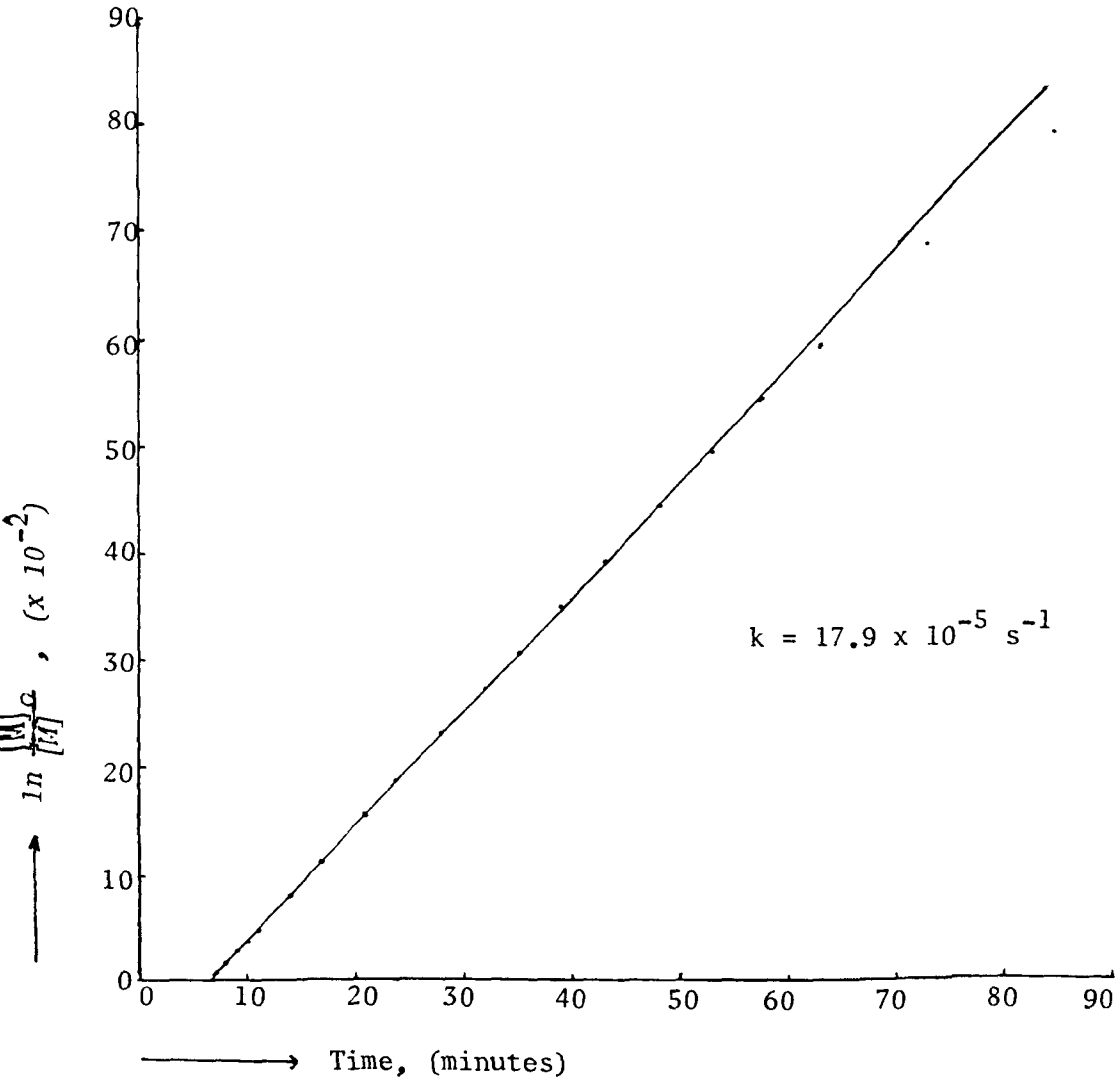


Figure 6.4D Relationship between natural logarithm of disappearance of HEMA in NR latex and time for the investigation of the reproducibility of the dilatometric technique

6.2.3 Experimental procedures

6.2.3.1 Gravimetric method

6.2.3.1.1 Determination of volatility of non-ionogenic hydrophilic monomers

Each of the monomers (ca. 1.5 g) was weighed into 60-ml jars. Portions of water (ca. 3.5 g) were added to each of the monomers. The samples were then placed into a vacuum oven and heated to 90 $\pm$ 1°C. The pressure was reduced, slowly at first to avoid flashing of the monomers, to 0.16 mm Hg. The drying of the monomers was continued to constant weight (3.5 hours). Determination of the volatilities of the monomers were carried out in duplicate. The volatilities of the monomers were calculated as follows:

$$\text{volatility (\% w/w)} = 100 - \left[\frac{M_1}{M_o}\right] \times 100 \quad \text{.....6.7}$$

where M_1 is the mass of residue after drying (g), and M_o is the mass of initial monomer (g). The average of two values was taken.

6.2.3.1.2 Determination of volatility of inhibitors /antioxidants in the presence of NR latex

Inhibitors/antioxidants (10 to 69 pphr) were added to separate portions (3 to 3.5 g) of 41.5% DRC NR latices in 75-ml jars. The inhibitors/antioxidants were prepared as 15% solutions in acetone. The samples were kept at 20 $\pm$ 2°C overnight and then heated in the vacuum oven at 90 $\pm$ 1°C for 6.5 to 8.5 hours. The determinations were carried out in duplicate. The volatilities of the inhibitors/antioxidants were calculated as follows:

$$\text{volatility (\% w/w)} = 100 - \left[\frac{M_3 - M_4}{M_2}\right] \times 100 \quad \text{.....6.8}$$

where M_2 is the initial mass of inhibitor/antioxidant (g), M_4 is the mass of dry rubber (g), and M_3 is the mass of residue after evaporation (g).

6.2.3.1.3 Determination of effectiveness of inhibitors/ antioxidants in NR latex

(i) **Inhibitors/antioxidants added to NR latex containing a monomer prior to addition of redox initiator**

HEA (40 pphr) was added to separate portions (2-3.5 g) of 42% TSC NR latex, followed by the initiator (2 to 5 pphr), and the inhibitors/antioxidants (17 to 18 pphr). The HEA was added as a 15% aqueous solution, the potassium persulphate and sodium metabisulphite as 2 % w/w aqueous solutions, and the inhibitors/antioxidants as 5-15% w/w acetone solution. Each of the latices was kept overnight and heated in the vacuum oven (0.16 mm Hg) at 90 $\pm$ 1°C for 6.5 - 8.5 hours. The effectiveness of inhibitors/antioxidants was calculated as follows:

Effectiveness (% w/w) =

$$100 - \left[\frac{M_1 - M_2 - M_4 - M_5}{M_o}\right] \times 100 \quad \text{.....6.9}$$

where M_o is the mass of the monomer (g), M_1 is the mass of residue after evaporation (g), M_4 is the mass of rubber, (g), M_5 is the mass of redox initiator (g), and M_2 is the mass of inhibitor/antioxidant (g).

(ii) **Monomer added to NR latex containing a redox initiator prior to addition of Nonox DPPD**

Based on the results in the previous section, Nonox DPPD and DPPH were found to be the most effective inhibitors. For economic reasons, Nonox DPPD was used as the inhibitor throughout this work. Potassium persulphate (0.98 pphr) and sodium metabisulphite (0.98 pphr) were added to 20.39% TSC NR latex. The potassium persulphate and sodium metabisulphite were each prepared as 2% w/w aqueous solutions. The sample was stirred thoroughly using a glass rod and kept at 25 $\pm$ 1°C for 23 hours. The actual TSC of the latex was

determined in duplicate. Each of the monomers (30-31 pphr) was added to separate portions (5 g) of the latices, followed by Nonox DPPD (0.3 to 0.4 pphr). Each of the monomers was added undiluted, whereas Nonox DPPD was prepared as 2% w/w IMS solution. The latices were then heated in an oven at 70°C for 14 hours, and further dried in the vacuum oven (0.16 mm H_g) at 90°C for 15 hours. The determination was carried out in duplicate. The effectiveness of the inhibitor under these conditions was calculated using Equation 6.9.

6.2.3.2 Dilatometric method

6.2.3.2.1 General procedure

(i) NR latex was measured into a 50-ml conical flask and heated in a water-bath (30.1 ± 0.1°C) for 15 to 20 minutes. The following three solutions were then prepared separately:

a. 10-20% w/w monomers in 1.5% aqueous ammonia solution

b. a 4% w/w potassium persulphate in 1.5% aqueous ammonia solution

c. a 4% w/w sodium metabisulphite in 1.5% aqueous ammonia solution

The solutions were then heated in a water-bath at 30.1 ± 0.1°C for 15 to 20 minutes.

(ii) The potassium persulphate and sodium metabisulphite solutions were then added to the latex, and heated in the water-bath at 30°C for about 1 minute. Each of the monomer solutions was added to a separate portions of the latices containing the redox initiator, and the time recorded as the beginning of the polymerisation. Each of the latices was heated in the water-bath at 30°C and stirred thoroughly using a glass rod for about 1 minute. At the same time, any bubbles present in the flask were removed using cellulose paper.

(iii) The Veridia capillary was heated and then cooled to about 30°C. Silicone grease was coated on to the joint of the capillary. The reaction mixture was then placed in a weighed plastic container. The capillary was then inserted gently into the flask. At the same time, about 1 g out of 60 g of the sample would overflow. The joint between the flask and the capillary was immediately secured by means of a rubber band. If there was a bubble, either in the flask or in the capillary, the experiment was abandoned. The sample which overflowed around the flask was collected and weighed so that the actual mass of monomer in the dilatometer could be calculated. The dilatometer was then placed in the water-bath at a constant temperature of 30.00 ± 0.04°C and stirred using a magnetic stirrer.

(iv) The height of the meniscus of the sample was immediately recorded using a travelling microscope. The change of height of the meniscus was then recorded every minute until the height of the meniscus was constant. This was taken as the initial height (h_o) of the meniscus. The decrease in height (h_t) of the meniscus was then recorded every minute for the first 20 minutes. A further reading was then carried out every two, three or five minutes, depending upon the rate of polymerisation. The polymerisation was stopped when the change in height of the meniscus became insignificant. In the case of higher concentrations of HEMA and HPMA, a 60-watt lamp was sometimes required to read the meniscus, because of the opaque nature of the sample in the capillary.

(v) The conversion of the monomers at time t was calculated as follows

Conversion at time t =

$$\frac{7.069 \times \rho_m \times \rho_p}{M_m(\rho_p - \rho_m)} \times (h_o - h_t) \quad \text{.....6.10}$$

where ρ_m is the density of the monomer (g/cm^3), ρ_p is the density of polymer (g/cm^3), M_m is the

mass of monomer (g), h_o is the original height of the sample in the capillary (cm), h_t is the height of the sample in the capillary (cm) at time t. The density of monomers and polymers was determined at 30°C (Appendices 9A and 9B). The derivation of Equation 6.10 is given in Appendix 10.

(vi) The fluidity and any visible creaming of the products were observed whenever possible. The pH of the initial and final products were also recorded whenever possible. The above procedure was used throughout this work, unless otherwise stated.

6.2.3.2.2 Polymerisation of non-ionogenic hydrophilic monomers both in aqueous solution and in aqueous ammonia solution

Solutions of monomers and initiator were prepared in distilled water containing the potassium persulphate (2.04×10^{-3} mol/l solution) and sodium metabisulphite (2.90×10^{-3} mol/l solution). The concentration of each of the monomers was ca. 0.2 mol/l. The conversion of monomers was followed using the dilatometer at 30 ± 0.03°C for up to 1.5 hours. The pH and appearance of the products, and the details of the monomer and initiator concentrations, are given in Appendix 11A. Polymerisations of the monomers in the presence of the redox initiator in a 1.5% aqueous ammonia solution were also carried out under comparable conditions. The pH and appearance of the products, together with details of the monomer and initiator concentrations are given in Appendix 11B.

6.2.3.2.3 Preliminary investigation of rate of conversion of non-ionogenic hydrophilic monomers in NR latex using distilled water as diluent

The monomers and initiator were prepared in aqueous solution. The concentration of each of the monomers polymerised in NR latex was ca. 0.1 mol/l latex, and the concentrations of potassium persulphate and sodium metabisulphite initiator were ca. 8.8×10^{-3} and ca. 11.3×10^{-3} mol/l latex respectively. The polymerisations were carried out at 30 ± 0.03°C for up to 23 hours in a dilatometer. The DRC of the total reaction mixtures was 15.0%. The pH and values for the DRCs of the products,

together with details of the monomer and initiator concentrations, are given in Appendix 12.

6.2.3.2.4 Effect of nature of diluent upon rate of polymerisation of HPA in NR latex

Solutions of the monomer and initiator were prepared separately in:

(i) distilled water
(ii) a 0.5% aqueous ammonia solution
(iii) a 1.5% aqueous ammonia solution

These solutions were added to separate portions of NR latex (Batch C). The concentration of monomer in the latices was ca. 0.2 mol/l latex. The concentrations of potassium persulphate and sodium metabisulphite were ca. 3.1×10^{-3} and ca. 4.3×10^{-3} mol/l latex respectively. The polymerisations were carried out in the dilatometer at $30 \pm 0.03^{o}C$ for up to 6-7 hours. The DRC of the total reaction mixtures was about 24.7%. The pH and values for the DRCs of the products, together with details of the monomer and initiator concentrations, are given in Appendix 13.

6.2.3.2.5 Effect of type of non-ionogenic hydrophilic monomers upon rate of conversion in NR latex using aqueous ammonia solution as diluent

The solutions of monomers and initiator were prepared in 1.5% aqueous ammonia solution. The initial concentration of each of the monomers in NR latex was kept constant at ca. 0.2 mol/l latex, as were the concentrations of potassium persulphate (ca. 3.1×10^{-3} mol/l latex) and sodium metabisulphite (4.3×10^{-3} mol/l latex). The DRC of the total reaction mixtures was kept constant at 24.8%. The polymerisations were carried out in the dilatometer at a constant temperature ($30 \pm 0.03^{o}C$) for up to 5.5 hours. The pH and values for the DRC of the products, together with details of the monomer and initiator concentrations, are given in Appendix 14.

6.2.3.2.6 Effect of varying sodium lauryl sulphate (SLS) concentration upon rate of polymerisation of HPMA in NR latex

NR latices containing SLS (0 pphr, 1 pphr) were prepared and matured for about one week at 20°C. The monomer and initiator were prepared in the manner described previously [Section 6.2.3.2.1 (i)]. The concentration of each of the monomers was ca. 0.2 mol/l latex. The concentrations of potassium persulphate and sodium metabisulphite were 3.14×10^{-3} and 4.33 mol/l latex respectively. The DRC of the total reaction mixtures was about 24.9%. The polymerisations were carried out in the dilatometer at 30 ± 0.03°C for up to 5 hours. The pH and values for the DRCs of the total reaction mixtures, together with details of the monomer and initiator concentrations, are given in Appendix 15.

6.2.3.2.7 Effect of initial monomer concentration upon the rate of polymerisation of non-ionogenic hydrophilic monomers in NR latex

The solutions of monomers and initiator were prepared as described previously [Section 6.2.3.1 (i)]. The concentrations of potassium persulphate and sodium metabisulphite were 2.09×10^{-3} and 2.89×10^{-3} mol/l latex respectively. The initial concentration ranges for each of the monomers, $[M]_o$ are as follows:

HEA	0.2 to 0.5 mol/l latex
HPA	0.2 to 0.5 mol/l latex
HEMA	0.2 to 0.3 mol/l latex
HPMA	0.2 to 0.3 mol/l latex

The quantities of redox initiator and monomers added to the latices were such that the DRCs of the total reaction mixtures were 24.8%. The polymerisations were carried out in dilatometers at 30 ± 0.03°C for up to 3 hours. The calculation of rate of polymerisation, R_p, for each monomer, and the order of reaction with respect to initial monomer concentration, is given in Section 8.3.6. The pH and values for the DRCs of the total reaction mixtures, together with details of the of the monomer and initiator concentrations, are given in Appendix 16.

6.2.3.2.8 Determination of order of reaction with respect to monomer concentration, [M], during the course of polymerisation of non-ionogenic hydrophilic monomers in NR latex

The monomers and initiator were prepared as described previously [Section 6.2.3.2.1 (i)]. The concentration of each of the monomers was ca. 0.2 mol/l latex with the exception of HPA, for which the concentration was 0.5 mol/l latex. This concentration for HPA was chosen because it displayed the longest straight line in the conversion vs. time curve. Each of the monomers was polymerised in the presence of potassium persulphate (ca. 2.1×10^{-3} mol/l latex) and sodium metabisulphite (2.9×10^{-3} mol/l latex). The DRCs of the total reaction mixtures were 24.7%. The polymerisations were carried out in the dilatometer at 30 $\pm$ 0.03°C for up to 3 hours. The disappearance of each of the monomers during polymerisation was plotted against time using the various rate equations shown in Table 6.10. The order of reaction with respect to monomer concentration during the polymerisation reaction was established on the basis of the plot which gave the best straight line. The pH and values for the DRCs of the products, together with details of the monomer and initiator concentrations are given in Appendix 17.

Table 6.10 Rate equations applied to data for disappearance of monomers during polymerisation in NR latex (130)

order of reaction	rate equation for disappearance of monomer
0	$kt = [M]_o - [M]$
1	$kt = \ln \frac{[M]_o}{[M]}$
2	$kt = \frac{1}{[M]} - \frac{1}{[M]_o}$
3	$kt = \frac{1}{2[M]^2} - \frac{1}{2[M]_o^2}$

In each entry, $[M]_o$ is the initial monomer concentration (in mol/l latex), [M] is the monomer concentration at time t (in mol/l latex), k is the rate coefficient, and t is the time.

6.2.3.2.9 Effect of initial redox initiator concentration upon rate of polymerisation of non-ionogenic hydrophilic monomers in NR latex

The solutions of monomers and initiator were prepared as described previously [Section 6.2.3.2.1 (i)]. The concentrations of potassium persulphate and sodium metabisulphite ranged from ca. 1.3×10^{-3} to 5.2×10^{-3} and from 1.8×10^{-3} to 7.2×10^{-3} mol/l latex respectively. The monomer concentration in the latices was ca. 0.2 mol/l latex. The addition of monomers, initiator and a 1.5% aqueous ammonia solution to the latices was such that the DRCs of the reaction mixtures were 24.7%. The polymerisations were carried out in the dilatometer at ($30 \pm 0.03^{o}C$) for up to 3 hours. The methods of calculation of the rates of polymerisation, R_p , and orders of reaction with respect to initiator concentration are given in Section 8.3.8. The pH and values for the DRCs of the total reaction mixtures, together with details of the monomer and initiator concentrations, are given in Appendix 18.

6.2.3.2.10 Effect of dry rubber content (DRC) upon rate of polymerisation of non-ionogenic hydrophilic monomers in NR latex

The solutions of monomers and initiator were prepared as described previously [Section 6.2.3.2.1 (i)]. The amounts of potassium persulphate and sodium metabisulphite added to separate portions of NR latex were kept constant at 2.08×10^{-3} and 2.87 mol/l latex respectively. The concentration of the monomers in the latices containing the redox initiator was ca. 0.2 mol/l latex. The monomers, initiator and a 1.5% aqueous ammonia solution added to the latices were such that the DRCs of the latices ranged from 14 to 30%. The polymerisations were carried out in the dilatometer at $30 \pm 0.03^{o}C$ for up to 2 hours. The methods of calculation of the rates of polymerisations, and the orders of reaction with respect to DRC are given in Section 8.3.9. The pH values and the DRCs of the products, together with details of the monomer and initiator concentrations, are given in Appendix 19.

6.3 Characterisation of materials obtained by graft copolymerisations in NR latex

6.3.1 Experimental Procedure

6.3.1.1 Preliminary investigation on solubility of non-ionogenic hydrophilic polymers and NR

Due to the unusual solubility behaviour of the homopolymers, the non-ionogenic hydrophilic monomers were polymerised under various conditions as follows:

(i) **Polymerisations in aqueous solution and in a 1.5% aqueous ammonia solution using redox initiator**

The monomers (3.5 g) were each dissolved in portions of the aqueous solution (46.5 g) in 125-ml jars. To each solution were added potassium persulphate [0.5 parts by weight per hundred parts by weight of monomer (pphmon)] prepared as a 1% w/w aqueous solution, and sodium metabisulphite (0.5 pphmon) prepared as a 1% w/w aqueous solution. The polymerisations were carried out at 25^{o}C for 19 hours. Any precipitation of the polymers formed which occurred during and after polymerisation was observed visually. Polymerisations of the monomers in aqueous ammonia solution as the medium were carried out under similar conditions.

(ii) **Polymerisations in serum obtained from NR latex by ultracentrifugation using a redox initiator**

It was observed that PHEA and PHPA prepared in ammonia solution were soluble, whereas PHEMA and PHPMA were insoluble (Section 7.11.6). In this work, only HEMA and HPMA were polymerised in the serum. The monomers (2.5 g) were each dissolved in portions of the serum (29.6 g) in 125-ml jars. To each solution were added potassium persulphate (0.7 pphmon) and sodium metabisulphite (0.7 pphmon). The polymerisations were carried out in a water-bath at 25 ^{o}C for 1 hour. Any precipitation of polymers formed which occurred during and after the polymerisation was observed visually.

(iii) **Polymerisations in a 0.06% aqueous sodium hydroxide solution using ACA as an initiator**

The monomers (3.5 g) were each dissolved in portions of the solution (46.5 g) in 125-ml jars. To each solution was added ACA (1 pphmon). The polymerisations were carried out in a water-bath at 60^{o}C for 17 hours. Any precipitation of polymers formed which occurred during and after polymerisation was observed visually.

(iv) **Polymerisations in IMS using ACA as initiator**

The monomers (3.5 g) were each added to portions of IMS (46.0 g) in 25-ml jars. To each solution was added ACA (1 pphmon). The polymerisations were carried out in a water-bath at 60^{o}C for 17 hours. Any precipitation of polymers formed which occurred during and after polymerisation was observed visually.

(v) **Polymerisations in aqueous solution in presence of NR petroleum-ether solution and other non-polar solvents using a redox initiator**

The aim of this experiment was to simulate the polymerisation of the monomers in NR latex. NR dissolved in petroleum ether-toluene (1.42% w/w) (Appendix 20) was used as a model for the rubber phase in the reaction mixture. This experiment would enable one to observe visually whether the polymers precipitate in the aqueous phase in the presence of a rubber phase. The monomers (HEMA or HPMA) (3.50 g) were each dissolved in portions of distilled water (38.8 g) in 125-ml jars. The NR solution (15.50 g) were added to each portion of monomer solution, the amount being equivalent to 24% hydrocarbon content. The mixtures were stirred thoroughly for 1 minute using a magnetic stirrer. Potassium persulphate (2.11 pphmon) prepared as 2% w/w aqueous solution, and sodium metabisulphite (2.11 pphmon) prepared as 2% w/w aqueous solution were added to separate portion of the reaction mixtures. The amount of the redox initiator in the mixtures was equal to 1.43 parts by weight per hundred parts by weight of hydrocarbon (pphh). The polymerisations were

carried out at 20°C with constant stirring for 17-21 hours, and stored for 5-7 days at 20°C. The solubility of the products was observed visually. Polymerisations of the monomers using a solution of NR in petroleum ether-toluene solution were carried out under similar condition.

6.3.1.2 Solubility of homopolymers of non-ionogenic hydrophilic monomers in various solvents

To investigate the solubility of the polymers, the products obtained in using the procedures described in Sections 6.3.1.1 (i), (iii), and (iv) were dried in an air-oven (70°C) for 10.5 hours and then in a vacuum oven (0.16 mm Hg; 75-85°C) to constant weight (21 hours). Special attention was given to PHEMA and PHPMA, in order to establish whether crosslinking had occurred during polymerisation.

(i) Solubility of PHEMA and PHPMA, prepared by procedures described in Sections 6.3.1.1 (i), (iii), and (iv), in various solvents

Attempts were made to dissolve each of the polymers (0.5 g) separately in:

a. THF and IMSA (Section 6.1.1.3) (100 g)
b. distilled water (100 g)
c. IMSA (100 g)
d. THF (100 g)
e. allyl alcohol (100 g)

The samples were kept in an oven (40°C) for 18-23 days. The solubility of the polymers in each of the solvents was observed visually. Further investigations of the possibility of crosslinking of the polymers prepared in Section 6.3.1.1.(iv) were carried out. These polymers were added to distilled water using the procedures described previously. The swollen-polymers (PHEMA and PHPMA) were then dried in an oven (100°C) overnight, then in the vacuum oven (0.16 mm Hg; at 90°C) to constant weight (3.5 hours). The recovery of the polymers was calculated. The dry polymers were then added to the IMSA and kept at 40°C overnight. Because the polymers were

completely soluble in the IMSA, no attempt was made to redissolve the polymers in any other solvents.

(ii) **Solubility of PHEMA and PHPMA, prepared by procedures described in Section 6.3.1.1.(v), in IMSA**

The undried polymers obtained directly from a polymerisation (3.7 to 5.2 g) were each added to portions of IMSA (50.0 g). The actual mass of dry polymers was calculated from the equilibrium water absorption obtained from the previous work (Section 6.3.1.1.v). The samples were kept at 20°C overnight. The solubilities of the polymers were observed visually.

6.3.1.3 Separation of added polymers in NR latex

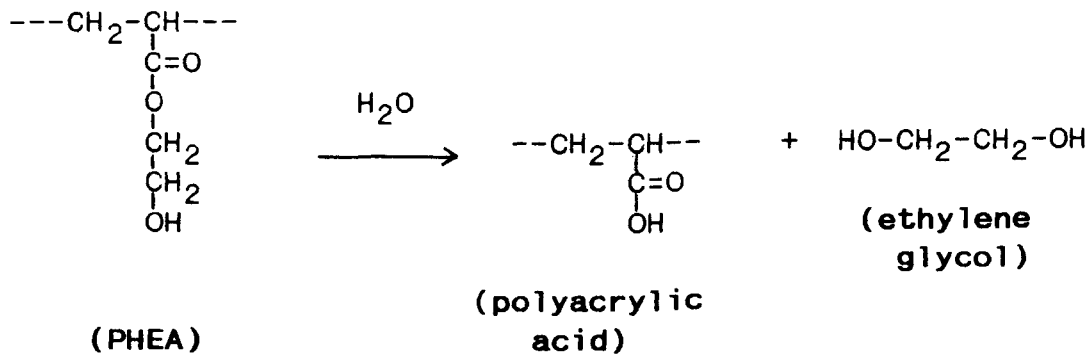
Water-soluble polymers (PHEA and PHPA) which can be added to NR latex were chosen as representative of the polymers for finding the best conditions for separation of the polymers from NR latex, because the other two polymers (PHEMA and PHPMA) are insoluble in aqueous solution. PHEA and PHPA were each dissolved in water to form solutions 7.81% and 7.25% w/w respectively. The polymer solutions (3.5 g) were each added to 15.59% TSC NR latices (5.0 g). The samples were thoroughly stirred using a glass rod, and stored at 20°C for 4 days. The samples (3 to 5 g) were then dried in a fume cupboard at 20°C for 16 hours, by which time thin pastes had formed. The pastes were then coagulated using few drops of IMSA solution until a clear serum was obtained. Each of the wet films obtained from the coagulation was then pressed a few times with a roller and washed thoroughly using tap water. The films were then soaked in IMSA (100 g) at 20°C for 6 days. Each of the films was rewashed thoroughly with tap water for about 5 minutes and dried in a fume cupboard at 20°C for 19 hours. The wet films were then dried in an oven (100°C) for 4 to 5.5 hours. A latex containing no added polymer was used as a control. The extent of separation was defined as the amount of the added polymers recovered, and was calculated as follows:

$$\text{polymer recovered (\% w/w)} = 100 - \left[\frac{M_{10} - M_{11}}{M_9}\right] \times 100 \quad \ldots 6.11$$

where M_9 is the mass of added polymer (g), M_{10} is the mass of actual dry film in NR latex and polymer (g), and M_{11} is the mass of residue after extraction and evaporation (g).

6.3.1.4 Investigation of hydrolysis of homopolymers of non-ionogenic hydrophilic monomers dissolved in IMSA solution and in aqueous ammonia solution

It was found that added polymers in NR latex could be extracted satisfactorily using IMSA solution over 6 days at 20 $\pm$ 2°C (Section 9.11.2). For the purpose of separating the homopolymers, the samples were frequently allowed to stand in contact with IMSA (pH ca. 2.5) for more than 2 weeks at 20 $\pm$ 2°C. Therefore it was desirable to investigate whether the polymers would hydrolyse in the presence of IMSA solution at a low pH (ca. 2.5). For example, if PHEA hydrolysed, one would expect that polyacrylic acid and ethylene glycol would be formed;



The boiling point of ethylene glycol is 187°C, and of propylene glycol is 198°C. These boiling points of the glycols are lower than those of the non-ionogenic hydrophilic monomers, these being in the range 222 - 230°C. Therefore one would expect that the glycols would evaporate under prolonged drying in the vacuum (0.16 mm Hg) which was used to evaporate completely the monomers. Thus, if the PHEA hydrolysed completely (100% hydrolysis), a mass loss of 37.93% from the original polymer would be expected. The estimation of the mass loss is given by:

$$\text{mass loss (\%)} = \left[\frac{MM_p - MM_a}{MM_p}\right] \times 100\% \quad \text{.....6.12}$$

where MM_p is the molecular mass of the repeat unit of PHEA (116), and MM_a is the molecular mass of the repeat unit of polyacrylic acid (72). Two methods were used to investigate

the extent of the hydrolysis of the polymers, namely, a gravimetric method and a titration method.

(i) **Gravimetric method**

The polymers were prepared as described previously [Section 6.3.1.1.(iv)]. The polymers 0.5 g) were each added to IMSA solution (ca. 50 ml) in 120-ml jars. The samples were allowed to stand for about 3 weeks at 20 $\pm$ 2°C. The samples were then dried in an oven at 80°C for 8 hours, and then in a vacuum oven (0.16 mm Hg) at 90°C for 19 hours. IMSA solutions containing no polymer were prepared as a control. It was found that the residue of the IMSA solutions after evaporation was negligible, being less than 0.02 % w/w. Each of the determinations was carried out in duplicate. The mass loss of the polymers after drying to constant weight was calculated as follows:

mass loss of polymer (% w/w)

$$= \left[\frac{M_{16} - M_{17}}{M_{16}} \right] \times 100 \quad \text{.....6.13}$$

where M_{16} is the mass of the sample (g), and M_{17} is the mass of the residue after drying. An investigation of the possible hydrolysis of the polymers in alkaline solution was also carried out by adding the polymers to aqueous ammonia solution (pH ca. 10). The procedure used was the same as for IMSA as solvent.

(ii) **Titration method**

The polymers were prepared as described previously [Section 6.3.1.1.(iv)]. The polymers 1.0 g) were each added to IMSA solution (50 ml) in 120-ml jars. The samples were allowed to stand for about 2 weeks at 20°C. IMSA solution containing no polymer was prepared as a control. A sample (5.00 ml) was pipetted and added to a 200-ml beaker containing 50 ml water. The sample was then titrated using a standard solution of 0.10 M NaOH in the presence of phenolphthalen

(PP) as indicator. The titration was stopped when the colour of the samples changed to red. The titration was carried out in duplicate. The extent of hydrolysis of PHEA was calculated as follows:

(% hydrolysis) =

$$\frac{0.10 \times (V_1 - V_o) \times 72 \times 50/5 \times 116/72}{M_{18} \times 1000} \times 100\% \quad \text{.....6.14}$$

$$= \frac{V_1 - V_o}{M_{18}} \times 11.6 \quad \text{.....6.15}$$

where V_o is the volume of NaOH for the blank (ml), V_1 is the volume of NaOH for the sample (ml), M_{18} is the mass of the sample (g), 72 is the molecular mass of the repeat unit of the PHEA, 50/5 is the dilution factor, 116/72 is the factor for 100% hydrolysis. Equation 6.15 was also used to calculate the extent of hydrolysis of the other polymers, but the factors used were 14.0 for PHPA, 13.0 for PHEMA and 15.4 for PHPMA in place of the factor 11.6 for PHEA.

6.3.1.5 Insolubility of homopolymers of non-ionogenic hydrophilic monomers in non-polar solvents (PE/toluene)

The polymers (0.5 g) were each added to portions of PE/toluene (1:1 by volume) (100 g). The samples were kept in an oven (40°C) for 66 days. The insoluble polymers were then removed from the solvent and dried. In this experiment, the insolubility of the polymers was defined as the amount of polymer recovered after drying in an oven (100°C) for 45 minutes and then in the vacuum oven (0.16 mm Hg) at 20°C for 2-5 hours. The insolubility was calculated as follows:

$$\text{polymer recovered (\% w/w)} = \frac{M_9}{M_8} \times 100 \quad \text{.....6.16}$$

where M_8 is the mass of added polymer (g), and M_9 is the mass of dry polymer (g).

6.3.1.6 Solubility of NR film in polar and non-polar solvents

NR films were prepared by casting NR latex on to separate ceramic plates. The films were then dried either at 20°C for 1 to 2 weeks, or at 20°C for 1 to 2 weeks and then in the vacuum oven at 30°C for 30 minutes, or at 20°C for 1 to 2 weeks and then in the vacuum oven at 50°C for 30 minutes.

(i) **Non-polar solvent**

The NR films (0.5 g) were added to the PE/toluene solutions (50-150 g). The samples were then kept either

a. at room temperature (20°C) for up to 3.5 months,
b. in an oven (40°C) for up to 63 days, or
c. at 20°C for up to 11 days, followed by maturing in an oven (40°C) for up to 55 days.

The solubility of the products in the solvent was observed visually.

(ii) **Polar solvents**

The NR films (1 to 3 g) were added to IMSA (100 g). Two samples were kept at 20°C for 3.5 months and the others were kept in an oven (40°C) for 26 days. The films were then taken out of the solvent and dried in an oven (100°C) for 3.5 hours. The insolubility of the products was determined as described previously (Section 6.3.1.5).

6.3.1.7 Characterisation of modified NR latex

6.3.1.7.1 Monomer conversion

Nonox DPPD (0.4 pphr), prepared as a 2% IMS solution, was added to the modified latices (3-5 g). The samples were then dried in an air-oven (70°C) for 3-4 hours, and then in a vacuum oven (0.16 mm Hg) at 90°C until a constant mass was obtained (16-18 hours). The conversion of monomer to polymer was calculated as follows:

$$\text{conversion (\% w/w)} = \frac{M_{10} - M_{11}}{M_o} \times 100 \quad \text{.....6.17}$$

where M_o is the mass of the monomer (g), M_{10} is the mass of residue after evaporation (g), and M_{11} is the total mass of the solids of NR latex plus inhibitor, initiator and soap, if any, (g).

6.3.1.7.2 Determination of homopolymers

Modified NR latices (3-5 g) having a known extent of polymerisation were dried in a fume cupboard (20°C) until thin pastes were obtained. The pastes were then coagulated completely using a few drops of IMSA solution. The homopolymers were extracted as described previously (Section 6.3.1.3). Four determinations for each sample were carried out. Two samples were used to continue the determination of free NR in the samples. The samples were not dried in the oven (to avoid oxidation) after separation of the homopolymers (Section 6.3.1.7.3). The homopolymer content was calculated as follows:

$$\text{homopolymer (\% w/w/)} = \frac{(M_o \times C) - (M_{12} - M_{13})}{M_o} \times 100 \quad \text{...6.18}$$

where M_o is the mass of monomer (g), C is the conversion of monomer (%), M_{12} is the total mass of dry rubber and polymer after extraction and drying (g), and M_{13} is the mass of dry rubber in the sample.

6.3.1.7.3 Separation of free NR

After separation of the homopolymer and monomer as described previously (Section 6.3.1.7.1/2), the samples were dried in a fume cupboard (20 $\pm$ 2°C) until completely dry. The dry samples were then dissolved in petroleum ether/toluene (1:1 by volume) (100 g). The samples were then kept in an oven (40°C) until the NR film control was completely dissolved. The free NR was calculated as follows:

$$\text{free NR (\% w/w)} = \frac{M_{14} - M_{15}}{M_{19}} \times 100 \quad \text{.....6.19}$$

where M_{19} is the total mass of solids of NR latex and monomer (g), M_{14} is the mass of sample after separation of monomer, homopolymer, added soap (if any), and initiator (g), and M_{15} is the mass of residue after extraction and drying (g).

6.3.1.8 Investigation of grafting mechanism via transfer reactions in NR latex

This investigation was carried out using an organic initiator (ACA) which is soluble in aqueous solutions. Being similar to AZBN in structure, the radicals from ACA would be expected not to attack the NR molecule directly. Portions of NR latex (ca. 109 g) containing SLS (2 pphr) were measured into 500-ml reaction vessels. ACA (0.87 pphr) was added to each of the NR latices. The mixtures were then stirred thoroughly using a magnetic stirrer. The four monomers were then added to the latices in the quantities shown in Table 6.11. The polymerisations were carried out in a water-bath at 62-65^{o}C for about 18 hours with constant magnetic stirring. The determinations of conversion of monomers to polymer, and the characterisation of homopolymers, were carried out as described previously (Section 6.3.1.7). The grafting mechanism via transfer reactions involving NR in NR latex, if any, was established by the presence of graft copolymer in the products. Selected physical properties of the products, as described in Section 6.5, were also determined.

Table 6.11 Amounts of monomers added to NR latex and dry rubber content of reaction mixtures for investigation of transfer reactions involving NR in NR latex

monomer	concentration[x)] (% w/w)	level (pphr)	DRC (%)
HEA	9.0	20.19	24.95
HPA	9.1	20.35	24.92
HEMA	4.6	10.21	24.97
HPMA	4.7	11.17	24.96

x) aqueous solution

6.4 Polymerisation of non-ionogenic hydrophilic monomers in NR latex

6.4.1 Investigation of the hydrolysis of non-ionogenic hydrophilic monomers in aqueous ammonia solution

The undiluted monomers (8.0 g) were added to separate portions of a 2% aqueous ammonia solution (50.0 g) in 150-ml bottles. The samples were stirred thoroughly using a glass rod. The initial pH of each sample was determined immediately after stirring. The bottles were then closed to prevent evaporation of ammonia, and were placed in a water-bath at 30°C with constant magnetic stirring. The pH of the solutions was recorded about every 1.5 hours for the first 6-7 hours, and then after 23 and 47 hours time respectively. A 2% aqueous ammonia solution containing no monomer was used as control.

6.4.2 Effect of added PHEA, PHPA upon creaming of NR latex

Samples of NR latex (40-50 g) were weighed into 250-ml bottles. Appropriate of volumes of a 1.5% aqueous ammonia solution were added to the samples to reduce the DRC of the total reaction mixture, including the added polymers, to 25%. The required amounts of the polymers to give 0, 30 and 50 pphr respectively, dissolved in 1.5% aqueous ammonia solution, were added to the diluted latices. The mixtures were stirred thoroughly using a clean glass rod and kept for about 4 months at 20$\pm$ 0.02°C. The amount of serum layer which had formed after 4 months was observed. The extent of creaming was calculated as follows:

$$\text{extent of creaming (\%)} = \frac{H_s}{H_o} \times 100 \quad \text{.....6.14}$$

where H_o is the height of the initial latex sample, and H_s is the height of the serum layer.

6.4.3 Determination of maximum quantity of non-ionogenic hydrophilic monomers that could be polymerised in NR latex using a redox initiator

6.4.3.1 Polymerisation of HEMA in presence of SLS

Of the four monomers, HPMA and HEMA were the most effective destabilisers for NR latex. HEMA was selected

first for investigation, and inferences concerning the other monomers were then drawn from the results for HEMA. These inferences were subsequently verified. The formulation used to investigate the maximum amount of HEMA which could be polymerised in NR latex at 25% DRC in the reaction mixture is given in Table 6.12. Portions of a 10-20% aqueous solution (0 to 6 pphr) were added to separate portions of NR latex and matured for 12 to 90 days at 20°C prior to use.

Table 6.12 Formulation used to investigate maximum amount of HEMA which could be polymerised in NR latex at 30°C

ingredient	dry parts by weight
NR latex (as 59.99% DRC)	100.0
SLS (as 10-20% w/w aqueous solution)	0 to 6
NH_4OH (as 2% v/v aqueous solution)	variable
$K_2S_2O_8$ (as 4% w/w)[x)]	0.2 to 1.5
$Na_2S_2O_5$ (as 4% w/w)[x)]	0.2 to 1.5
HEMA (as 20% w/w)[x)]	9.6 to 40.5
or	
HEMA (as 30% w/w)[x)]	40.5 to 60.3
total mass, (g)	75.0
DRC	25.0

x) in 2% v/v ammonia solution

The procedure for the polymerisations was as follows: Portions of NR latex (ca. 31.3 g) were placed in 120-ml bottles. The requisite amounts of ammonia and potassium persulphate were added to the latices. The samples were stirred thoroughly using a glass rod for about 1 minute. The requisite amount of sodium metabisulphite was added to the samples and stirred again for about 1 minute. The requisite amount of HEMA was then added to the samples. The amounts of each ingredient added were adjusted so that the total mass of the reaction mixtures was always 75.0 g with DRCs of the total reaction mixture of 25.0%. The bottles containing the samples were closed tightly and placed in a water-bath at 30.0°C for about 24 hours with constant magnetic stirring. The pH of the samples before, during (if necessary), and after polymerisation was recorded. The stability of the samples was observed

visually. The extent of any serum layer was also observed.

6.4.3.2 Polymerisation of HEA, HPA, and HPMA in presence of SLS

The formulation used to investigate the maximum amount of HEA, HPA and HPMA which could be polymerised in NR latex in the presence of SLS was similar to that used for HEMA (Section 6.4.3.1), with the following differences:

(i) The NR latex containing SLS (0 to 6 pphr) was matured for 5 to 90 days at 20 ± 0.02°C prior to use.

(ii) The amounts of monomers added to NR latex were as shown in Table 6.13.

Table 6.13 Amounts of HEA, HPA, and HPMA polymerised in NR latex at 30°C

monomer	concentration[x] (% w/w)	dry parts by weight
HEA	30	30.0 to 50.5
	50	75.0 to 100.0
HPA	30	40.3 to 50.5
	50	75.0 to 99.9
HPMA[xx]	20	40.5 to 50.6

[x] in 2% v/v aqueous ammonia
[xx] as a mixture

The conditions for polymerisation and the assessment of the colloid stability of the products were as described previously (Section 6.4.3.1).

6.4.4 Effect of pH upon creaming of crude graft copolymer latices

Portions (100 g) of crude NR/PHEA graft-copolymer latex and crude NR/PHPA graft-copolymer latex as prepared previously (Section 6.4.3.2) were added to 250-ml bottles. The initial pH of the latices after polymerisations was ca. 6. A 35% ammonia solution was added to the latices to raise the pH to ca. 10. The latices were then allowed to stand for 34 days. The extent of the creaming was observed over

periods of 10 and 34 days. Crude graft copolymer latices containing no added ammonia were prepared as controls.

6.4.5 Effect of dry rubber content (DRC) upon conversion and efficiency of grafting of monomers polymerised in NR latex in absence of SLS

The formulation used to investigate the effect of varying the DRC upon the conversion and efficiency of grafting of the monomers when polymerised in NR latex in the absence of the SLS is given in Table 6.14. The procedure for the polymerisations was as follows: The requisite quantities of NR latex and ammonia solution were placed in 250-ml bottles. To these were added portions of potassium persulphate (2.1×10^{-3} mol/l latex). The mixtures were stirred thoroughly for about 1 minute. Portions of sodium metabisulphite (2.97×10^{-3} mol/l latex) were then added to the latices, and the mixtures stirred thoroughly for a further time. Then the monomers (0.50 mol/l latex) were added to the mixtures. The total mass of the final mixtures was 113.0 g. The DRCs were 15.0, 25.0, and 35.0% respectively. The samples were placed in a water bath at 30.0°C for about 24 hours with constant magnetic stirring. The colloid stability of the products was assessed by observing any flocculation or coagulation. Any separation of serum was noted. The conversion of monomer to polymer, and the determination of homopolymer content, were carried out as described previously (Section 6.3.1.7).

Table 6.14 Formulation used to investigate effect of dry rubber content (DRC) upon conversion and efficiency of grafting of monomers polymerised in NR latex in absence of SLS

ingredient	level (mol/l latex)		
NR latex	variable	variable	variable
NH_4OH (2% v/v)	variable	variable	variable
$K_2S_2O_8$ (4% w/w)[x]	2.09×10^{-3}	2.09×10^{-3}	2.09×10^{-3}
$Na_2S_2O_5$ (4% w/w)[x]	2.97×10^{-3}	2.09×10^{-3}	2.09×10^{-3}
monomer (20% w/w)[x]	0.50	0.50	0.50
total mass, (g)	113.0	113.0	113.0
DRC, (%)	15.0	25.0	35.0

[x] in a 2% aqueous ammonia solution

6.4.6 Effect of activation of NR latex upon conversion and efficiency of grafting of monomers polymerised in NR latex in presence of SLS

Portions of NR latex containing SLS (3.66 pphr) were placed in 2-l reaction vessels. The latices were then diluted with 1.5% w/w aqueous ammonia solution as described previously (Section 6.4.3). The diluted latices were then 'activated' by adding a 4% potassium persulphate solution to give 0.27 to 1.10 pphr, and stirred for 25 to 80 minutes. The activation process was believed to occur during the additional time the initiator was in contact with the NR latex prior to the addition of monomer addition. After this activation time, 4% aqueous sodium metabisulphite solution was added to the latex to give 0.27 to 1.10 pphr. The mixtures were stirred for 5 to 18 minutes at 30°C. The preparation of the initiator solutions was carried out as described previously. To these latex mixtures were added the quantities of monomers shown in Table 6.15. The polymerisations were carried out in a water-bath at 30.0°C for about 23 hours with constant magnetic stirring. The pH values before and after polymerisations were recorded. The colloid stability of the products and the extent of creaming were also noted. The conversion and efficiency of grafting were determined as previously (Section 6.3.1.7). In addition, selected physical properties of the products were also determined as described in Section 6.5.

Table 6.15 Level and concentration of the monomers added to the activated NR latex

monomer	concentration of solution (% w/w)[x)]	dry parts per 100 DRC
HEA	20-30	10-50
HPA	20-30	10-50
HEMA	20	10-30
HPMA	20	10-30

[x)] in a 2% v/v aqueous ammonia solution

6.5 Selected physical properties of modified NR latices and modified NR films

6.5.1 Additional test equipment

6.5.1.1 Instron testing machine model 1026

6.5.1.2 Monsanto Rheometer 100

6.5.2 Experimental procedures

6.5.2.1 Mechanical stability time (MST)

Portions of modified NR latex (25% DRC)(85.0 g) were heated to 35°C prior to carrying out the MST testing as described in Section 6.1.2.1. NR latices (25% DRC) containing SLS (0 and 3.66 pphr) were used as controls. Because of excessive foaming of the controls during the test, attempts were made to reduce the stability of the latices by adding 5% w/w aqueous sodium chloride solution (9 pphr) or 5% w/w w/w aqueous potassium chloride solution (9 pphr) prior to the MST test. However, these additions did not overcome the foaming problem.

6.5.2.2 Coagulation behaviour

Portions of the modified latices (2.0 g) were measured into 120-ml bottles. The coagulant solutions shown in Table 6.16 were prepared. The amount of the coagulant solutions added to separate portions of the latices was 250 pphr. The stability of the latices, such as flocculation, coagulation and creaming, was observed visually.

Table 6.16 Coagulant solutions used to investigate coagulation behaviour of modified NR latices

coagulant	concentration (% w/w)	coagulant	concentration (%w/w)
CH_3COOH	5	KCl	5
CTMB	5	$MnCl_2$	5
CH_3OH	5	$MgCl_2$	5
IMS	5	$ZnCl_2$	5
acetone	5	$CaCl_2$	5
LiCl	5	$BaCl_2$	5
NaCl	5	$FeCl_3$	5

6.5.2.3 Vulcanisation behaviour

6.5.2.3.1 Effect of added PHEA and PHPA upon vulcanisation behaviour of NR film

The procedure for blending the polymers with NR latex is given in Section 6.4.2. The blends were compounded with vulcanising agents as shown in Table 6.17. The preparation of the vulcanising agents (20% w/w aqueous dispersion) is described in Appendix 21. In the case of dicumyl peroxide as a vulcanising agent, the samples were matured for 2 days at 20°C prior to casting. The latex compounds were each cast on to glass plates and dried in a fume cupboard at 20°C for 2 days. The glass plates were coated with a release agent and dried prior to use. Each sample dried film was folded 5-7 times and pressed using a roller. Samples (10-15 g) were punched rom the folded film. Films from NR latices containing no polymers were prepared as controls. The vulcanisation behaviour of the films was investigated using a Monsanto Rheometer 100 heating at 140°C for about 1.5 hours.

Table 6.17 Formulation used for investigation of vulcanisation behaviour of blend of PHEA/NR and PHPA/NR

ingredient	dry parts per 100 DRC	
	compound-1	compound-2
NR latex containing PHEA or PHPA	100.00	100.00
S	2.75	-
ZnO	5.50	-
stearic acid	1.10	-
CBS	1.10	-
TMTD	0.33	-
dicumyl peroxide[xx)]	-	2.50

[x)] as 20% w/w aqueous dispersion
[xx)] as 25% w/w toluene solution

6.5.2.3.2 Effect of nature of accelerator upon vulcanisation behaviour of NR film at 100°C

The vulcanisation of NR films prepared from NR latex is usually carried out in an oven at low temperature (100°C) using a zinc dithiocarbamate, such as zinc

diethyldithiocarbamate (ZDC), as accelerator. Previous work (6) showed that, with the exception of crude NR/HPMA graft-copolymer latex, the tensile strength of the modified NR latices using ZDC as accelerator were lower than that of the control NR latex. Therefore attempts were made to investigate the effect of other type of accelerators upon selected physical properties of the modified NR. To investigate the effect of the nature of the accelerator upon vulcanisation behaviour at low temperature (100°C), two compounds containing different accelerators, namely, ZDC and a mixture of n-cyclohexyl-2 benzthiazole sulphenamide (CBS) and tetramethyl thiuram disulphide (TMTD), were prepared. Portions of NR latex were compounded with the vulcanising ingredients as shown in Table 6.18.

Table 6.18 Formulations used to investigate the effect of nature of accelerator upon vulcanisation behaviour of films from NR latex

ingredient	dry parts per 100 parts DRC	
	compound-1	compound-3
NR latex	100.00	100.00
S	2.75	2.00
ZnO	5.50	3.00
CBS	1.10	-
stearic acid	1.10	-
TMTD	0.33	-
ZDC	-	1.00

The preparation of the vulcanising agents containing ZDC (50% w/w aqueous dispersion) is described in Appendix 22. The requisite amounts of the dispersion were added to the latices and stirred using a glass rod. The samples were matured overnight at 20°C prior to casting. The latex compounds were each cast on to glass plates and dried in a fume cupboard at 20°C for 3 days. The dried film of each sample was folded 3-5 times and pressed using a roller. Samples (10-15 g) were punched from the folded film. The vulcanisation behaviour of the NR films was investigated using Monsanto Rheometer 100 heating at 100°C.

6.5.2.3.3 Vulcanisation behaviour of modified NR films

The preparation of samples for investigating the vulcanisation behaviour of the modified NR films was carried out as described previously (Section 6.5.2.3.1), except that no experiments were carried out using dicumyl peroxide as vulcanising agent.

6.5.2.4 Determination of stress-strain behaviour

The formulation-1 shown in Table 6.17 was used to investigate the tensile properties of vulcanised films from the modified NR latices. The procedure for preparing the samples was as follows: The curing agents (ca. 4 g) were added to the modified latices (ca. 30 g) and the mixture stirred thoroughly using a clean glass rod. Air bubbles were removed from the surface of the samples by scavenging with filter paper. The samples were carefully filtered using a muslin cloth (5 to 6 layers) to eliminate the small remaining air bubbles, and then cast on glass plates in a fume cupboard. The glass plates were previously coated with a release agent. NR latices containing no additives were prepared as controls. The samples were dried in the fume cupboard for 2-3 days. When vulcanised at 140^{o}C for 30 minutes, the film of the modified NR latices turned black and became very sticky, becoming almost impossible to remove from the glass plates. To overcome these problems, the temperature of the vulcanisation was reduced to 100^{o}C but extending the heating to 1.5 hours, which gave satisfactory films. The vulcanised films were slightly dusted with zinc stearate powder and then kept in a desiccator. Test-pieces were die-cut from the film of the vulcanisate using an ISO cutter. At least three test-pieces from each sample were punched for the determination of modulus at 100%, and 300%, elongation at break, and tensile strength. The test-pieces were of the dumbbell type as described in BS 903: Part A2: 1971. A punch with the nominal width of 4 mm was used. The mean value of three thickness measurements was taken as the thickness of the test-pieces. The moduli at 100% and 300% extention, the elongation at break, and the tensile strength of the test-pieces were determined using an Instron tensometer model 1026. The rate of the cross-head separation was 500 mm/minute. For each sample, at least three test-pieces were tested and average values calculated.

6.5.2.5 Determination of resistance to liquids

(i) Water absorption

Samples 1 mm thick, 4 mm wide and of variable length were cut. The films (0.5 to 1.6 g) were vacuum dried (0.16 mm Hg) at 60°C for about 15 minutes. The samples were cooled and re-weighed (0.5 to 1.6 g) before immersing in distilled water (ca. 100 g) for about 2 months at 20°C. The water absorption was calculated as follows:

$$\text{water absorption (\% w/w)} = \frac{M_{16} - M_o}{M_o} \times 100 \quad ..6.15$$

where M_o is the original mass of the sample, and M_{16} is the mass of the swollen sample. Films from NR latices containing no additives were prepared as controls.

(ii) Oil uptake

As for the determination of water-absorption determination, the samples (ca. 1 g) (1 mm thick, 4 mm wide and variable length) were vacuum-dried (0.16 mm Hg) at 60°C for about 15 minutes. The films were then immersed in (ca. 100 ml) of an isooctane:toluene (70:30 by volume) mixture for 7 days at 20 ± 2°C in the dark. The oil uptake was calculated as follows:

$$\text{oil uptake (g solvent/g sample)} = \frac{M_{17} - M_o}{M_o} \quad ..6.16$$

where M_o is the mass of the original sample (g), and M_{17} is the mass of the swollen sample. Films from NR latices containing no other additives were prepared as controls.

6.5.2.6 Dipping behaviour

In this work, the dry-coagulant and heat-sensitised dipping behaviours of the modified latices were investigated. Attempts were made to heat-sensitise the latices by the zinc-ammine system, and also by PVME.

6.5.2.6.1 Dry-coagulant dipping

The formulation for the coagulant used to investigate dry-coagulant dipping behaviour is given in Table 6.19. The procedure for the dry-coagulant process was as follows: Boiling tubes were used as formers throughout the dipping experiments. Clean formers were heated to 75°C and immersed in the coagulant solution. The formers were removed slowly and dried at 75°C for about 5 minutes. The cool formers were each immersed in the modified latices (Table 6.20) for 0.5, 1.2, and 3 minutes respectively. The appearance of the deposits on the formers was observed to drying. However, after withdrawal of the formers, the deposits of the samples were found to run down the side of the formers. No attempt was made to vulcanise the films.

Table 6.19 Formulation of coagulant solution for dry-coagulant dipping

ingredient	parts by weight
$CaCl_2 . 6 H_2O$	15.0
$Ca(NO_3)_2 . 4 H_2O$	15.0
CTAB	0.1
IMS	60.0

6.5.2.6.2 Heat-sensitisation of modified NR latices using PVME as a heat-sensitiser

The formulation used for the heat sensitisation of the modified NR latices is given in Table 6.21. The procedure for preparing the latex compounds was as follows: The requisite amounts of the dispersion of S, ZnO, CBS and TMTD (Appendix 23) and the PVME were added to the latices and allowed to mature overnight at 20°C. The pH of the latex compound was adjusted to 9.0 by adding either a 10% ammonia solution or a 5% formaldehyde solution. Air bubbles were removed from from the latex by scavenging the surface with a filter paper. The procedure used to assess the heat sensitivity of the latex compounds was as follows. The clean formers were filled with boiling water and immersed in the latex compound. The dwell times were 0.5, 1.0, 2 and 3 minutes respectively. NR latices containing no PVME were prepared as controls. The appearance of the products was

observed visually. It was observed that deposits ran down the side of the formers. No attempt was made to vulcanise the films.

Table 6.20 Formulation of modified NR latices for dipping behaviour

monomer	level (pphr)	SLS (pphr)	initiator system	conversion (%)	efficiency of grafting (% w/w)
control	-	0.00	-	-	-
control	-	2.00	-	-	-
control	-	3.66	-	-	-
HEA	20.19	2.00	ACA	51.9	85.4
HPA	20.35	2.00	ACA	51.5	50.8
HEMA	10.21	2.00	ACA	44.4	64.9
HPMA	11.17	2.00	ACA	51.4	100.0
HEA	9.98	3.66	redox	60.9	0.5
	49.85	3.66	redox	35.3	0.0
HPA	9.98	3.66	redox	60.9	0.5
	39.71	3.66	redox	69.7	0.0
HEMA	10.05	3.66	redox	44.7	23.1
HPMA	10.05	3.66	redox	42.5	32.6

Table 6.21 Formulation used for heat-sensitisation of modified NR latex using PVME as sensitiser

ingredient		dry parts by weight
modified NR latex (as 25% DRC)		100.00
S	x)	2.75
ZnO	x)	2.75
CBS	x)	1.10
TMTD	x)	0.33
PVME[xx)]		3.00

x) as 18% w/w aqueous dispersion
xx) as a 15% aqueous solution

6.5.2.6.3 Heat sensitisation of modified NR latices using zinc-ammine system

The formulation used to investigate the heat sensitisation of the modified NR latices by the zinc-ammine system is given in Table 6.22. The procedure for preparing the latex compounds was as follows: The requisite amounts of the dispersion of S, ZnO, CBS and TMTD (Appendix 23) and ammonium acetate were added to the latices and stirred thoroughly using a glass rod. The mixtures were then allowed to mature overnight at 20 $\pm$ 0.02^{o}C. Air bubbles were removed from the surface of the mixture by means of a filter paper. The procedure used to assess the dipping behaviour of the latices was carried out as follows: The clean formers were filled with boiling water and immersed in the latex compounds. The dwell times ranged from 0.5 to 2 minutes. The formers, together with their deposits, were withdrawn slowly and rotated to even out irregularities. It was observed that the deposits obtained from all the modified NR latices, except those obtained from the crude NR/PHPMA graft-copolymer latex, ran down the side of the formers. This also proved to be the case with the controls containing added SLS (2-3.66 pphr). The deposits of the crude NR/PHPMA graft-copolymer were dried in oven at 40^{o}C for 30 minutes, then vulcanised at 100^{o}C for about 30 minutes. When vulcanised at 140^{o}C, the modified latices turned black and could not easily be removed from the formers. The temperature was reduced to 100^{o}C to overcome this problem. Although this temperature was low for curing the NR and modified NR films using the vulcanising system shown in Table 6.22, it did produce satisfactory films for the modified NR latex, and also for the control latex not containing SLS. NR latices, containing SLS (0, 2 and 3.66 pphr), but containing no other additives were prepared as controls. The vulcanised films were stripped from the formers and lightly dusted with zinc stearate powder. The thickness of the films was measured using a Mercer Gauge. The mean value of at least three readings was taken as the thickness of the film.

Table 6.22 Formulation of latex compound for investigating heat-sensitisation of modified NR latices using zinc-ammine system

ingredient	(dry parts by wight)
modified NR latex	100.00
S x)	2.75
ZnO x)	2.75
CBS x)	1.10
TMTD x)	0.33
ammonium acetate (20% w/w)	0.55

x) as 18% w/w aqueous dispersion

6.5.2.6.4 Combination of dry-coagulant dipping and heat-sensitisation

Because the deposits ran down the formers using both the dry-coagulant and heat-sensitised processes, attempts were made to investigate the dipping behaviour of the modified NR latices using the combination of

i) the dry-coagulant and the zinc-ammine system as heat sensitiser

ii) the dry-coagulant and PVME as heat sensitiser

The clean formers were immersed in to the dry-coagulant and dried as described previously. The formers were then filled with boiling water and immersed into the latex compound containing either zinc-ammine ions or PVME as heat sensitiser. All of the modified NR latices also ran down the side of the formers with the exception of the crude NR/PHPMA graft-copolymer. The films were dried in an oven at 40^{o}C for 30 minutes and then vulcanised as described previously (Section 6.5.2.6.3).

Chapter 7

Investigation of effects of non-ionogenic hydrophilic monomers, their polymers, and initiators upon colloid stability of NR latex

7.1 Introduction

The monomers, redox initiator and polymers, added to NR latex, would be expected to affect the colloid stability of the latex. Preliminary studies were carried out to confirm if this was the case, and to quantify such effects. Further studies would then made to investigate ways of reducing any destabilisation that was observed. The results of this work are summarised in the Sections 7.2 to 7.10, which describe:

(i) the effects of additing non-ionogenic hydrophilic monomers to NR latex,

(ii) the partitioning of the monomers between water and n-dodecane phases,

(iii) the effects of adding redox initiator to the latex,

(iv) the effects of maturation and dilution,

(v) the effects of adding homopolymers of non-ionogenic hydrophilic polymers to the latex.

All the results are then discussed in Section 7.11.

7.2 Effect of added non-ionogenic hydrophilic monomers upon colloid stability of NR latex in presence of stabilisers

Table 7.1 shows the results of experiments undertaken to investigate the effects of added non-ionogenic hydrophilic monomers upon the colloid stability of NR latex. It was observed visually that the monomers act as destabilisers. The NR latex (55.0 % final TSC), which had been stabilised previously by adding non-ionogenic stabilisers (up to 8 pphr) or ionic stabilisers (up to 8 pphr) and then matured for 2-7 days at 20^{o}C, was greatly destabilised by adding small quantities of the monomers (2-4 pphr). The hydroxyalkyl methacrylates (HEMA and HPMA) would at least partly coagulate the latex overnight. The hydroxyalkyl

acrylates (HEA and HPA) showed no visual signs of coagulating the latex. However, the mechanical stability times (MST) of the samples were much lower than that of the control latex.

7.3 Partition coefficients of non-ionogenic hydrophilic monomers between water and n-dodecane phases

The results are shown in Table 7.2. Of the four non-ionogenic hydrophilic monomers, only one (HPMA) showed a partition between the water and n-dodecane, the value being K = 0.49 at 25^{o}C. The other monomers are totally miscible with water.

7.4 Effect of added non-ionogenic hydrophilic monomers upon mechanical stability time (MST) of NR latex in absence of a stabiliser

The results are shown in Figure 7.1 and Table 7.3. It was subsequently found that the monomers initially increased the MST of the latex until it reached a point where the MST showed a maximum value. Further addition of monomers then decreased the MST significantly. The concentrations of the monomers which give maximum MST values, together with the concentrations which give an MST equivalent to that of the initial control latex $[MST]_o$ are shown in Table 7.4. The effectiveness of the monomers in enhancing, and also in subsequently reducing, the MST of NR latex is in the following order: HPMA > HEMA > HPA > HEA.

7.5 Effect of maturation upon mechanical stability time (MST) of NR latex in presence of non-ionogenic hydrophilic monomers

The results are shown in Figures 7.2, 7.3, and Tables 7.5, 7.6. It was found that maturation of NR latex in the presence of the monomers decreased significantly the MST of the latex over a short period of time (less than 20 hours), and that further slower reductions occurred with further maturation. The effectiveness of the monomers in reducing the MST of NR latex was found to be in the following order: HEA> HPA > HEMA > HPMA>.

7.6 Effect of added potassium persulphate-sodium metabisulphite upon mechanical stability time (MST) of NR latex before maturation

The results are shown in Figure 7.4 and Table 7.7. The MST of NR latex decreased progressively as the concentration of redox initiator was increased, until the concentration reached a 1.50 pphr (1:1 by weight ratio of the two components of the redox initiator) when the latex was partly coagulated. The thickness of the double layer surrounding the rubber particles would be reduced by increasing the concentration of the redox initiator. The results of calculations of double-layer thickness are shown in Figure 7.5. These calculations were based on the assumption that the ionic strength contribution from the initial latex was derived mainly from the electrolytes which gave rise to the VFA number, the latter being 0.02 g/100 g total solids for the latex used.

7.7 Effect of added redox initiator and monomer upon mechanical stability time (MST) of NR latex

The results are shown in Figure 7.6 and Table 7.8. The addition of the redox initiator at 0.75 pphr reduced the MST to about half that of the control latex. The addition of the monomers at 2 pphr increased the MST of the latex. The ratios of the MSTs of the latices containing 2 pphr of monomers to that of the control latex are given in Table 7.9. However, as expected, a mixture of redox initiator and each monomer caused the MST of the latex to fall below that of the latex containing each respective monomer only.

7.8 Effect of maturation upon mechanical stability time (MST) of NR latex containing both monomers and redox initiator

The results are shown in Figure 7.7 and Table 7.10. Maturation of NR latex containing both monomers and redox initiator caused the MST to decrease progressively over a short period of time (less than 20 hours), but the decrease slowed over a further longer period of time in the case of the latices containing HEA-initiator and HPA-initiator. The MST of the latices containing HEMA-initiator and HPMA-initiator decreased over a period of less than 20 hours and then increased slowly with time.

7.9 Effect of dilution upon mechanical stability time (MST) of NR latex containing non-ionogenic hydrophilic monomers and initiator before maturation

The results are shown in Figures 7.8, 7.9 and Table 7.11. Dilution of NR latex, either containing monomer and initiator or in the absence of these additives increased the MST of the latex. However, plots of the ratios of MST of NR latices containing monomer and initiator, MST(m), to the MST of the corresponding latex not containing monomer and initiator, MST(o), versus TSC shows that the monomer-initiator mixtures tend to decrease the enhancement of the MST accompanying dilution of the latex, except in the case of the latex containing HEA and initiator (Figure 7.9).

7.10 Effect of added homopolymers of non-ionogenic hydrophilic monomers upon mechanical stability time (MST) of NR latex

The results are shown in Figure 7.10 and Table 7.12. They are presented as ratios of the MST of NR latices containing polymer, MST(p), to that of the corresponding latices not containing polymer, MST(o). The results show that PHPA (0.1 pphr) increased the MST of NR latex, whereas the other three polymers initially decreased the MST below that of the control latex. The effectiveness of the three polymers in reducing the MST of the latex is in the following order: PHEMA > PHEA > PHPMA. However, at a higher concentration (0.2 pphr), the MST of the latex increased to value above that of control latex, except in the case of PHEMA.

7.11 Discussion of results

7.11.1 Introduction

To the best of the present author's knowledge, no information has been published on the effects of monomers or initiators upon the colloid stability, particularly, the mechanical stability, of NR latex. This is despite the fact that many monomers have been graft copolymerised in NR latex.

7.11.2 Effect of non-ionogenic hydrophilic monomers and maturation upon the stability of NR latex

In the first stage of the investigation of the effect of the added monomers to NR latex (55.0% DRC mixtures), it was observed that, at small levels of added HEMA and HPMA (2-4 pphr), the latex partly coagulated overnight even though the latex contained previously-added stabilisers (up to 8 pphr) such as Texofor A-60, Texofor FP-300 and sodium lauryl sulphate. The other monomers (HEA and HPA) when added to the latex showed no visual signs of coagulating, but the MST was lower than that of the control latex (Table 7.1). These observations strongly suggested that the monomers act as destabilisers for NR latex. There are two possible explanations for the destabilisation of the latex:

(i) The monomers are hydrophilic in nature, and reduce the extent of the hydration layer at the surface of the rubber particles, thereby reducing the stability of the latex.

(ii) The monomers might react with the indigenous stabilisers of the latex, such as proteinaceous substances and fatty-acid anions, although it is difficult to suggest a mechanism for such reactions.

As mentioned in Section 3.2.3, Minoura (87) investigated the effect of varying the length of the alkyl group of an alcohol, i.e., methanol, ethanol, and propanol, upon the MST of NR latex. At low alcohol concentrations, the MST of the latex increased progressively with increasing amount of added alcohol. However, at certain levels of added alcohol, the alcohols are no longer able to increase the MST of the latex. In this project, the effect of the non-ionogenic hydrophilic monomers containing an -OH group upon MST before maturation also showed that, at low concentrations, the monomers increased substantially the MST of NR latex until it reached a maximum value (Figure 7.1), i.e., 1,650 seconds for HEA, 2,295 seconds for HPA, 3,998 seconds for HEMA, and 3,948 seconds for HPMA above that of the control latex. This strongly suggests that the monomers rapidly adsorbed on to the particle surfaces, perhaps bringing about a thickening of the adsorbed layers, possibly contributing to steric stabilisation, and enhancing hydration. One would expect that the ethylenic

and alkyl functional groups of the monomers are more likely adsorb on to the surface of the particles than the hydroxyl groups, which would tend to remain in the aqueous phase. There is also the possibility that the monomers might become associated with the surface layers through hydrogen bonding involving the OH group. In the case of HPMA, this monomer might partly dissolve into the rubber phase, as it showed a tendency to dissolve in n-dodecane in the presence of water (Table 7.2).

As regards the ethylenic groups in these monomers, the methacrylate group (3 C atoms) is more hydrophobic than the acrylate group (2 C atoms). Consequently, the hydroxyalkyl methacrylates (HPMA and HEMA) might be adsorbed more, and cover more of the surface of the particles, than would HPA and HEA under comparable conditions. It is therefore interesting that the MSTs of the latices containing HPMA and HEMA were greater than those of latices containing HPA and HEA. It was also observed that the MST of the latices containing monomers having a propyl group (HPMA and HPA) were greater than those of the latices containing the monomers having an ethyl group (HEMA and HEA). This may be as a consequence of thicker adsorbed layers at particle surfaces brought about by the propyl group being adsorbed more than the ethyl group. Another interesting aspect of the hydroxyalkyl acrylates is that they had to be added in higher concentrations to reach the maximum MST value than did the hydroxyalkyl methacrylates. A possible explanation for this is that these monomers were less adsorbed on to the particle surfaces. To achieve the MST maximum, the monomers had to be added such that the rubber particles became well covered by the monomers, requiring higher monomer concentrations than in the case of HEMA and HPMA.

When further additions of the monomers beyond those corresponding to the MST maximum values were made, the monomers were no longer able to increase the MST. In fact, the MST decreased progressively as the monomer concentrations were increased. Possible explanations of this are that mentioned earlier in this section (p.141). An additional factor may be the effect of reduction of the dielectric constant in the presence of added monomers upon the thickness of the double layer ($1/\kappa$) surrounding the rubber particles. This would also be expected to bring about destabilisation of the latex. The presence of the monomers would result in lower dielectric constant than in

the absence of the monomers. The thickness of the double layer could be calculated as follows in cgs units:

$$1/\kappa = \sqrt{\frac{D\ k\ T}{8\ \pi\ e^2\ I}} \quad \text{.....7.1}$$

where $1/\kappa$ is the thickness of double layer (cm), k is the Boltzman constant (1.38×10^{-16} erg.$^{o}K^{-}$), e is the electronic charge (4.80×10^{-10} esu), T is the absolute temperature ($298^{o}K$), D is the dielectric constant of the dispersion medium, and I is the ionic strength of the dispersion medium (ions/cm^3). The ionic strength is defined as follows,

$$I = 0.5 \sum m_i . z_i^2 \quad \text{.....7.2}$$

where m_i is the concentration of each ionic species (ions/cm^3), and z_i is the valency of each ionic species. It was assumed that the contribution to the total ionic strength made by the initial NR latex was due to the electrolytes assessed by the VFA no. of the latex (ca. 0.02 g/100 g rubber). Based on this VFA no., the ionic strength of the latex was calculated 24.50×10^{17} ions/cm^3 (Appendix 8). Substituting the values of k, T, e, and I in to the Equation 7.1, the thickness of the double layer surrounding particles in NR latex is then related to the dielectric constant of the dispersion medium by the equation

$$1/\kappa = 5.39 \times 10^{-8} \sqrt{D} \quad \text{.....7.3}$$

Based on the dielectric constant of compounds similar to the monomers, one can estimate that the monomers would have a dielectric constant of ca. 17. It was assumed that the dielectric constant of the dispersion medium of the initial latex is similar to the dielectric constant of water (78). The calculation of D for the aqueous phase was based on the assumption that the monomers partition entirely in the aqueous phase, and that a simple "law of mixture" is applicable. The results of the calculation of D and $1/\kappa$ at different levels of added monomer are shown in Table 7.13. From this table, it is evidence that the change of double layer thickness in the presence of the monomers (up to 14 pphr) is very small, being 6.1% . The conclusion was reached that the compression of the double layer with increasing monomers due to effects upon the dielectric

constant was negligible, and that the MST of NR latex was not affected by reduction of dielectric constant at the monomer concentrations investigated.

Rather surprisingly, the MST of NR latex in the presence of the monomers decreased substantially in over a short period of time, and then decreased slower with further time (Figures 7.2, 7.3). The following are the possible explanations: The monomers (16% w/w) in a 2% aqueous ammonia solution in fact undergo hydrolysis at 30°C (Figure 10.1). The susceptibility of the monomers to hydrolyse under such conditions was in the following order : HEA > HPA > HEMA > HPMA. It was to be expected that the monomers would also hydrolyse in NR latex preserved with ammonia to produce the corresponding acids and alcohols. In these circumstances, there are three processes which might decrease the MST of NR latex during maturation:

(i) The thickness of adsorbed layers brought about by the monomers gradually decreased while hydrolysis of the monomers was occurring, thereby reducing the MST of the latex.

(ii) The alcohols produced during hydrolysis, together with the rest of the unhydrolysed monomers, continued to dehydrate the hydration layer by mean of a hydrogen bonding reaction, thereby reducing the MST of the latex.

(iii) The acids produced during the hydrolysis of the monomers decreased the pH and increased the ionic strength of the latices to some extent, thereby reducing the MST of the latex.

It is probably significant that the susceptibility of the monomers to hydrolysis (HEA > HPA > HEMA > HPMA) is the same order as the effectiveness of the monomers in reducing the MST of NR latex after maturation, i.e., HEA > HPA > HEMA > HPMA.

7.11.3 Effect of redox initiator upon MST of NR latex

The redox initiator contains various ions such as Na^+, K^+, $S_2O_8^=$, and $HSO_3^=$ (from $S_2O_5^=$). As expected, addition of the redox initiator decreased the MST of NR latex (Figure 7.4). This was attributed to the increase in ionic strength (I) of the dispersion medium, thereby compressing the electric

double layer. This would decrease the repulsive potential energy (V_R), thereby reducing colloid stability. The effect of added redox initiator upon the compression of the thickness of rubber particles was calculated. The results are shown in Figure 7.5. The calculation of the thickness of the double layer is based on Equation 7.1. It was assumed that the dielectric constant, D, of the dispersion medium of NR latex is similar to that of water (78). The thickness of the double layer surrounding the rubber particles is then related to the ionic strength by the equation

$$1/K = 744.47 \sqrt{\frac{1}{I}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 7.4$$

The calculation of ionic strength, I, and the thickness of the double layer, $1/K$, at various levels of added redox initiator, is given in Appendix 8. Other factors, such as the formation of acids brought about by 1) decomposition of the initiator, and 2) reaction between persulphate radicals and hydrogen atoms removed from rubber molecules, might decrease pH of the latex to some extent. This would also decrease the MST of NR latex.

7.11.4 Combined effect of monomers and redox initiator upon MST of NR latex

When the monomers were added to NR latex containing the redox initiator, the MST of NR latex increased again (Figure 7.6). However, the MST values did not return to those of the NR latex plus monomer only. After maturation (Figure 7.7), the MST of the monomer-initiator mixtures decreased substantially over a short period of time (< 20 hours). Thereafter, the MST of NR latex might increase or decrease, depending upon the monomer present. In the case of HEA and HPA, the MST decreased slowly with time, suggesting that hydration was occurring slowly during the maturation. In the case of HEMA and HPMA, the MST increased gradually with time. Possible explanations for this are:

(i) The HEMA and HPMA are slower to hydrolyse than are HEA and HPA, so that the concentrations of these monomers were higher than those of HEA and HPA under comparable conditions (Figure 10.1).

(ii) The monomers might polymerise to some extent during the maturation period, to produce either a homopolymer or a graft copolymer. This might increase the MST of NR latex to some extent (Figure 7.10). This possibility will be discussed in Section 7.11.6.

7.11.5 Effect of dilution upon MST of NR latex containing both monomer and initiator

All previous workers have found the MST of NR latex to increase with decreasing TSC (77, 80, 81). This accords with the results of the present investigation. Figure 7.8 shows that, as the TSC of NR latices containing monomer and initiator decreases, the MST of the latices increases progressively. This is not surprising, because the average distance between the rubber particles increases with decreasing TSC of the latices, thereby decreasing the number of particles collisions. However, the plot of ratios of MST of NR latices containing monomer and initiator, MST(m), to that of the latices not containing monomer and initiator, MST(o), suggests that the monomer-initiator mixtures tend to decrease the enhancement of the MST upon decreasing the TSC, except in the case of the HEA-initiator-mixture (Figure 7.9). This might be as a consequence of the desorption of the monomers from the surface of the rubber particles to the aqueous phase.

7.11.6 Effect of homopolymers of non-ionogenic hydrophilic monomers upon MST of NR latices

The polymers derived from the non-ionogenic hydrophilic monomers behave differently from the monomers themselves. Generally, at low concentration (0.1 pphr), the polymers decreased the MST of the latex, with the exception of PHPA. The MST then increased as the polymer concentration (0.2 pphr) increased (Figure 7.10). For the purpose of discussion, it is convenient to divide the polymers into two groups:

(i) Those polymers, PHEA and PHPA, which are soluble in the aqueous phase of NR latex.

(ii) Those polymers, PHEMA and PHPMA, which are insoluble in the aqueous phase of NR latex.

At low concentrations, the water-soluble polymers had a less detrimental effect upon the MST than did the non-water-soluble polymers. The non-water-soluble polymers would be expected to precipitate in the aqueous phase and then desorb the indigenous stabilisers from the latex particles on to their surfaces, thereby decreasing the MST. This is probably similar to the results obtained by Blackley et al. (95). Blackley et al. concluded that ethoxylates having species which are essentially insoluble in water, but which can form dispersions of high specific surface area, and thus adsorb latex stabilisers, and may be this mechanism reduce the MST of NR latex. Thus both PHEMA and PHPMA decreased the MST more than did PHEA and PHPA respectively at low concentrations. The hydroxy ethyl polymers decreased the MST more than did the hydroxy propyl polymers. This was attributed to the fact that the propyl polymers were more hydrophobic than the ethyl polymers, thereby increasing the MST. Of the four polymers, PHPA, which is water-soluble and more hydrophobic than PHEA, was the most effective stabiliser for NR latex at the concentrations studied. This polymer would be most easily absorbed on to the particle surfaces, thereby providing steric stabilisation and an enhanced hydration layer. The new adsorbed layers overcome any displacement of the indigenous stabilisers, thereby increasing MST. However, the water-soluble PHEA decreased the MST at low concentrations. This might be attributed to particle bridging of the rubber particles as a consequence of an insufficient polymer concentration to cover the rubber particles, thereby decreasing the MST. At higher concentrations, however, there would be sufficient polymer to cover the rubber particles, and the new adsorbed layers are sufficient to overcome any displacement of the indigenous stabilisers, thereby increasing the MST.

If PHPMA and PHEMA were soluble in water, it would be expected that these polymers would increase the MST of NR latex above that in the presence PHPA. This is because they are more hydrophobic and they would be expected to be more adsorbed on to the particle surfaces than PHPA. Because of their insolubility in the aqueous phase, these polymers would desorb the indigenous stabilisers, thereby decreasing the MST. The effectiveness of the polymers in reducing the MST was in the following order : PHEMA > PHPMA. Unexpectedly, at higher concentrations (0.2 pphr), the polymers slightly increased the MST. In the case of PHEMA, the increase in MST was still below that of the control

NR. In the case of PHPMA, which is more hydrophobic than PHEMA, the MST was slightly above that of the control latex. To some extent, these water-insoluble polymers had the ability to stabilise the latex even though their ability to enhance the MST was much lower than that of the water-soluble polymers. Because of practical difficulties, it was impossible to study the effect of added water-insoluble polymers at higher concentrations, because the latex coagulated when the polymers were added to NR latex in IMS solution. The coagulation was probably a consequence of the high concentration of IMS in the latex when the polymers (10% w/w in IMS) were added to the latex at higher concentrations.

Table 7.1 Effect of non-ionogenic hydrophilic monomers upon colloid stability of NR latex in presence of stabilisers

A. stabiliser																										
Texofor A-60, pphr...	-	-	-	-	-	1.5	1.5	1.5	1.5	1.5	4	4	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Texofor FP-300, pphr.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	8	8	8	-
SLS, pphr.....	-	-	-	-	-	-	-	-	-	-	-	-	1.5	1.5	1.5	1.5	1.5	1.5	1.5	8	8	8	-	-	-	-
maturation (20°C), (days).....	*	-	-	-	-	6	4	6	6	7	2	3	3	3	3	6	6	7	7	7	7	7	7	7	7	4
B. monomer																										
HEMA, pphr.....	-	2	-	-	-	-	2	-	-	-	2	-	-	2	-	-	-	4	-	-	4	-	-	4	-	4
HPMA, pphr.....	-	-	2	-	-	-	-	2	-	-	-	2	-	-	2	-	-	-	4	-	-	4	-	-	4	-
HEA, pphr.....	-	-	-	2	-	-	-	-	2	-	-	-	-	-	-	2	-	-	-	-	-	-	-	-	-	-
HPA, pphr.....	-	-	-	-	2	-	-	-	-	2	-	-	-	-	-	-	2	-	-	-	-	-	-	-	-	-
maturation (20°C), (days).....	*	4	4	4	4	5	1	1	5	5	5	5	5	1	1	5	5	3	3	3	3	3	3	3	3	4
observation.....	L	PC	PC	L	L	L	PC	PC	L	L	CC	HV	L	PC	PC	L	L	CC	CC	L	CC	CC	L	CC	CC	CC
MST, seconds	1020	-	-	240	405	F	-	-	60	45	-	-	F	-	-	120	160	-	-	F	-	-	>2500	-	-	-

* :1-2 months; L = liquid; PC = partly coagulated; HV = highly viscous;
CC = completely coagulated; F = foaming.

Table 7.2 Partition coefficient of non-ionogenic hydrophilic monomers between aqueous phase and n-dodecane

material	volume (ml)				partition coefficient, K, at 25°C
n-dodecane	1.40	1.40	1.40	1.40	-
distilled water	4.00	4.00	4.00	4.00	-
monomer					
HEA	0.60	-	-	-	∽
HPA	-	0.60	-	-	∽
HEMA	-	-	0.60	-	∽
HPMA	-	-	-	0.60	0.49

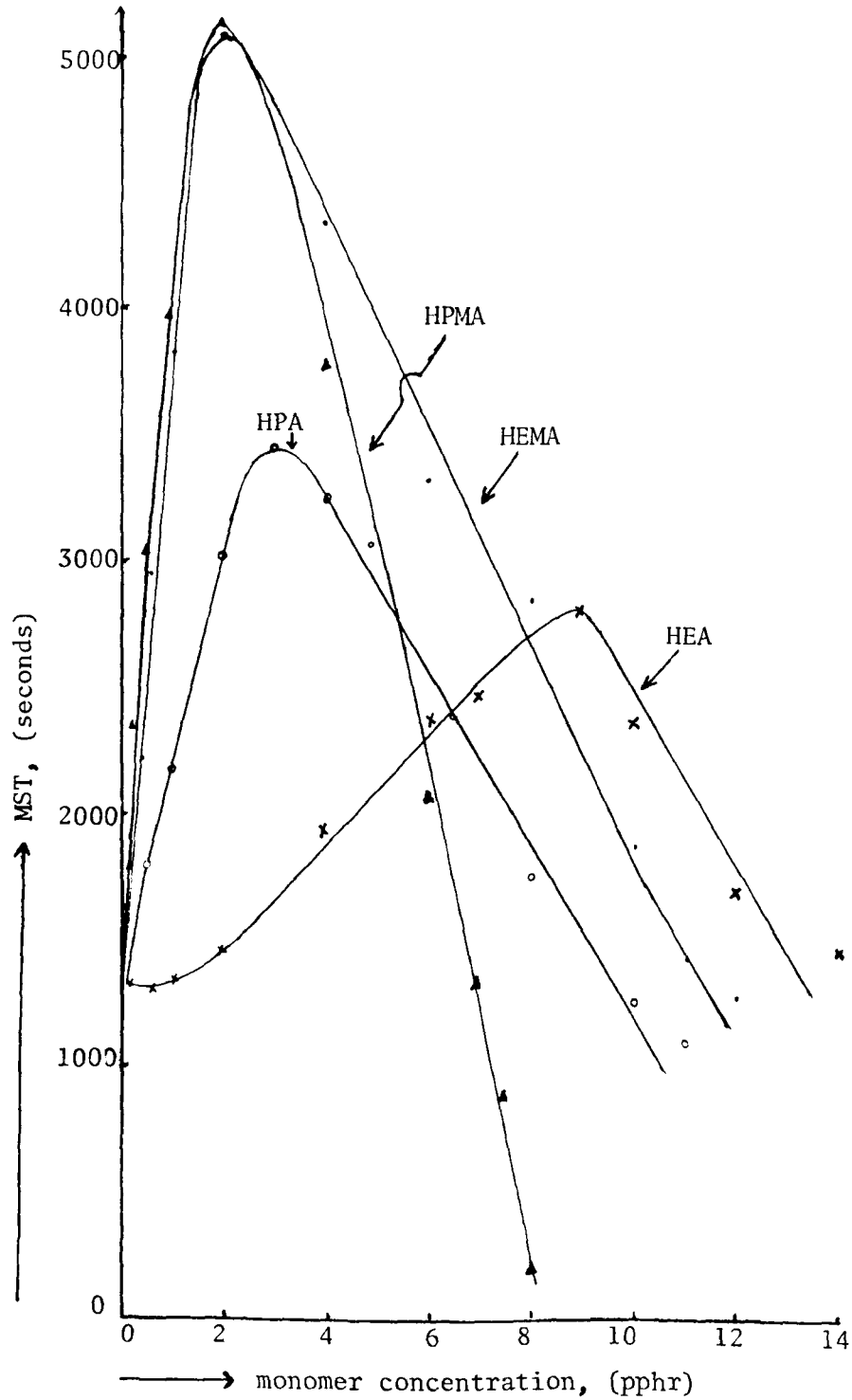


Figure 7.1 Effect of non-ionogenic hydrophilic monomers upon mechanical stability time (MST) of NR latex before maturation

Table 7.3 Effect of non-ionogenic hydrophilic monomers upon mechanical stability (MST) of NR latex before maturation

concentration (pphr)	MST (seconds)			
	HPMA	HEMA	HPA	HEA
0.00	1,240	1,240	1,240	1,240
0.06	1,630	1,425	1,455	1,333
0.13	1,785	1,545	1,395	1,305
0.25	2,370	2,445	-	-
0.50	3,030	2,940	1,800	1,290
1.00	3,940	3,820	2,160	1,335
2.00	5,088	5,138	3,005	1,440
3.00	-	-	3,435	-
4.00	3,765	4,335	3,245	1,920
5.00	3,060	-	-	-
6.00	2,095	3,300	-	2,368
6.50	-	-	2,390	-
7.00	-	-	1,320	2,470
7.50	855	-	-	-
8.00	180	2,843	1,750	-
9.00	-	-	-	2,865
10.00	-	1,860	1,230	2,345
11.00	-	1,411	1,080	-
12.00	-	1,275	-	1,673
14.00	-	-	1,440	1,440

Table 7.4 Concentration of non-ionogenic hydrophilic monomers which give maximum MST, together with concentrations which give MST equivalent that of initial control latex

monomer	optimum monomer concentration (pphr)	maximum MST (seconds)	concentration when MST=$[MST]_o$ (pphr)
control	-	1140	-
HEA	9.0	2790	13.5
HPA	3.0	3435	9.8
HEMA	2.0	5138	11.4
HPMA	2.0	5088	7.0

MST = MST of NR latices containing sufficient monomer at time t

MST max. = MST of NR latices containing sufficient monomer at beginning of maturation

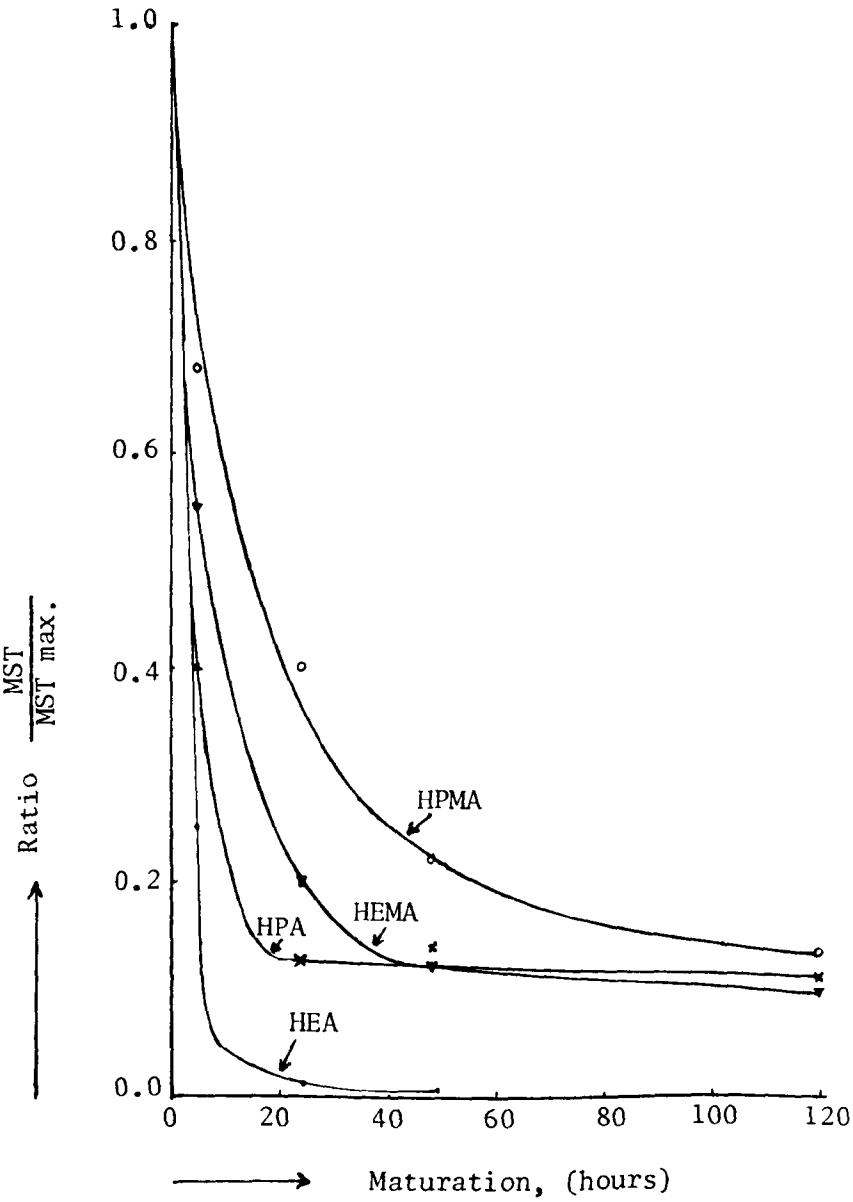


Figure 7.2 Effect of maturation upon mechanical stability time (MST) of NR latex containing sufficient non-ionogenic hydrophilic monomers to give maximum MST

Table 7.5 Effect of maturation upon mechanical stability of NR latex containing sufficient non-ionogenic hydrophilic monomers to give maximum MST

maturation (hours)	MST				ratio $\frac{MST}{MST_{max}}$ x)			
	HEA	HPA	HEMA	HPMA	HEA	HPA	HEMA	HPMA
0	2,790	3,435	5,138	5,088	1.000	1.000	1.000	1.000
4.5	707	1,383	2,823	3,483	0.253	0.403	0.549	0.685
24	35	495	1,003	2,055	0.013	0.128	0.195	0.404
48	5	495	600	1,140	0.002	0.144	0.117	0.224
120	-	385	505	678	-	0.112	0.098	0.133

x) MST_{max} is the maximum MST of NR latex containing sufficient of non-ionogenic hydrophilic monomer at the beginning of the maturation.

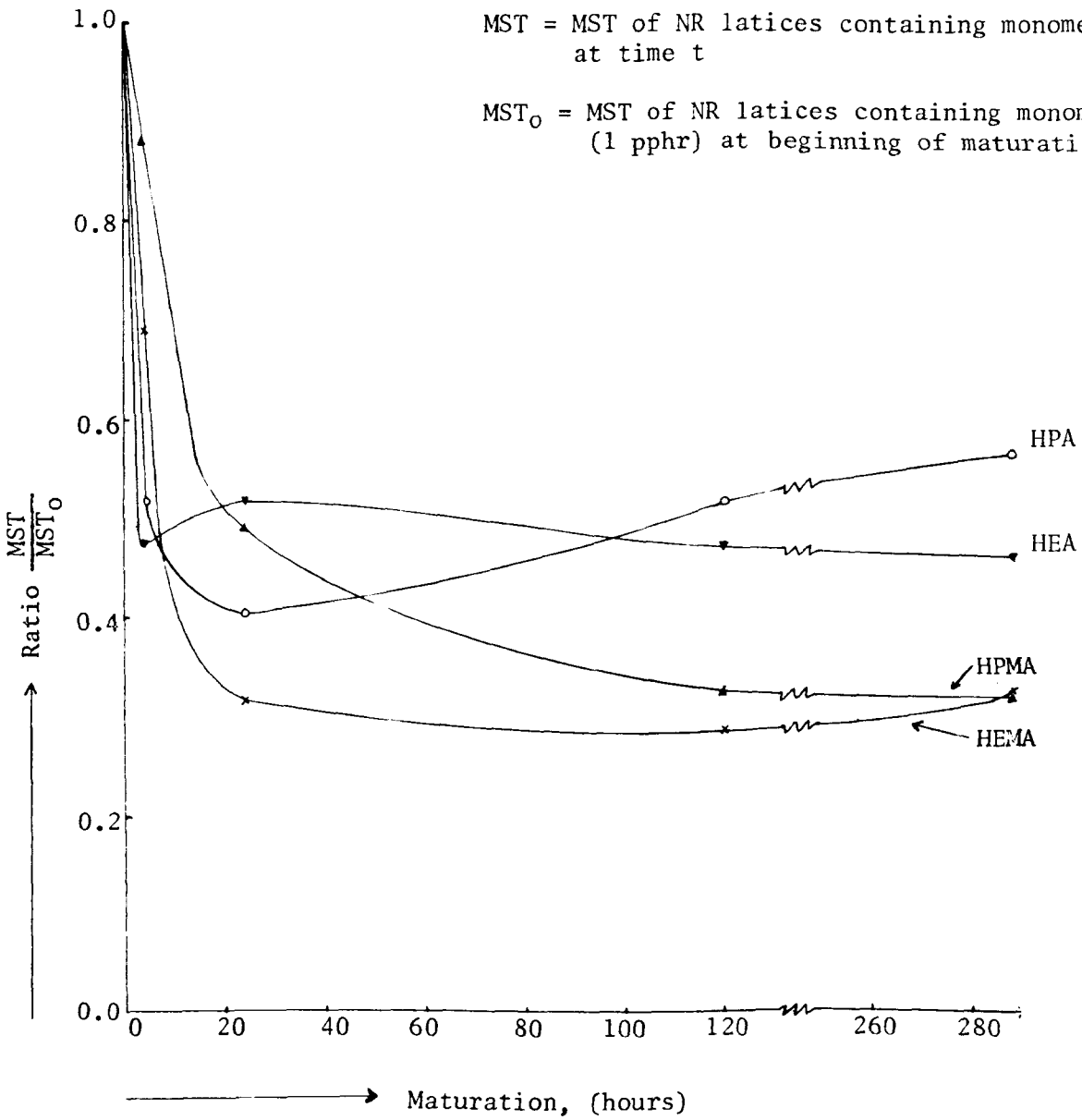


Figure 7.3 Effect of maturation upon mechanical stability time (MST) of NR latex in presence of low level of non-ionogenic hydrophilic monomers

Table 7.6 Effect of maturation upon mechanical stability time (MST) of NR latex in presence of low levels of non-ionogenic hydrophilic monomers

maturation (hours)	MST				ratio $\frac{MST}{MST_o}$ [x]			
	HEA	HPA	HEMA	HPMA	HEA	HPA	HEMA	HPMA
0	1,980	2,625	3,600	4,350	1.000	1.000	1.000	1.000
4	945	1,365	2,500	3,840	0.477	0.520	0.694	0.883
24	1,030	1,070	1,140	2,145	0.520	0.408	0.316	0.493
120	945	1,365	1,035	1,425	0.477	0.520	0.288	0.327
288	920	1,485	1,175	1,400	0.465	0.566	0.326	0.322

[x] MST_o is the MST of the NR latex at the beginning of the polymerisation

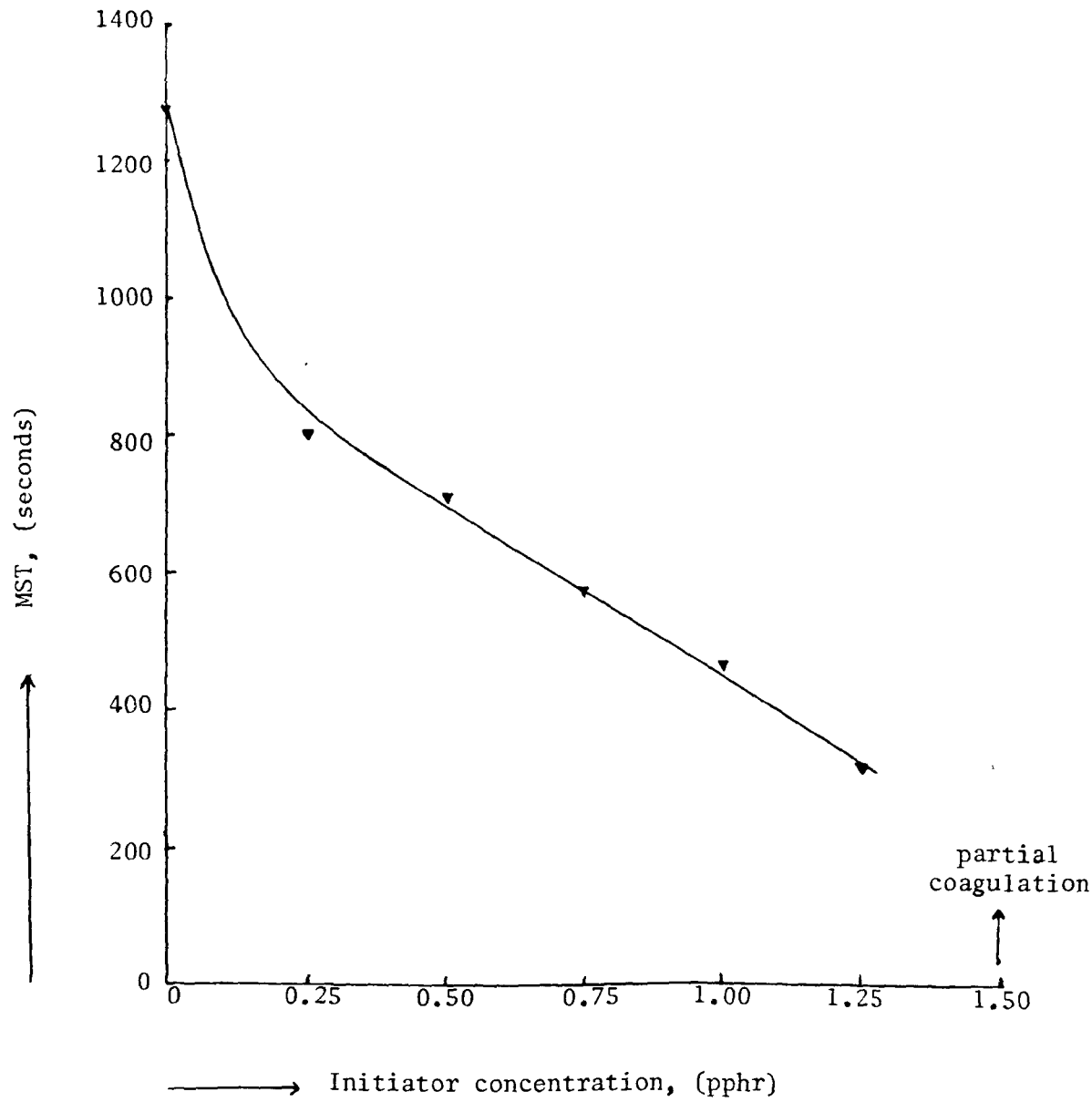


Figure 7.4 Effect of potassium persulphate-sodium metabisulphite upon mechanical stability time(MST) of NR latex before maturation

Table 7.7 Effect of potassium persulphate-sodium metabisulphite upon mechanical stability time (MST) of NR latex before maturation

concentration[x] (pphr)	MST (seconds)
0.00	1,240
0.25	800
0.50	710
0.75	570
1.00	463
1.25	318
1.50	partly coagulated

x) ratio $K_2S_2O_8$: $Na_2S_2O_8$ (1:1 by weight)

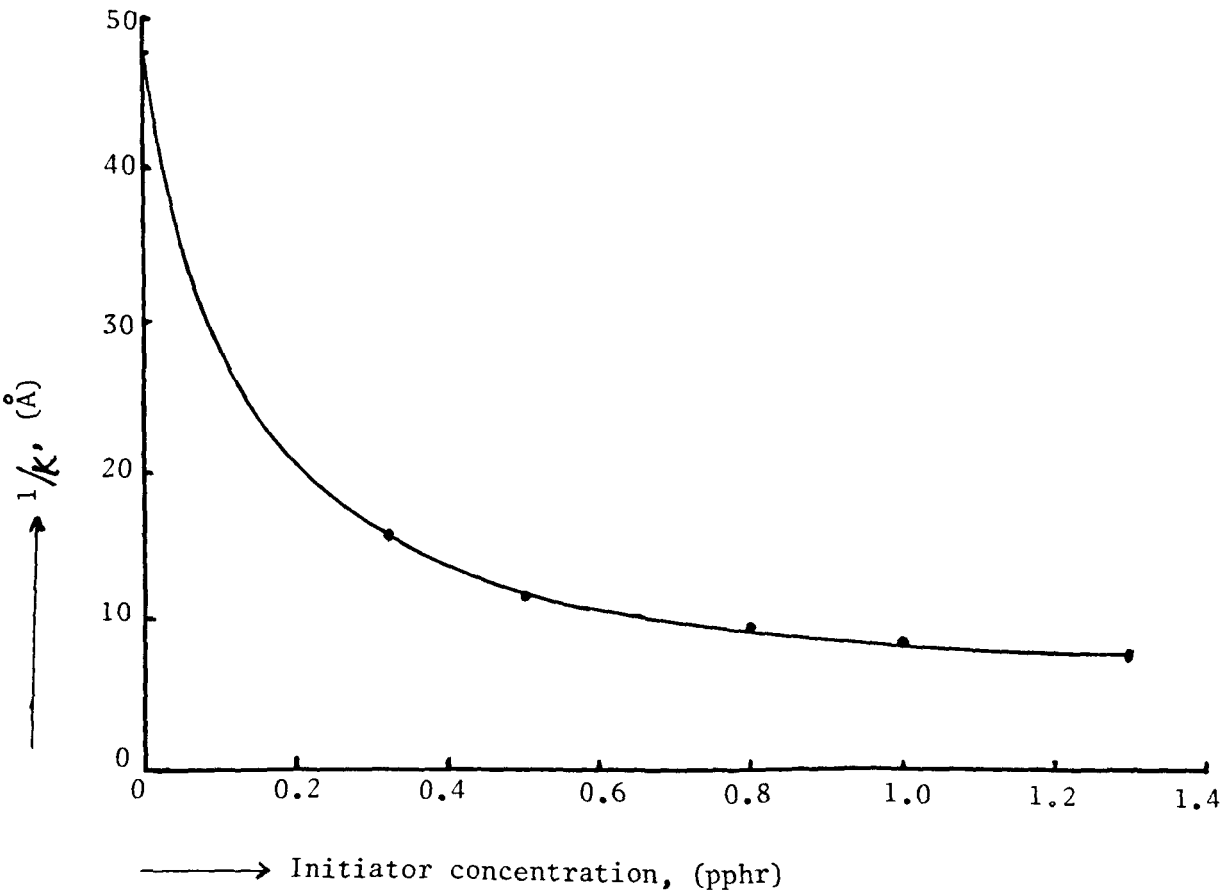


Figure 7.5 Effect of added redox initiator upon thickness of double layer surrounding particles in NR latex

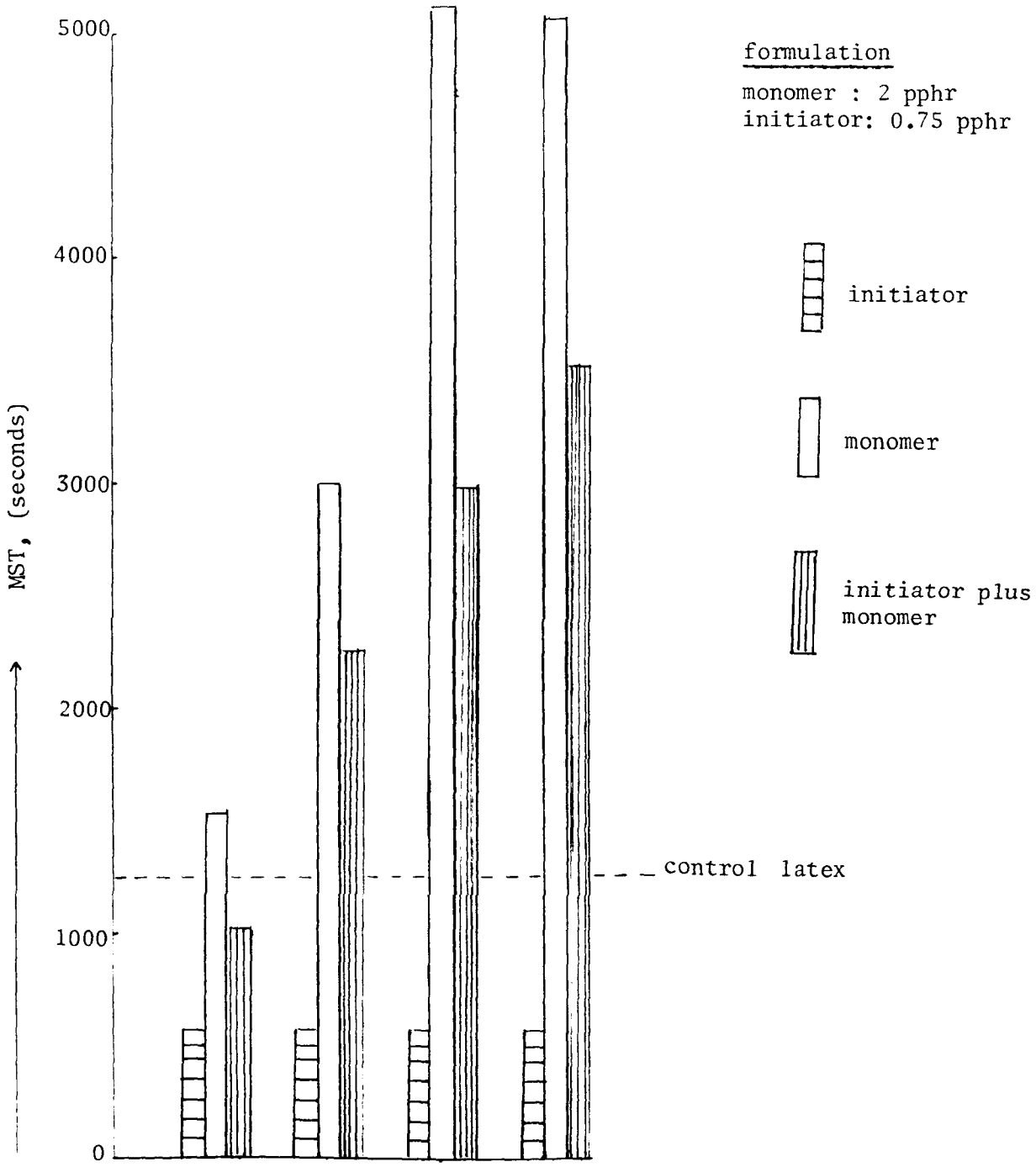


Figure 7.6 Effect of initiator, monomers, and the combination of initiator and monomers upon mechanical stability time (MST) of NR latex before maturation

Table 7.8 Effect of initiator, monomers, and the combination of initiator and monomers upon mechanical stability time (MST) of NR latex before maturation

	MST (seconds)
control	1,240
initiator	570
HEA	1,537
HPA	3,005
HEMA	5,138
HPMA	5,088
initiator + HEA	1,028
initiator + HPA	2,273
initiator + HEMA	2,985
initiator + HPMA	3,525

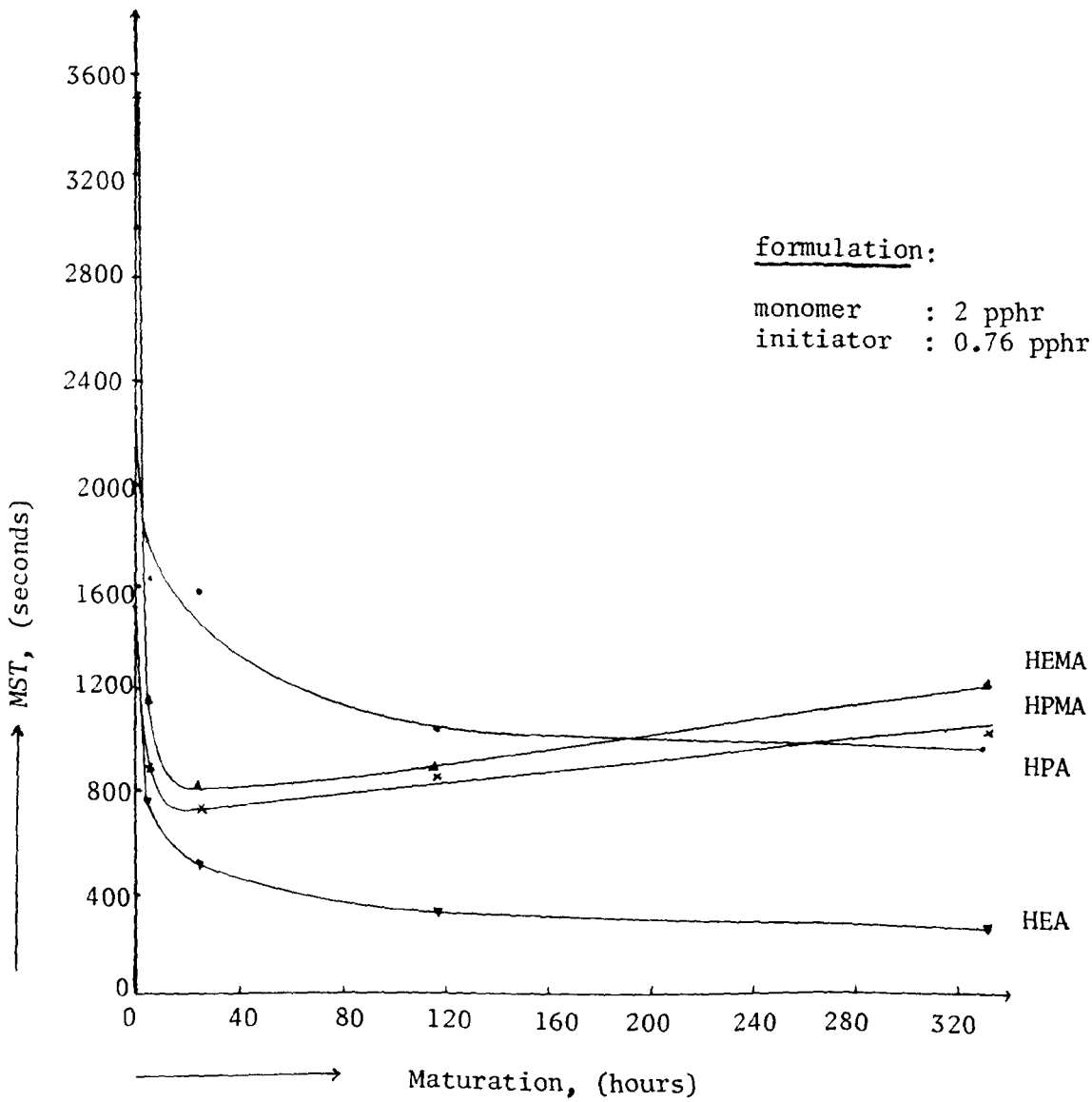


Figure 7.7 Effect of maturation upon mechanical stability time (MST) of NR latex containing both monomers and redox initiator

Table 7.9 Ratios of MST of latices containing 2 pphr of monomers to that of control latex

monomer	ratio of MSTs of latex containing monomer to that of control latex
HEA	1.21
HPA	2.38
HEMA	4.06
HPMA	4.02

Table 7.10 Effect of maturation upon mechanical stability time (MST) of NR latex containing both monomers and redox initiator

maturation (hours)	MST (seconds)			
	initiator + HEA	initiator + HPA	initiator + HEMA	initiator + HPMA
0	1,028	2,273	2,985	3,525
4	750	1,620	1,148	875
22	510	1,590	810	720
116	315	1,035	882	870
330	250	990	1,208	1,038

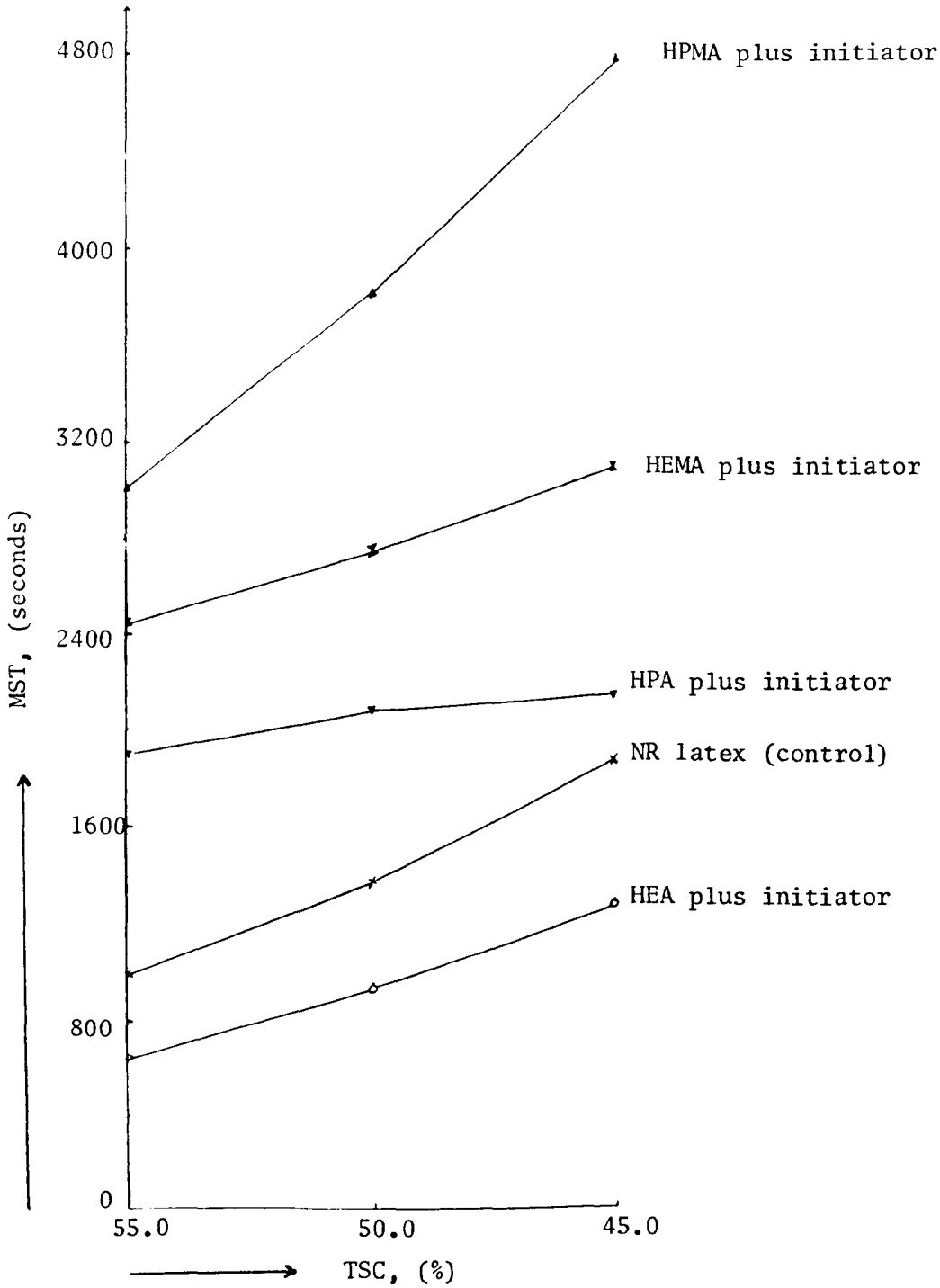


Figure 7.8 Effect of dilution upon mechanical stability time (MST) of NR latex containing non-ionogenic hydrophilic monomer-initiator before maturation

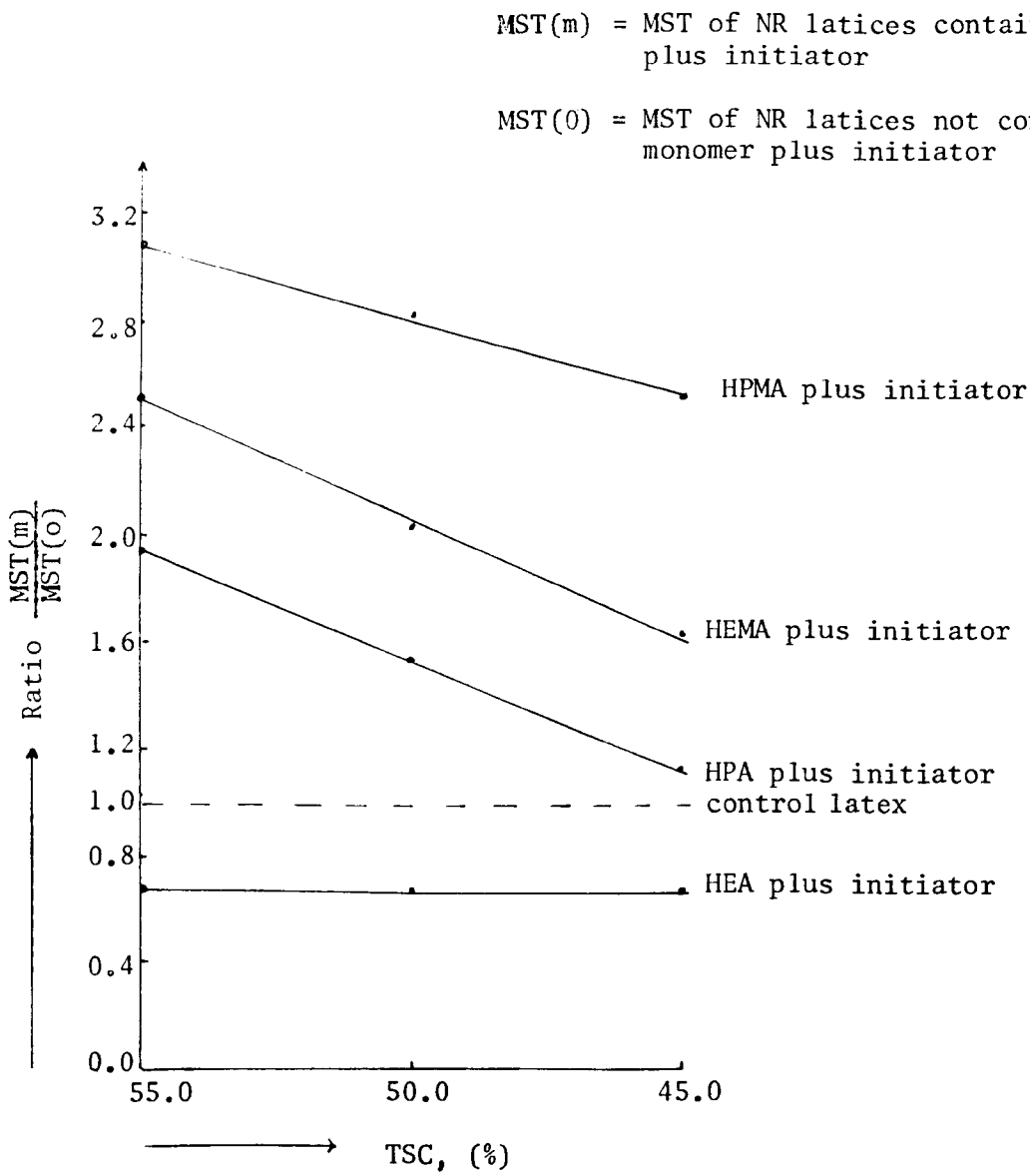


Figure 7.9 Effect of dilution upon ratio of MST of NR latices containing both monomer and initiator to that of MST of NR latices not containing monomer or initiator

Table 7.11 Effect of dilution upon mechanical stability time (MST) of NR latex containing non-ionogenic hydrophilic monomer-initiator mixtures before maturation

TSC (%)	control	HEA	HPA	HEMA	HPMA
45.0	1,883	1,253	2,120	3,070	4,770
50.0	1,343	915	2,068	2,725	3,788
55.0	970	630	1,895	2,440	2,983

MST(p)=MST of NR latices containing polymer

MST(c)=MST of control latices

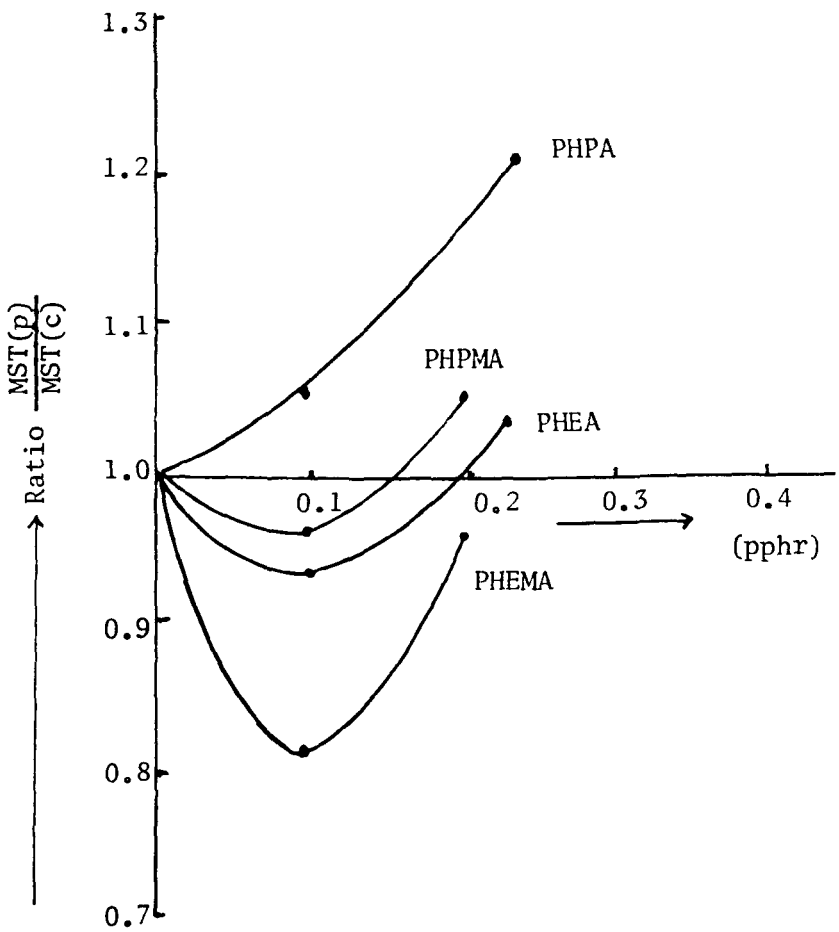


Figure 7.10 Effect of non-ionogenic hydrophilic polymers upon mechanical stability time (MST) of NR latex after maturation for more than 3 weeks

Table 7.12 Effect of homopolymers of non-ionogenic hydrophilic monomers upon mechanical stability time (MST) of NR latex for more than 3 weeks maturation at room temperature

i) PHEA and PHPA

level (pphr)	MST(C)[x]	MST(P)[x]		Ratio MST(P)/MST(C)	
		PHEA	PHPA	PHEA	PHPA
0.00	1,375	-	-	1.00	1.00
0.10	-	1,293	-	0.94	-
0.10	-	-	1,458	-	1.06
0.23	-	1,444	-	1.05	-
0.23	-	-	1,678	-	1.22

x) MST(C) is the MST of the control latex.
MST(P) is the MST of NR latex in the presence of the polymer.

ii) PHEMA and PHPMA

IMS (pphr)	polymer		MST[x] (C)	MST[x] (IMS)	MST[x] (P+IMS)	MST[x] (P)	ratio MST(P)/MST(C)
	PHEMA (pphr)	PHPMA (pphr)					
0.00	0.00	0.00	1,375	-	-	-	1.00
0.90	-	-	-	1,925	-	-	-
1.80	-	-	-	2,270	-	-	-
0.91	0.10	-		-	1,670	1,120	0.81
1.80	0.20	-		-	2,218	1,323	0.96
0.90	-	0.10		-	1,865	1,345	0.96
1.81	-	0.20		-	2,337	1,442	1.05

x)
-MST(C) is the MST of the control latex.
-MST(IMS) is the MST of NR latex in the presence of IMS.
-MST(P+IMS) is the MST of NR latex in the presence of IMS plus polymer.
-MST(P) is the MST of NR latex in the presence of polymer.

Chapter 8

Kinetic studies of polymerisation of non-ionogenic hydrophilic monomers in NR latex

8.1 Introduction

The conversions of the monomers to polymers in NR latex were followed using two methods:

(i) a gravimetric method (Section 8.2)
(ii) a dilatometric method (Section 8.3)

The results of the gravimetric method are summarised in Sections 8.2.1 to 8.2.3, and the results are discussed in Section 8.2.4. The results of the dilatometric method are summarised in Sections 8.3.1 to 8.3.9, and these results are discussed in Section 8.3.10.

8.2 Gravimetric method

8.2.1 Volatility of the non-ionogenic hydrophilic monomers

The results are shown in Table 8.1. It was observed that, despite their high boiling points, the monomers could be satisfactorily evaporated to 99.9% removal by heating at 90^{o}C in a vacuum oven (0.16 mm Hg) for 3.5 hours.

8.2.2 Volatility of inhibitors/antioxidants in presence of NR latex

The volatilities of fourteen inhibitors/antioxidants were investigated. The results are shown in Table 8.2. Six of them, namely, Nonox DN, Flexzone 3C, Nonox EXN, Antioxidant 2246, Nonox DPPD and DPPH, when added to NR latex (10 - 70 pphr) were effectively non-volatile, with a weight loss of less than 1% when heated under 0.16 mm Hg pressure at 90^{o}C for 8 hours.

8.2.3 Effectiveness of inhibitors/antioxidants

The results are shown in Table 8.3. It was found that, despite being added at high concentration (42-68 pphr), none of the inhibitors/antioxidants could stop the polymerisation of the monomers in NR latex in the presence of the redox initiator (2-4.5 pphr), even if the inhibitors/antioxidants were added to the latex prior to

the initiator. The conversions were in the range 6 to 80%. The most effective inhibitors /antioxidants investigated were DPPH and Nonox DPPD. Further results concerning the use of these compounds are in Table 8.4. It was observed that, if the redox initiator (ca. 2 pphr) was added to the latex and kept overnight prior to the addition of Nonox DPPD at low concentrations (ca. 0.4%), the conversions of the monomers were of the order of 0.8% for HEMA and HPMA, and 3% for HEA and HPA.

8.2.4 Discussion of gravimetric method

The monomers contain hydroxyl [-OH] and ester [-C(=O)-O-] groups which form hydrogen bonds with water. The presence of such bonds in the monomers gave the characteristic high boiling points (Section 6.11.2). In these circumstances, it was necessary has to use a vacuum drier to evaporate them completely. It was found that, using a vacuum drier (0.16 mm Hg) at 90^{o}C for 3.5 hours, the monomers were satisfactorily evaporated (99.9%).

This observation indicated that the gravimetric method could be used to determine the monomer conversions, providing that the evaporation was not hindered by the polymers present. This hindrance might occur if a sample contains NR particles in which the monomers might become trapped during coagulation of the latex. In this case, the evaporation of the monomers might take longer than in the absence of rubber. In addition, polymerisation may occur as a consequence of this prolonged heating. To avoid such polymerisation, an inhibitor/antioxidant should be added to the sample prior to drying. The most common inhibitors used are hydroquinone, and tertiary butyl catechol. Unfortunately, when these inhibitors were added to NR latex, they evaporated to an unacceptable level (16-19% weight loss) under the above drying conditions. Such loss of inhibitor might result in a lower calculated conversions than the true value and, of course, once evaporated they would be ineffective as inhibitors.

Inhibitors /antioxidants such as Nonox DPPD, Flexzone 3C, Nonox EXN, Antioxidant 2246, Nonox DN and DPPH showed no tendency to evaporate to an unacceptable level, the level being less than 1% (Table 8.2). The investigation of the ability of the inhibitors /antioxidants to suppress polymerisation of the monomers in NR latex gave the following order of effectiveness: DPPH > Nonox DPPD >

Flexzone 3C > nonox DN > Nonox EXN > Antioxidant 2246. The conversions were in the range 1.6 (DPPH) to 80.0% (Antioxidant 2246) (Tables 8.3 and 8.4). In the presence of the redox initiator, even the presence of the most effective inhibitors/antioxidants failed to stop the polymerisation, despite their being present in high concentration (51-69 pphr). Possible explanations are as follows:

(i) The propagation rate constant (k_p) of the monomers might be greater than the inhibition rate constant (k_{pz}) of the inhibitors/antioxidants, so that $k_p(M) > k_{pz}(Z)$ (Section 4.3).

(ii) The inhibition process may be partition-dependent. The inhibitors/antioxidants may be soluble in the rubber phase, whilst the initiators and monomers are soluble in the aqueous phase. In these circumstances, the inhibitors/antioxidants might suppress the polymerisation at the surface of particles, but not enter the aqueous phase, so that polymerisation can continue there.

(iii) The rate constant for the decomposition of the initiator (k_d) is greater than the rate constant for the inhibition process. Thus radicals would be formed faster than the inhibitor can react with them.

Typically a polymerisation would be run during the day and then left overnight to ensure complete reaction. Then the conversion of monomer to polymer was determined gravimetrically. To ensure no polymerisation occurred during prolong drying, a control experiment was carried out. The redox initiator was added to NR latex and kept overnight. The next morning, monomers and Nonox DPPD were added. The samples were then dried in the vacuum oven (0.16 mm Hg) to determine the conversion, if any, of the monomers to the corresponding polymers. As a result, the conversions of the monomers proved to be low, being of the order of 0.5 to 3%. This suggests that the initiator is mostly decomposed after this time. The antioxidant (Nonox DPPD) was then able to prevent any polymerisation during drying. This method was used to determine the conversion of the monomers at the end of a reaction, which was typically longer than 20 hours. This method, however, should not be

used to determine the conversion of the monomers during the polymerisation, and certainly not at the beginning of the polymerisation.

8.3 Dilatometric method

8.3.1 Polymerisation of non-ionogenic hydrophilic monomers in water and in aqueous ammonia solution

The results of the experiments undertaken to investigate the polymerisation of the hydrophilic monomers in water (pH ca. 5) and in aqueous ammonia solution (pH ca. 10) are shown in Figures 8.1A and 8.1B. It was observed that the polymerisation of the monomers in the water and in the aqueous ammonia solution produces "complex" conversion-time curves. The curves produced are neither straight nor hyperbolic lines, but they show a period where polymerisation appears to cease before continuing. This complex shape for the curves was reproducible for several polymerisations. Because all of the graft copolymerisation reactions were carried out in NR latex, it was more appropriate to investigate the reproducibility of the dilatometric technique by polymerising the monomer in NR latex than in water. It was found that the reproducibility of the dilatometric technique for measuring the conversion of the monomers polymerising in NR latex was satisfactory [Section 6.2.1.(viii)]. It was observed that at pH ca.5, the polymers from HPA, HEMA and HPMA precipitated from the aqueous solution at about 5% conversion, whereas the polymer from HEA remained soluble. At higher pH (ca. 10), however, the polymers from HPA and HEA remained soluble until complete reaction was achieved, whereas the polymers from HEMA and HPMA were observed to precipitate at about 5% conversion.

8.3.2 Polymerisation of non-ionogenic hydrophilic monomers in NR latex

Typical results are shown in Figure 8.2. The polymerisation of the monomers in NR latex produced "simple" conversion-time curves, different from those produced in water alone. The conversion rates for the monomers based upon < 3 hours reaction were in the following order: HEA > HPA > HPMA > HEMA.

8.3.3 Effect of added ammonia upon the rate of polymerisation of HPA in NR latex

The results are shown in Figure 8.3. The rate of polymerisation of HPA in NR latex increased with the quantity of ammonia present.

8.3.4 Polymerisation of non-ionogenic hydrophilic monomers in NR latex using aqueous ammonia solution (1.5%) as diluent

The results are shown in Figure 8.4. A comparison of the conversion rates for the polymerisation of the four monomers over the first two hours using aqueous ammonia solution, showed that the four monomers still followed the same pattern of relative reactivity, i.e., HEA > HPA > HPMA > HEMA, although the polymerisations were faster for each monomer compared to polymerisations when water was used as the diluent. It was observed that the polymerisation was rapid in the early stages of the reaction and subsequently substantially slowed.

8.3.5 Effect of added sodium lauryl sulphate (SLS) upon rate of polymerisation of HPMA in NR latex

The result is shown in Figure 8.5, which shows the conversion-time curves for the polymerisation of HPMA in the presence and in the absence of the SLS. The initial rate of polymerisation in the presence SLS was ca. 18% higher than in the absence of the SLS. However, the subsequent rate of polymerisation in the presence of the SLS declined than in the absence of the SLS. As a result, the conversion of monomer to polymer after ca. 50 minutes was higher in the absence of the SLS than in the presence of the SLS. The product in the absence of the SLS coagulated when left over night after polymerisation. The product in the presence of SLS (1 pphr) produced cream when left for 3 days after polymerisation.

8.3.6 Effect of initial monomer concentration $[M]_o$ upon rate of polymerisation (R_p) of non-ionogenic hydrophilic monomers in NR latex

Figures 8.6A to 8.6D show the results of the experiments undertaken to investigate the order of reaction with respect to initial monomer concentration, $[M]_o$, or the polymerisation of the monomers in NR latex using the redox

initiator at 30°C. The rate of the polymerisation for each of the monomer was found to be first-order with respect to initial monomer concentration. Thus the R_p for each monomer can be represented as follows:

$$R_p = k\,[M]_o$$

The values of R_p for each monomer were taken from the gradient of the plots of the disappearance of the monomer, $[M]_o$-[M], versus time at different levels of the initial monomer concentrations, $[M]_o$ being the initial monomer concentration, and [M] the monomer concentration at time t. The values of [M] at any time were obtained using Equation 6.5 [Section 6.2.1.2.(viii)]. The values of R_p obtained were then plotted versus the initial monomer concentrations $[M]_o$. A straight line was obtained for each monomer, which when extrapolated to zero monomer concentration passed through origin (zero rate) indicating that, for each monomer, the rate was first-order with respect to initial monomer concentration, within experimental error.

8.3.7 Determination of orders of reaction for rate of polymerisation (R_p) of non-ionogenic hydrophilic monomers with respect to monomer concentration ([M]) during the course of polymerisation in NR latex

Figures 8.7A and 8.7B show plots to test the orders of reaction with respect to monomer concentration, [M], during the course of polymerisation for the two hydroxyalkyl acrylates in NR latex using the redox initiator at 30°C. Figures 8.7C and 8.7D show similar plots for the two hydroxyalkyl methacrylates. The orders of reaction, n, with respect to monomer concentration, [M], during the course of polymerisation for each monomer were found to be as follows:

for HEA	n = 0	for conversions up to ca. 35%
for HPA	n = 0	for conversions up to ca. 30%
for HEMA	n = 1	for conversions up to ca. 48%
for HPMA	n = 2	for conversions up to ca. 41%

These are the values of n such that $Rp \propto [M]^n$. Clearly the value of n depends upon the monomer. The values for the two hydroxyalkyl methacrylates are greater than the values for the two hydroxyalkyl acrylates. In each case, the order of reaction was taken as that corresponding to the expression which gave a linear relationship to the highest conversion

when zero-, first- and second-order curves were fitted to data for individual polymerisations. Only HEMA gave a linear curve to high conversion for the first-order reaction, and this observation is in agreement with the results obtained in Section 8.3.6.

8.3.8 Effect of initial concentration of redox initiator ($[I]_o$) upon rate of polymerisation (R_p) of non-ionogenic hydrophilic monomers in NR latex

Figures 8.8A to 8.8D show the results of experiments undertaken to investigate the effect of initiator concentration upon the rate of polymerisation of the four monomers in NR latex. The following results were obtained for the orders of reaction with respect to initial initiator concentration, $[I]_o$,

for HEA $n = 0.50$
for HPA $n = 0.50$
for HEMA $n = 0.20$
for HPMA $n = o.50$

These are the values of n such that $Rp \propto [I]^n$. The values of R_p were taken from the gradient of the plots of disappearance of each of the monomer, $[M]_o$-[M], versus time at different levels of initial initiator concentrations, $[M]_o$ being the initial monomer concentration and [M] the monomer concentration at time t. The values of [M] were calculated using Equation 6.5 [Section 6.2.1.2 (viii)]. To test the half-order dependence with respect to initiator concentration, the values of R_p were plotted versus $[I]^{0.5}$. The monomers HEA, HPA and HPMA give straight lines which, when extrapolated to zero initiator concentration, passed through the origin (zero rate). This indicates that the rates of polymerisation of the three monomers were half-order within experimental error. In the case of HEMA, the line did not pass through the origin suggesting that the polymerisation occurred in the absence of the initiator which is not the case. To find the value of n value for this monomer, the values of log R_p were plotted versus log $[I]_o$. The value of n was taken from the gradient of the plot of log R_p versus log $[I]_o$.

8.3.9 Effect of dry rubber content (DRC) upon rate of polymerisation (R_p) of non-ionogenic hydrophilic monomers in NR latex

The results are shown in Figures 8.9A to 8.9D. Clearly, In the absence of rubber, the polymerisation of the four monomers would occur in the aqueous phase. Hence the rates of the polymerisation in NR latex, R_p, with respect to the DRC would be as follows:

$$R_p = (R_p)_o + k\,[DRC]^n$$

where $(R_p)_o$ is the rate of polymerisation in the absence of rubber (mol/l solution/s), [DRC] is the DRC of the total reaction mixture (% w/w by weight of latex), n is the order of the reaction, and k is the rate coefficient of the polymerisation. The values of R_p for each monomer were taken from the gradient of plots of the disappearance of each of the monomer, $[M]_o$-[M] versus time, $[M]_o$ being the initial monomer concentration, and [M] the monomer concentration at time t. The values of [M] were calculated using Equation 6.5 [Section 6.2.1.2.(viii)]. To test the first-order dependence with respect to the DRC, the values of R_p were plotted versus [DRC]. The four monomers gave straight lines suggesting that, for each monomer, the rate was first-order with respect to the DRC within experimental error.

As can be seen from the Figures 8.1 and 8.2, the shape of the curves obtained by polymerising the monomers in aqueous solutions, i.e., either in water or in an aqueous ammonia solution, is complex and they are not comparable with the simple shape of the curves when the monomers were polymerised in NR latex (Figures 8.2 and 8.4). In these circumstances, no attempt was made to calculate $(R_p)_o$ for these monomers in the aqueous solutions because the values of $(R_p)_o$ obtained when these monomers were polymerised in the aqueous solutions would not be comparable with the R_p obtained when the monomers were polymerised in NR latex. As can be seen from figures 8.9A and 8.9B, the lines which, when extrapolated to zero DRC did not pass through the origin. As mentioned earlier, in the absence of rubber, the polymerisation of the monomers would occur in the aqueous phase. To predict the rates of polymerisation in the aqueous phase, $(R_p)_o$, the lines were extrapolated to zero DRC. The values of $(R_p)_o$ were then taken from the intercepts of the extrapolation as follows:

for HEA $(R_p)_o = 41.0 \times 10^{-6}$ mol/l solution/s
for HPA $(R_p)_o = 23.0 \times 10^{-6}$ mol/l solution/s
for HEMA $(R_p)_o = 13.4 \times 10^{-6}$ mol/l solution/s
for HPMA $(R_p)_o = 11.6 \times 10^{-6}$ mol/l solution/s

These values of $(R_p)_o$ would be expected when the monomers were polymerised in the aqueous solutions.

8.3.10 Discussion of kinetics of polymerisation of non-ionogenic hydrophilic monomers in NR latex

8.3.10.1 Oders of reaction with respect to monomer concentration

As mentioned in Section 6.2.1.1, and Section 9.11.1, the monomers used for investigating the reaction kinetics were not purified. This was because 1) there was a possibility that crosslinking may occur during the purification process, and 2) the process itself would be too laborious. Therefore, it must not be overlooked that the impurities in the monomers, particularly inhibitor, might lead to side-reactions during polymerisation in aqueous solutions (Figures 8.1A and 8.1B). However, it was found that when the monomers were polymerised in NR latex, the conversion-time curves were simple (Figures 8.2 and 8.4) and satisfactorily reproducible (Section 6.2.1.2.(viii). A possible explanation for these differences in behaviour is that the rubber particles might act as the locus of polymerisation. This possibility will be discussed further subsequently. In this case, the inhibitor, p-methoxy phenol which is soluble in water, present in the monomers might not interfere with the reaction occurring at the surface of the rubber particles but would interfere with reaction occurring in the aqueous phase. In these circumstances, it is reasonable to assume that the initial polymerisation might predominantly occur at the surface of the rubber particles. If it was not the case, the shape of the curves would be complex, as shown by the polymerisation in water, as a consequence of the interference by the inhibitor which is soluble in water (Figures 8.1A and 8.1B). This will be discussed further subsequently.

Figure 8.3 shows that the pH of the latex affected the rate of polymerisation as follows:

diluent	pH at 30°C	Rp,(mol/l latex/s)
distilled water	9.00	1.76×10^{-5}
NH_4OH 0.5%	9.30	2.62×10^{-5}
NH_4OH 1.5%	10.12	3.70×10^{-5}

The rate of polymerisation increased as the pH of the latex increased. Possible explanations for this are as follows :

(i) The rate of decomposition of the redox initiator might be greater at a high pH than at a low pH, thereby increasing the rate of polymerisation.

(ii) At high pH, the colloid stability of the latex would be higher than that of a latex with a lower pH. High colloid stability of the latex may provide more favourable conditions for polymerisation than does lower colloid stability.

The reactivity and hydrophilicity of the monomers affected their rate of polymerisation in NR latex. The reactivity of the monomers when they were polymerised in NR latex was found to be in the following order (Figure 8.4): HEA > HPA > HPMA > HEMA. This suggests that the rate of combination of a polymer radical with monomer was higher for HEA than for HPA, HPMA and HEMA. An interesting feature is that HPMA reacted faster than HEMA whereas HEA reacted faster than HPA. A possible explanation of this is that HPMA is more hydrophobic than any of the monomers studied (Section 7.11.2). HPMA would therefore be adsorbed not only at the surface of particles, but also into the rubber phase. The concentration of HPMA at the surface would be expected to be higher than that of HEMA under comparable conditions. This would lead to a faster reaction of HPMA compared to HEMA. Further explanations of this observation will be discussed later in this section.

As HPMA partitioned between n-dodecane and water, it was thought that this monomer, in the presence of SLS (1 pphr), would show typical emulsion polymerisation behaviour. However, the polymerisation did not show the typical S-shaped emulsion polymerisation conversion-time curve

(Figure 8.5). There is no evidence of emulsion polymerisation of this monomer under the conditions used in this investigation, but in the heterogeneous system such as NR latex the possibility of the emulsion reaction should not be ignored. In the absence of the SLS, the product of the polymerisation of HPMA coagulated when left overnight after polymerisation. In the presence of the SLS (1 pphr), the product of the reaction produced cream when left for 3 days after polymerisation.

As mentioned in Section 8.3.6, the rate of polymerisation of the monomers was first-order with respect to initial monomer concentration, $[M]_o$ (Figures 8.6A to 8.6D). This suggests that the polymerisations behave as if they were true solution polymerisations. Based on these results solely, one might assume that the polymerisation occurred mainly in the aqueous phase of the NR latex. However, ammonium NR latex is a heterogeneous system containing a rubber phase and an aqueous phase (Section 1.1). In these circumstances, the order might deviate from the first-order dependence with respect to the initial monomer concentration because of the attraction/repulsion forces between the rubber particles and the monomers. As a matter of fact, the orders of the reaction for the four monomers with respect to monomer concentration, [M], during the course of the polymerisation were found to be zero-order for HEA and HPA, first-order for HEMA and second-order for HPMA (Figures 8.7A and 8.7B). This apparent contradiction between the first-order dependence upon the initial monomer concentrations, and zero-order obtained for the polymerisation of HEA and HPA in individual polymerisations is difficult to explain because, if they were truly zero-order, then the rate of polymerisation would not be dependent upon the initial monomer concentration. However, the apparent contradiction might be a consequence of the polymerisations occurring both at the surface of the rubber particles and in the aqueous phase at the same time. If this is the case, the polymerisation might predominantly take place at the surface as a consequence of the monomers being readily adsorbed on to the surface of the rubber particles (Section 7.11.2). Furthermore, if the locus of polymerisation was not at the surface, but truly in the aqueous phase, the shape of the curves would be complex as found when the monomers were polymerised in water (Section 8.3.1). The complexities are thought to be due to side reactions between inhibitor, which is water-soluble, and the monomers. If the initial polymerisations were

predominantly at the surface, possible explanations of the zero-order, first-order and second- order values obtained for HEA and HPA, HEMA and HPMA respectively are as follows:

(i) It is assumed that the monomers are adsorbed on to the surface of the rubber particles as clusters as shown in Figure 8.10A (page 212). The concentration of the monomer adsorbed on to the surface is dependent upon 1) the adsorbility of the monomers, and 2) the concentration of the monomer in the aqueous phase. It is expected that the effectiveness of monomer adsorption at the surface is in the following order: HEA < HPA < HEMA < HPMA. It is reasonable to assume that, under equilibrium conditions, the concentration of each of the monomers at the surface remains constant throughout out the reaction.

(ii) The redox initiator radicals (R.) present at the surface would attack monomers at the surface to produce oligomeric radicals. It would also be expected that the initiator radicals present in the aqueous phase would attack the monomers to produce oligomeric radicals. Most of these oligomeric radicals, however, would migrate to the surface of the rubber particles because they are more hydrophobic than the monomers. As mentioned in Section 7.11.2, it is the ethylenic and alkyl groups of the oligomeric radicals (designated as $\longrightarrow\!\!\bullet$) which are likely to move towards the space available at the surface as shown in Figure 8.10B. However, kinetic studies show different rate-orders for polymerisation depending upon the monomer concerned. Thus we need to consider the possible reasons for these different orders of reaction. The propagation mechanisms for the various monomers will now be considered.

a. Propagation mechanism for HEA and HPA

Both HEA and HPA were found to produce rate curves (Figures 8.10A to 8.10D) which are zero-order with respect to monomer concentration for the first ca. 35% conversion. This can be explained if the principal locus for polymerisation is at the

surface of rubber particles and that an equilibrium is established in which the monomer concentration at the surface becomes constant. The oligomeric radicals attracted to the surface would consume monomer which would then be replaced by further monomer from the aqueous phase (Figure 8.10C). Thus an equilibrium would be established at the surface with the monomer consumed at the surface during the polymerisation being replaced by monomer from the aqueous phase. These processes would continue until the surfaces of the rubber particles were almost covered by the polymer. This point is taken to be 35% conversion for HEA and 30% conversion for HPA (Figures 8.10A and 8.10B). In these circumstances, the monomers would disappear at a constant rate up to the conversion at which the surface was almost saturated. The apparent reaction rates for HEA and HPA were thus pseudo-zero-order with respect to monomer concentration, due to the monomer equilibrium at the surface of rubber particles.

Polymerisation in the aqueous phase would also be taking place concurrently with polymerisation at the surface. However, the polymerisation at the surface would be expected to be more rapid than that in the aqueous phase because 1) the oligomeric radicals and the monomer would be more concentrated at the surface, and 2) the ethylenic groups of the monomers would be attracted to the rubber particles surface rather than the hydroxyl groups. Thus, the incoming monomer would be oriented to approach a growing radical at the surface in the most favourable orientation for polymerisation to take place. The rubber particles would eventually be covered by polymer. Then no space would be available at the surface for incoming monomer from the aqueous phase (Figure 8.10D), the concentration of the monomer at the surface would no longer be constant. Thus, the rate of polymerisation would decrease as the concentration of the monomer at the surface decreased. The

polymerisation at this surface would cease when monomer could no longer reach the particle surface. The surface of the particles would then be well covered by the polymer (Figure 8.10E). At this stage, further polymerisation would take place in the aqueous phase. It is to be expected that the rate of polymerisation sharply reduced because of substantial decreasing of the monomer concentrations in the aqueous phase as a consequence of the monomers (ca. 35%) had been consumed during the surface polymerisation. As can be seen from the conversion-time curves (Figure 8.4), there is a substantial reduction in the rate of reaction after about 35% conversion. It is reasonable to assume that this reduction in rate after the initial linear rate corresponds to a reduction in polymerisation at the surface of particles, polymerisation still continuing in the aqueous phase.

The explanation of zero-order kinetics observed for HEA and HPA during the course of the polymerisation is probably an over-simplification. This is because one would expect HEMA and HPMA to be more readily adsorbed at the surface of rubber particles than HEA and HPA. Thus one would expect that the reaction order for HEMA and HPMA would also be zero-order. However, the results of the fitting of the various curves with data for individual polymerisations showed that the reaction-order was first-order for HEMA and second-order for HPMA. It is difficult to offer an explanation for this apparent contradiction from the discussion given below.

b. Propagation mechanism for HEMA

HEMA would be expected to follow a similar kinetic pattern to HEA and HPA, and hence also to show zero-order kinetics up to ca. 35% conversion. In fact, the polymerisation was found to be first-order for this monomer. As mentioned earlier, the polymer produced is

insoluble in the aqueous phase. This polymer precipitates in the aqueous phase and might form dispersions of high specific surface area and thus adsorb the latex stabilisers rather than cover the rubber particles itself. This explanation was similar to that proposed by Blackley et al. (95), who concluded that species fatty-alcohol ethoxylates which are essentially insoluble in water can nevertheless form dispersions and adsorb latex stabilisers. In this case, the concentration of the monomer at the surface during the polymerisation may not become constant, as the space for incoming monomer from the aqueous phase will not be restricted by the presence of the polymer and will always be available during polymerisation. As a result, the rate of polymerisation is first-order (up to 48% conversion) with respect to monomer concentration during the polymerisation. Alternatively, the mechanism could be straight-forward solution polymerisation showing first-order kinetics.

c. Propagation mechanism for HPMA

In the case of HPMA, the polymer (PHPMA) produced is also insoluble in the aqueous phase. As a result, the monomer would not be expected to show zero-order kinetics for the same reasons as suggested for HEMA. However, this monomer in fact followed a second-order reaction (up to 41% conversion). It is difficult at this stage to suggest a possible mechanism to explain this observation. However, HPMA is the only monomer likely to partition between the rubber and aqueous phase. If the rate of polymerisation was jointly proportional to the monomer concentration in the two phases, then one would expect that $R_p \propto [M]^2$, but how this might arise mechanistically is not clear.

In conclusion, it is noted that the phenomenon of zero-order kinetics for individual reactions but first-order

kinetics based upon different initial monomer concentrations is not unique to this work. Loh (150) obtained similar results when investigating the effect of zinc dibutyl dithiocarbamate upon the pre-vulcanisation of NR latex. This contradiction in kinetic behaviour appears to be peculiar to NR latex where a heterogeneous reaction exits. The phenomenon of second-order for individual reactions but first-order based upon the initial monomer concentrations might also be as a consequence of the heterogeneous reaction in NR latex. However, the present author is unable to offer satisfactory explanations for the apparent contradictions of the reaction-orders.

8.3.10.2 Order of reaction with respect to initiator concentration

Odian (99) stated that the kinetics of redox-initiated polymerisations depends upon the termination modes. If the termination is a bimolecular reaction between propagating radicals, the rate of polymerisation is expected to be half-order with respect to initiator concentration, as shown in Section 4.2. In some cases, the termination might be by monomolecular termination involving the propagating radicals and a component of the redox system. As mentioned in Section 4.2, the steady-state assumption implies that the rate of initiation is equal to the rate of termination. If the termination was dominated by bimolecular reaction between propagating radicals, the rate of polymerisation should be half-order with respect to initial concentration. In this experiment, it was observed that the rate of polymerisation with respect to initial initiator concentration for HEA, HPA and HPMA was 0.50 (Figures 8.8A, 8.8B, and 8.8D). This strongly suggests that the termination mode of the polymerisation for these three monomers using the redox initiator was by bimolecular reaction. For HEMA, however, the order of reaction with respect to initiator concentration between propagating radicals differed from that for the other monomers, being approximately 0.20 (Figure 8.8C). The present author is unable to suggest a possible explanation for this.

8.3.10.3 Order of reaction with respect to DRC

As mentioned in Section 4.7.1, Burfield and Ng (64) reported that the rate of polymerisation of methacrylamide in NR latex using potassium persulphate as initiator at $60^{0}C$ was first-order dependence with respect to the DRC. In

this work, it was also found that the rates of polymerisation of the non-ionogenic hydrophilic monomers were first-order dependence with respect to the DRC (Figures 8.9A to 8.9D). Burfield and Ng (64) stated that the first-order dependence of polymerisation rate on rubber hydrocarbon is not easily explained because the presence of the hydroperoxide groups on the rubber molecule might act as an initiator. This initiator would give rise to half-order. However, Burfield and Ng (64) gave two possible explanations for the first-order dependence with respect to the DRC (Section 4.7.1) as follows:

(i) The presence of reducing agent in NR latex such as Fe^{2+} could form a redox system with hydroperoxide present on the rubber molecule. The mechanism is re-written as follows:

$$Fe^{2+} + ROOH \xrightarrow{k_d} Fe^{3+} + RO. + OH^-$$

Since increasing the DRC will increase the concentration of both metal ion and rubber hydrocarbon, the rate of initiation would be second-order with the DRC. As a result, the overall rate of polymerisation would be first-order with respect to the DRC. In this work, however, it was found that the grafting efficiency of the polymerisation of HEA and HPA at $30^{o}C$ was virtually zero. In the case of HEMA and HPMA, only small amount of graft copolymers was obtained (Section 10.15.4). In these circumstances, the redox system was unlikely to occur. If the redox reaction occurred, the grafting efficiency of the four monomers would have been high for two reasons:

a. The growing radicals would cross-terminate with RO. to form graft copolymers.

b. The RO. would attack the monomers and subsequently produced graft copolymers.

(ii) The presence of non-rubber in the latex, such as amines, might bring about termination reactions that are first-order with respect to the DRC. The mechanism of the possible reaction is re-written as follows:

$$M_n\cdot + N \longrightarrow MH + S$$

where $M_n\cdot$ is the growing polymer radical, N is the non-rubber constituents, such as an amine, and S is a species which is incapable of re-initiating polymerisation, and MH is the homopolymer. This explanation accords to this work because the characterisation of the products of the polymerisation of the non-ionogenic hydrophilic monomers in the latex at 30°C using potassium persulphate-sodium metabisulphite initiator proved that these monomers were mostly converted to homopolymers rather than graft copolymers (Section 10.15.4)

As can be seen from the Figures 8.9A to 8.9D, the rate of polymerisation increased as the DRC increased. A possible explanation for this is as follows: Keeping the monomer concentration (21.5×10^{-2} mol/l latex), and the redox initiator concentration (4.9×10^{-3} mol/l latex) constant, but increasing the DRC from 15% to 30% would spontaneously result in:

i) A doubling of the surface area of the rubber particles. As a consequence, the proportion of monomer adsorbed at the particle surface would increase, although the actual concentration of adsorbed monomer might decrease.

ii) A corresponding reduction of volume of the aqueous phase. Thus the concentration of the monomer in the aqueous phase would also increase.

Thus the increase of rate with increase of DRC may be due to the combination of these two factors. In these circumstances, the presence of rubber in the latex would accelerate rather than retard the rate of polymerisation.

Table 8.1 Volatility of non-ionogenic hydrophilic monomers at 90°C under 0.16 mm Hg pressure for 3.5 hours in absence of NR latex

monomer	volatility (% w/w)
HEA	99.9
HPA	99.9
HEMA	99.9
HPMA	99.9

Table 8.2 Volatility of inhibitors/antioxidants at 90°C under 0.16 mm Hg pressure for 8.5 hours in presence of NR latex

No.	inhibitor/antioxidant	level (pphr)	volatility (% w/w)
1.	Nonox DPPD	68.45	0.2
2.	Flexzone 3-C	69.04	0.0
3.	Nonox EXN	61.42	0.0
4.	Antioxidant 2246	66.15	0.0
5.	Nonox DN	68.57	0.0
6.	DPPH	10.39	0.9
7.	Flectol H	68.45	1.5
8.	Nonox B	68.22	2.1
9.	Galvinoxyl	34.50	9.1
10.	4-tert-Butyl catechol	57.66	16.0
11.	Hydroquinone	31.60	18.6
12.	Santoflex AW	68.54	21.5
13.	Nonox WSL	69.34	42.5

Table 8.3 Effectiveness of inhibitors/antioxidants added to NR latex to which HEA (40 pphr) was added prior to the redox initiator (2-4.5 pphr)

No.	inhibitor/antioxidant	level (pphr)	conversion (% w/w)
1.	DPPH	42.82	6.85
2.	Nonox DPPD	51.34	8.63
3.	Flexzone 3-C	68.42	16.35
4.	Nonox DN	68.43	21.48
5.	Nonox EXN	60.44	43.52
6.	Antioxidant 2246	65.05	80.02

Table 8.4 Effectiveness of DPPH and Nonox DPPD added to NR latex to which the monomers (38-50 pphr) were added prior to the redox initiator (1-5 pphr)

monomer	inhibitor/antioxidant		level (pphr)	conversion (% w/w)
HEA	DPPH	-	25.94	8.29
	-	Nonox DPPD	50.32	2.95
HPA	DPPH	-	40.23	7.88
	-	Nonox DPPD	50.62	2.10
HEMA	DPPH	-	37.85	2.77
	-	Nonox DPPD	50.35	9.29
HPMA	DPPH	-	40.12	1.56
	-	Nonox DPPD	50.60	13.04

Table 8.5 Effectiveness of Nonox DPPD added to NR latex to which the redox initiator (1.96 pphr) added and kept for 23 hours at 30^{o}C prior to addition of the monomers (29-31 pphr)

monomer	inhibitor/antioxidant	level (pphr)	conversion (% w/w)
HEA	Nonox DPPD	0.39	3.30
HPA	Nonox DPPD	0.39	3.00
HEMA	Nonox DPPD	0.39	0.64
HPMA	Nonox DPPD	0.41	0.80

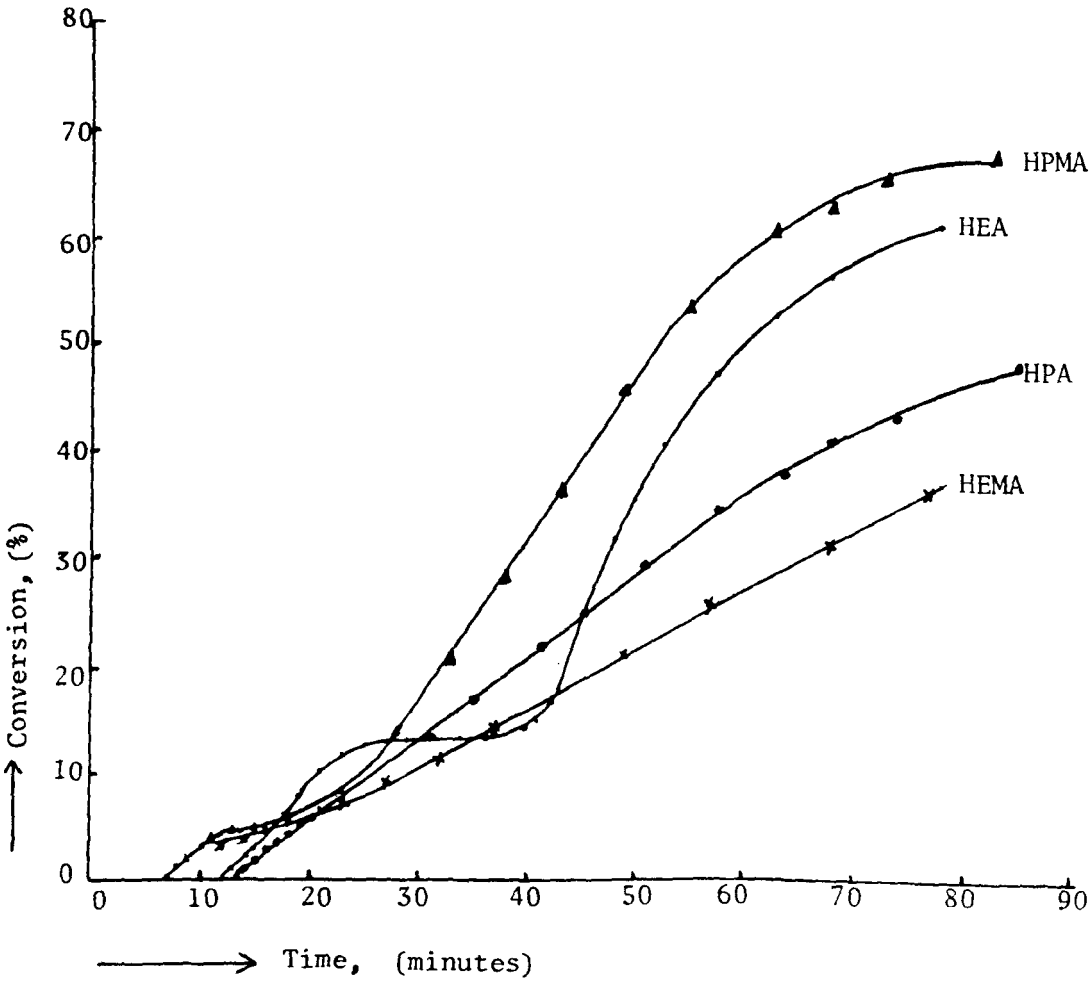


Figure 8.1A Conversion-time curves for non-ionogenic hydrophilic monomers in aqueous solution (pH ca. 5) at 30.00 ± 0.03°C

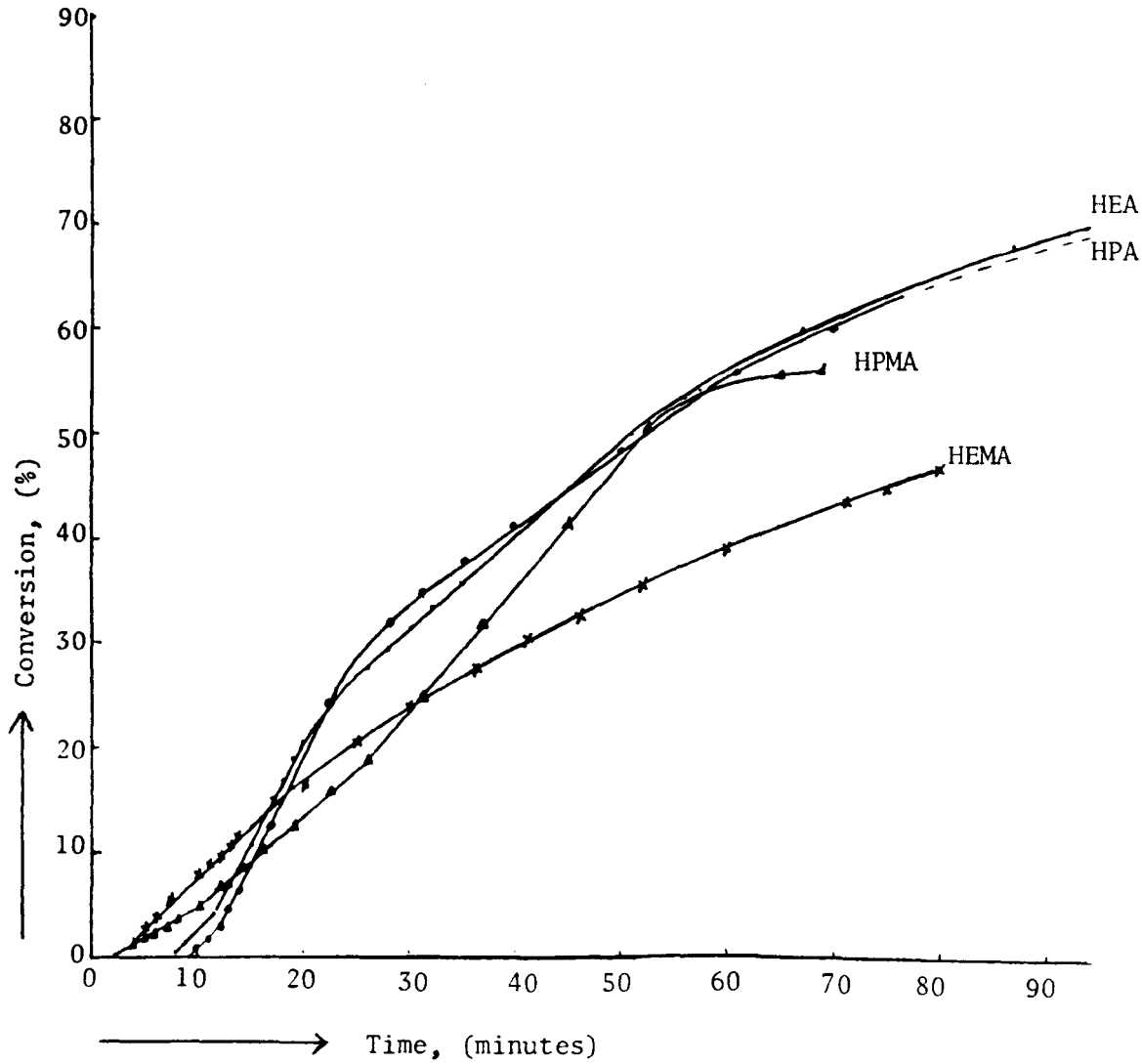


Figure 8.1B Conversion-time curves for non-ionogenic hydrophilic monomers in aqueous ammonia solution (pH ca. 10) at 30.00 ± 0.03°C

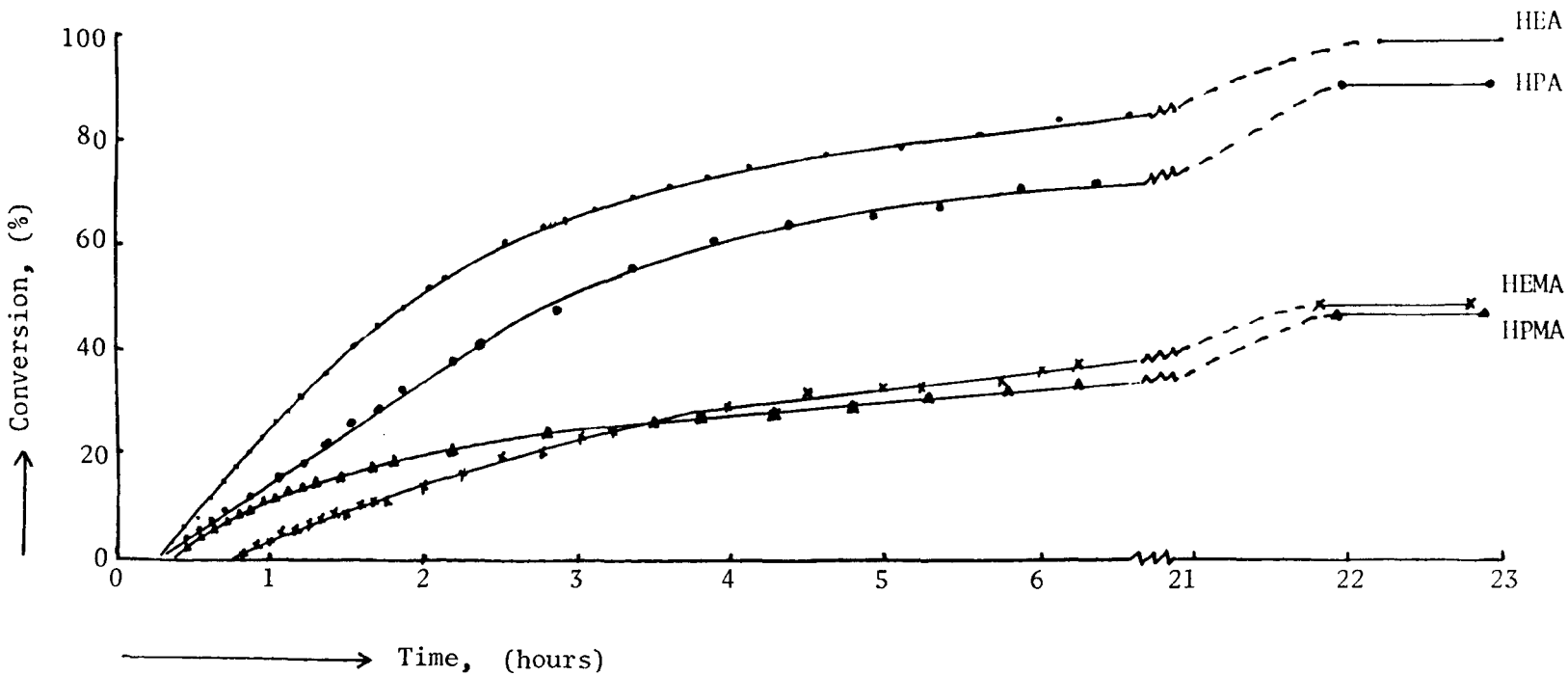
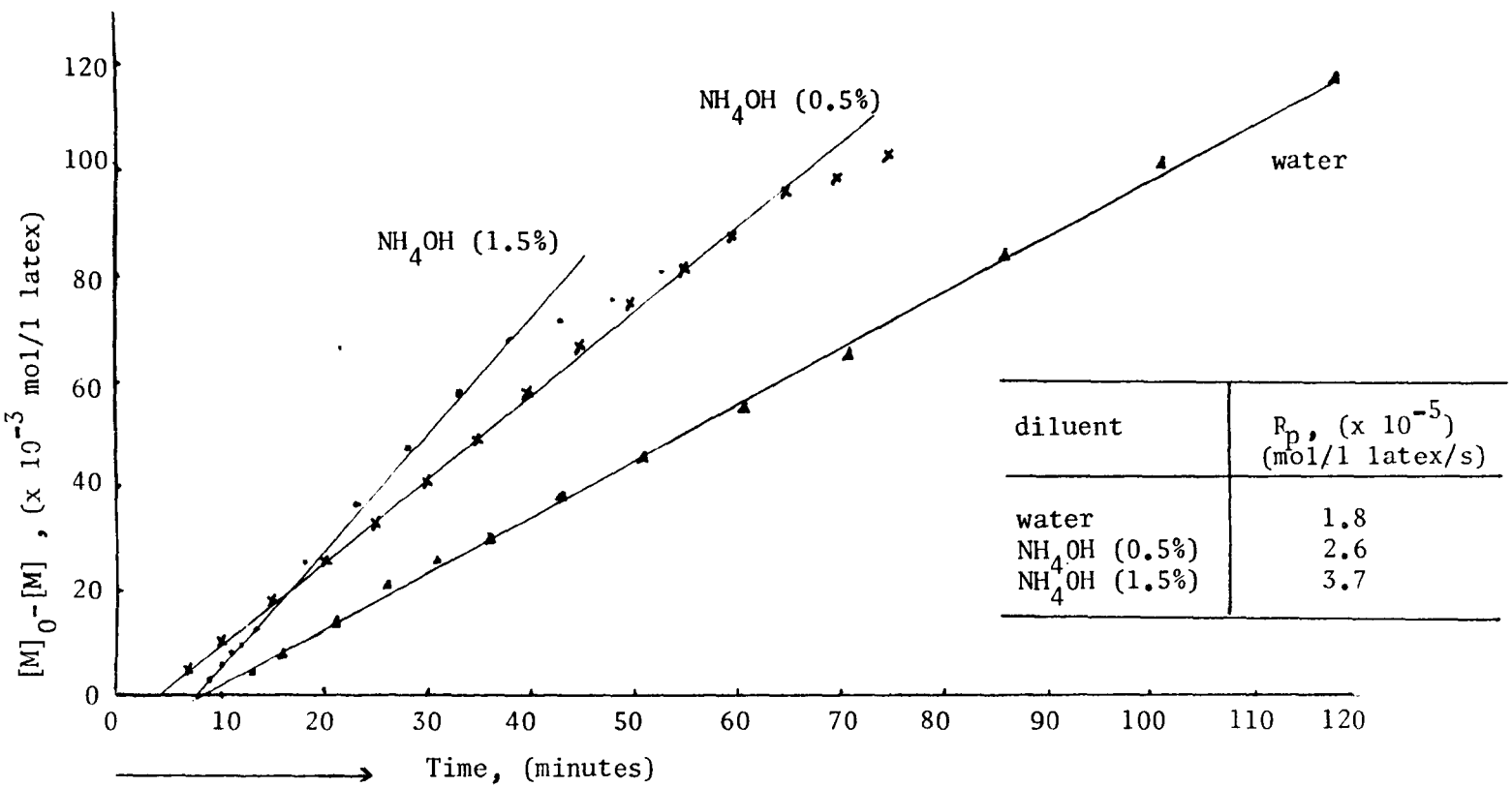


Figure 8.2 Conversion-time curves for non-ionogenic hydrophilic monomers in NR latex using distilled water as diluent at 30.00 ± 0.03°C



diluent	R_p, (x 10^{-5}) (mol/l latex/s)
water	1.8
NH_4OH (0.5%)	2.6
NH_4OH (1.5%)	3.7

Figure 8.3 Effect of added ammonia upon conversion-time curves for hydroxypropyl acrylate (HPA) polymerised in NR latex at 30.00 ± 0.03°C

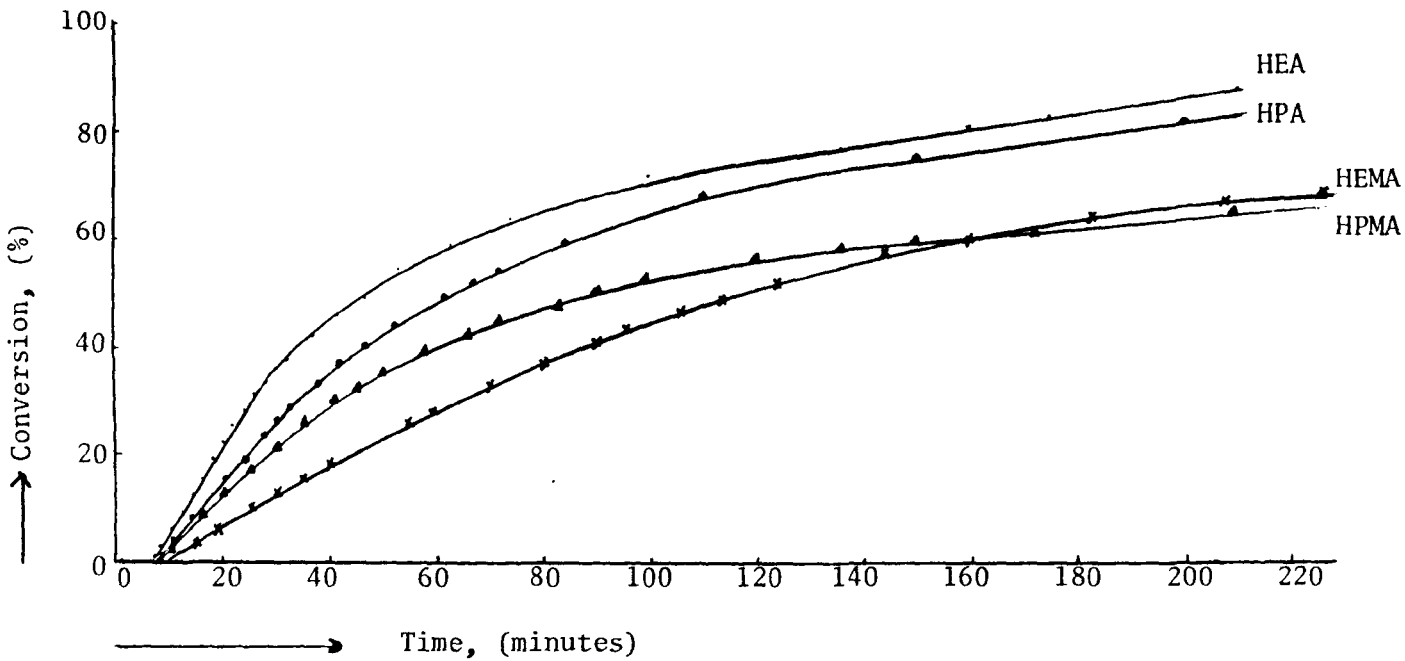


Figure 8.4 Conversion-time curves for non-ionogenic hydrophilic monomers polymerised in NR latex using aqueous ammonia solution (1.5%) as diluent at 30.00 ± 0.03°C

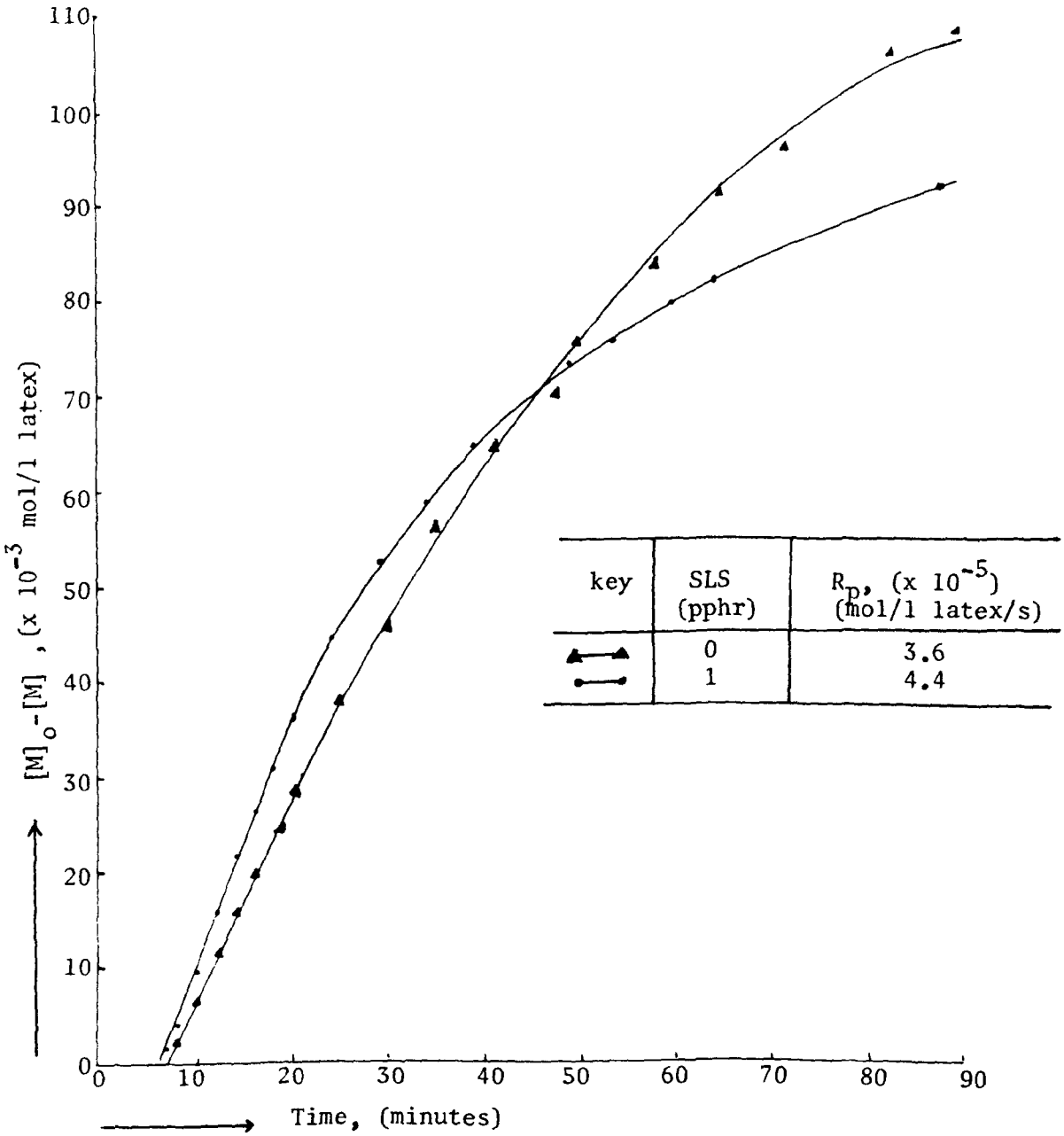
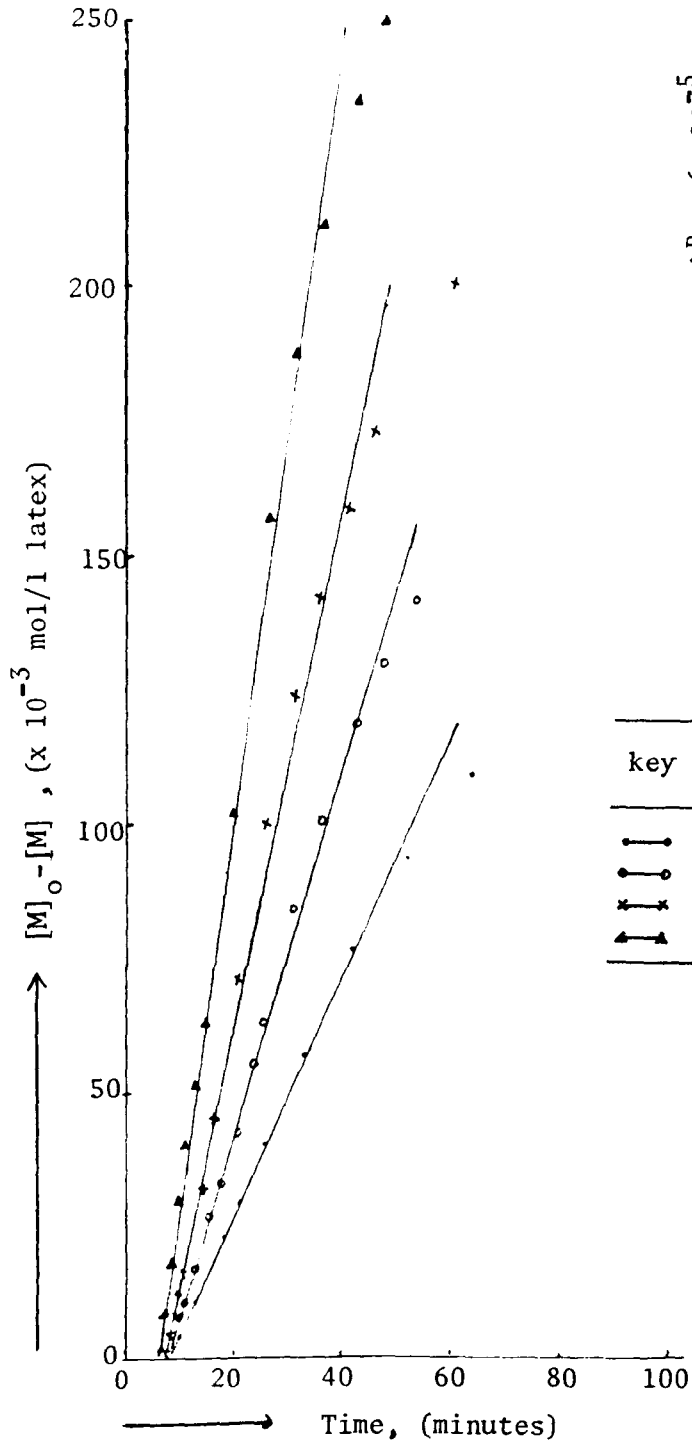
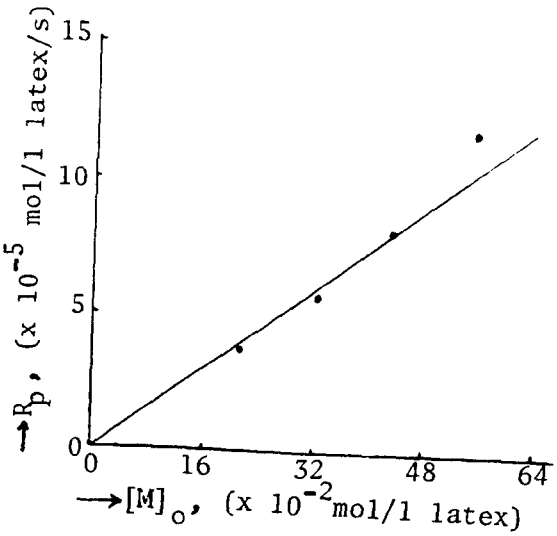


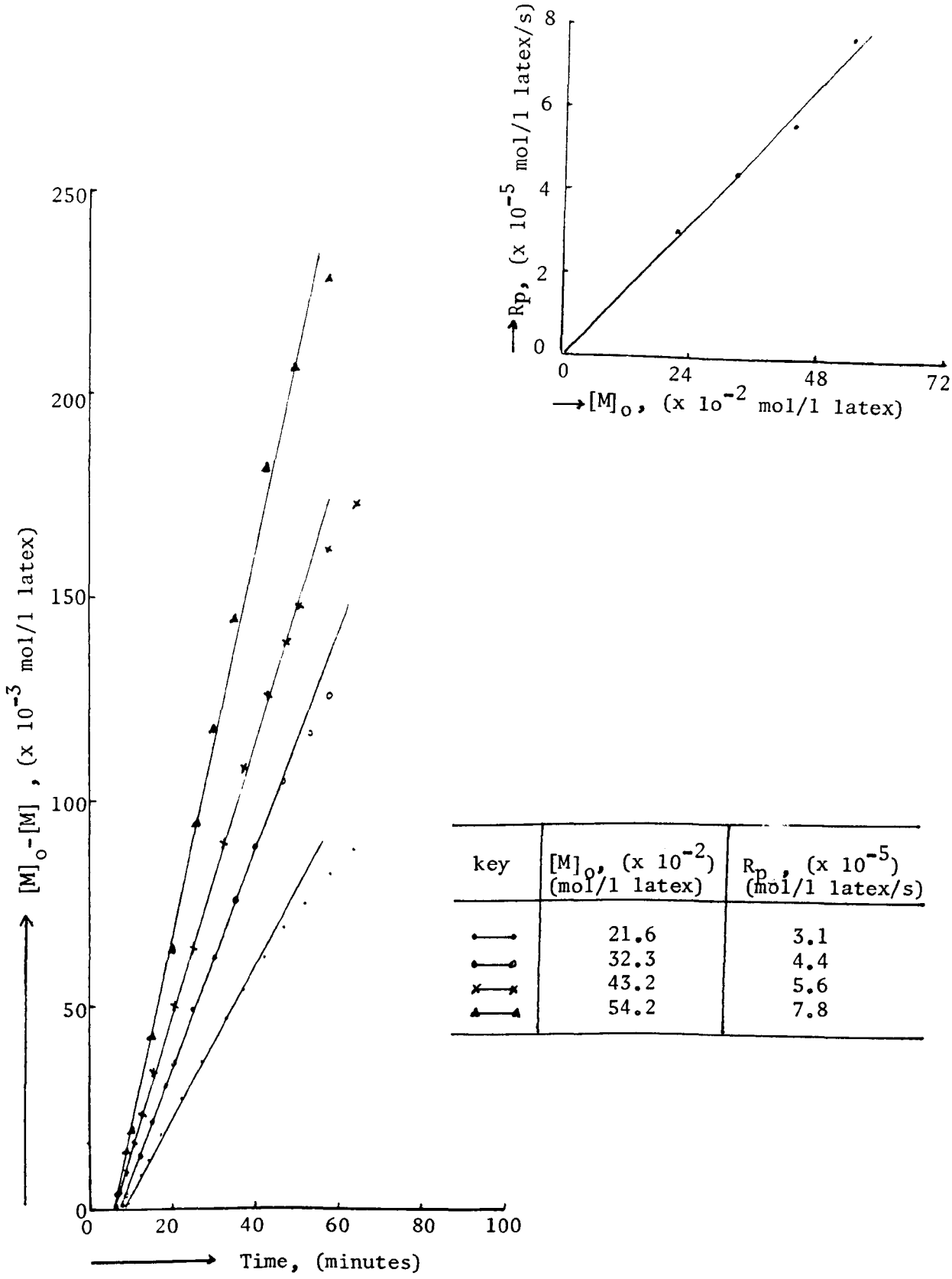
Figure 8.5 Effect of sodium lauryl sulphate (SLS) upon conversion-time curves for HPMA polymerised in NR latex at 30.00 ± 0.03°C





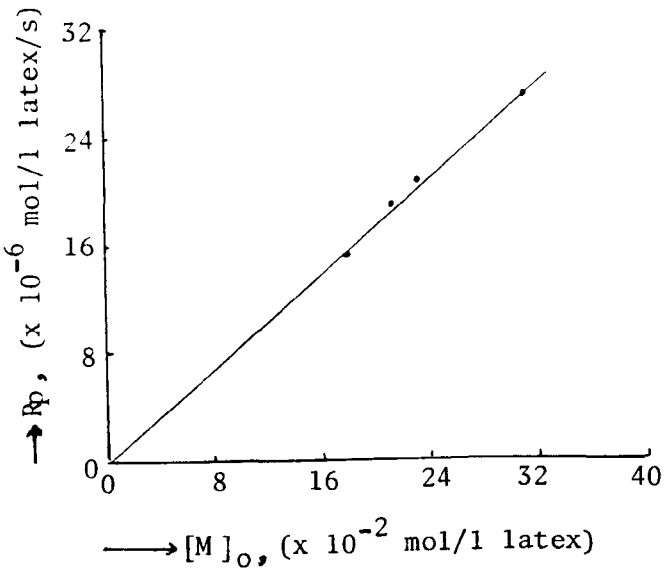
key	$[M]_o$, (x 10^{-2}) (mol/1 latex)	R_p, (x 10^{-5}) (mol/1 latex/s)
●—●	21.5	3.7
●—○	32.3	5.7
×—×	43.2	8.0
▲—▲	54.1	12.1

Figure 8.6A Determination of order of reaction for HEA with respect to initial monomer concentration in NR latex at 30.00 ± 0.03°C



key	$[M]_o$, (x 10^{-2}) (mol/l latex)	R_p, (x 10^{-5}) (mol/l latex/s)
●—●	21.6	3.1
●—○	32.3	4.4
×—×	43.2	5.6
▲—▲	54.2	7.8

Figure 8.6B Determination of order of reaction for HPA with respect to initial monomer concentration in NR latex at 30.00 ± 0.03°C



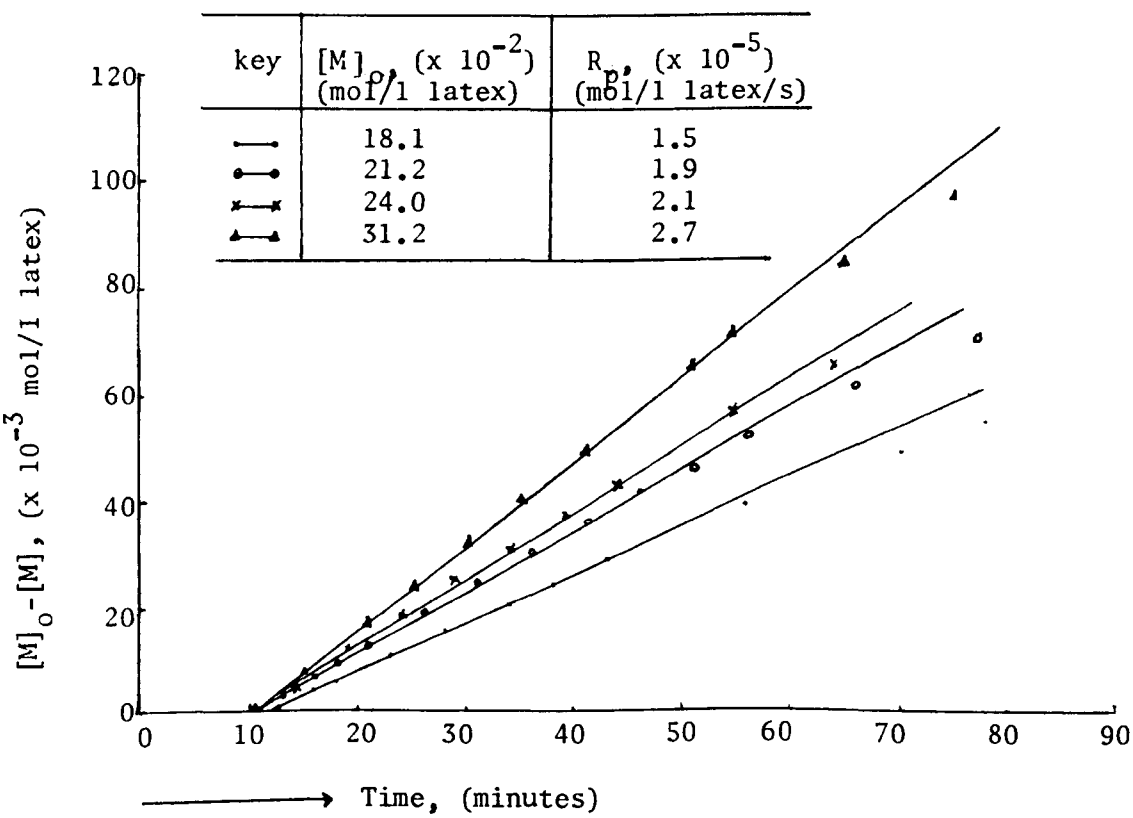
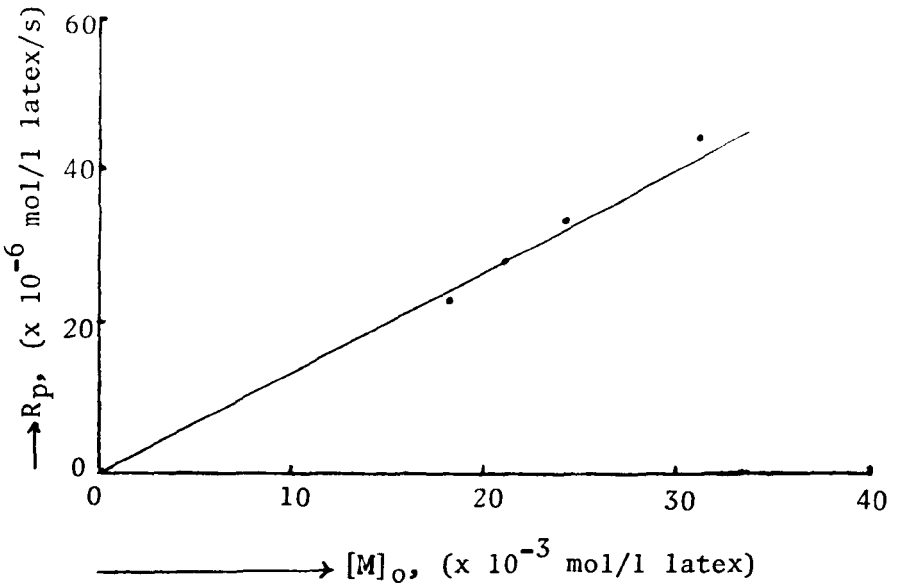
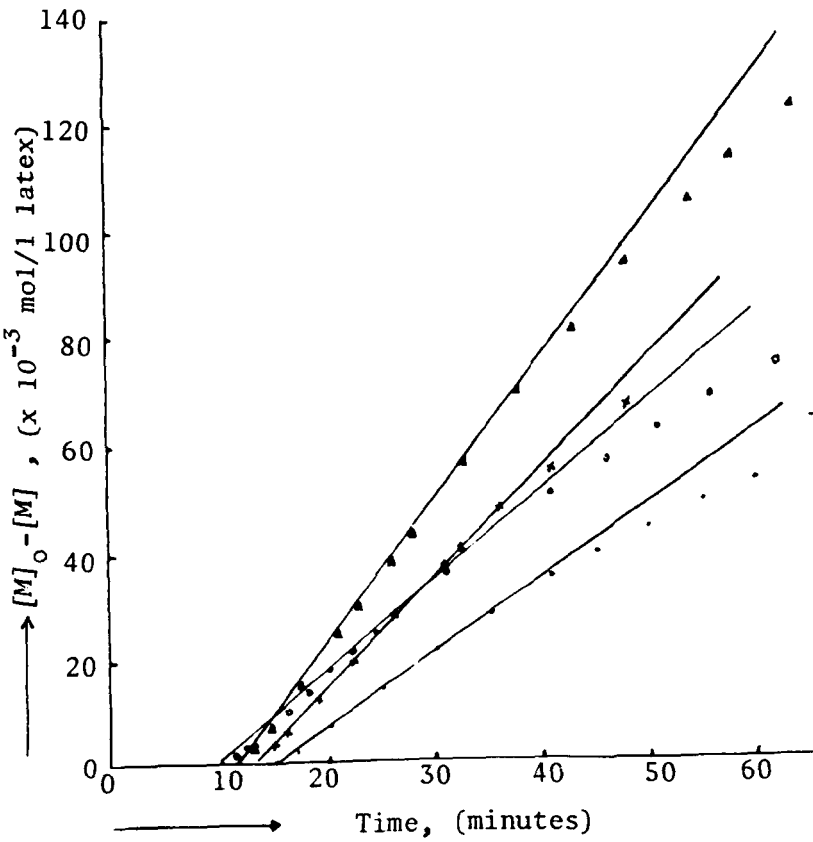


Figure 8.6C Determination of order of reaction for HEMA with respect to initial monomer concentration in NR latex at 30.00 ± 0.03°C





key	$[M]_o$, (x 10^{-2}) (mol/1 latex)	R_p, (x 10^{-5}) (mol/1 latex/s)
	18.1	2.3
	21.2	2.8
	24.2	3.3
	31.8	4.4

Figure 8.6D Determination of order of reaction for HPMA with respect to initial monomer concentration in NR latex at 30.00 ± 0.03°C

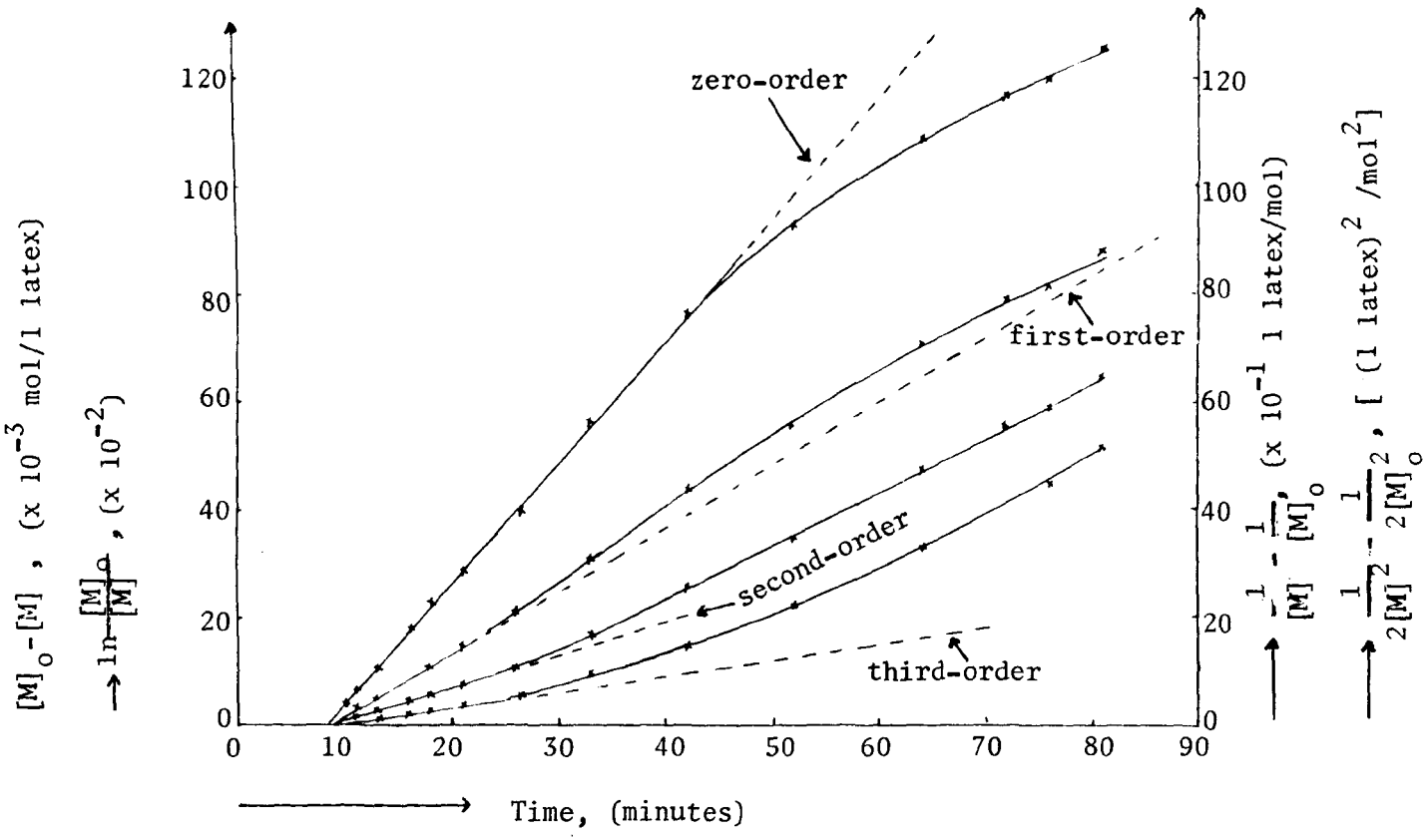


Figure 8.7A Determination of order of reaction for HEA with respect to monomer concentration at any instant during polymerisation in NR latex at 30.00 ± 0.03°C

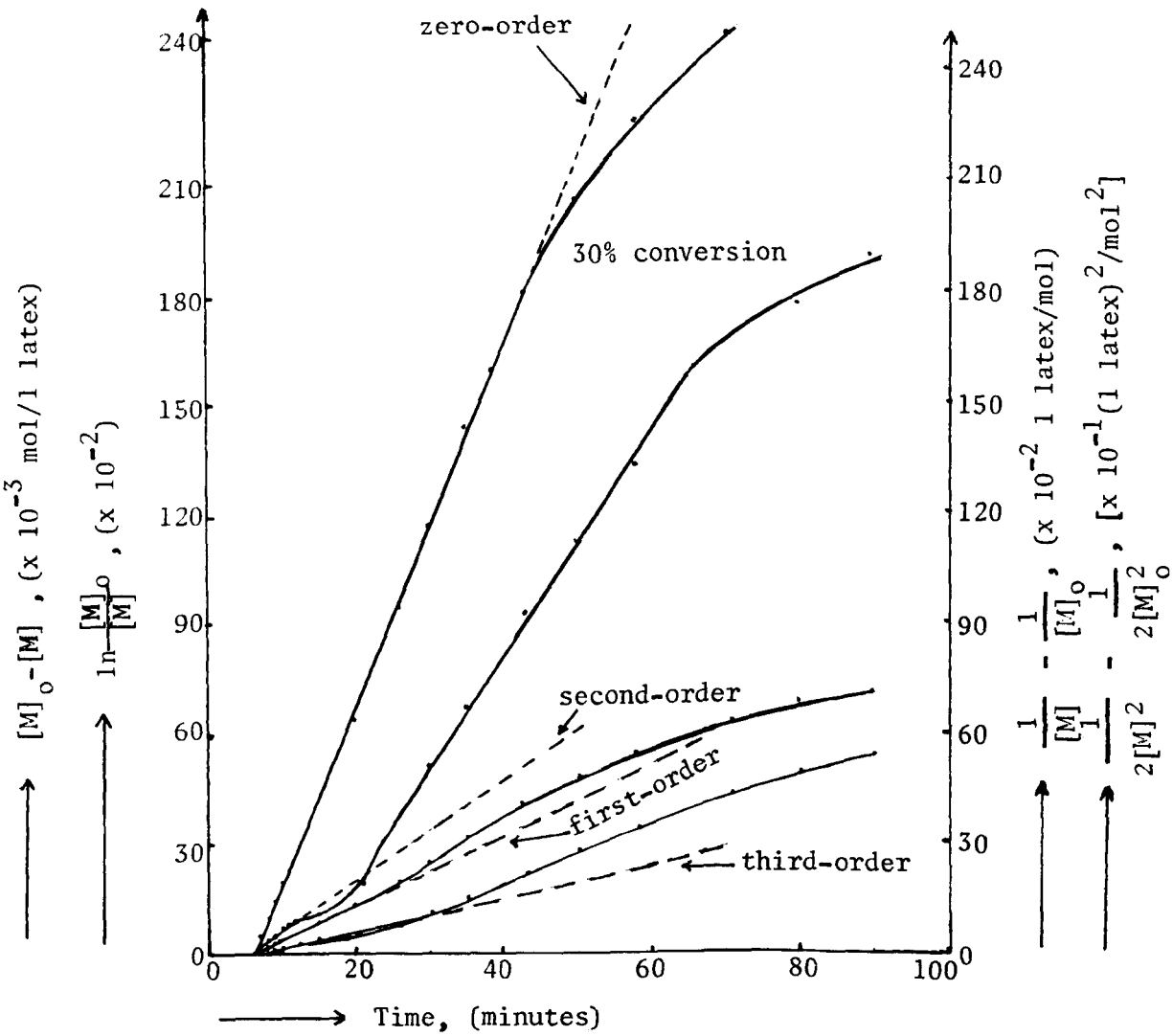


Figure 8.7B Determination of order of reaction for HPA with respect to monomer concentration at any instant during polymerisation in NR latex at 30.00 ± 0.03°C

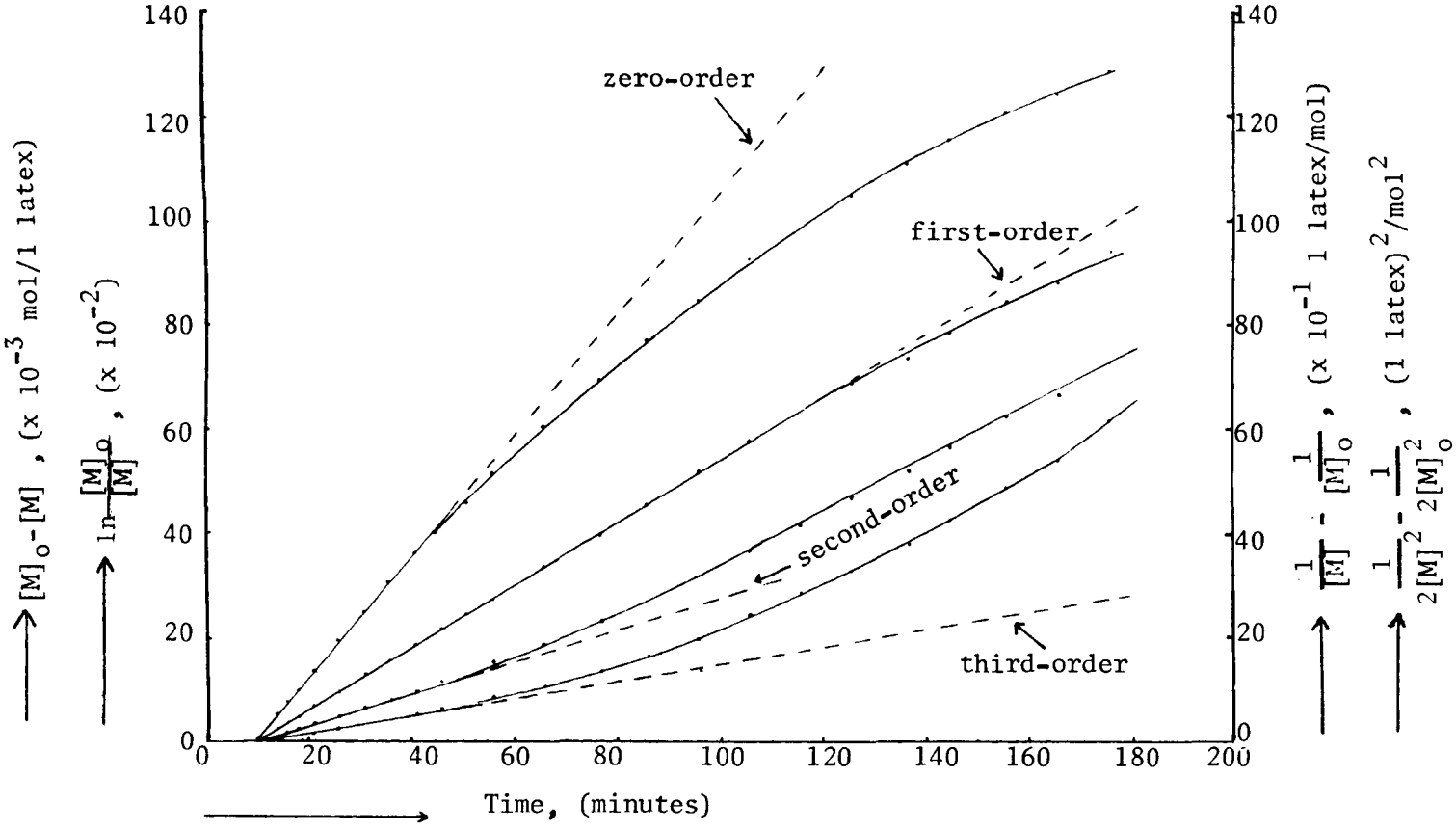


Figure 8.7C Determination of order of reaction for HEMA with respect to monomer concentration at any instant during polymerisation in NR latex at 30.00 ± 0.03°C

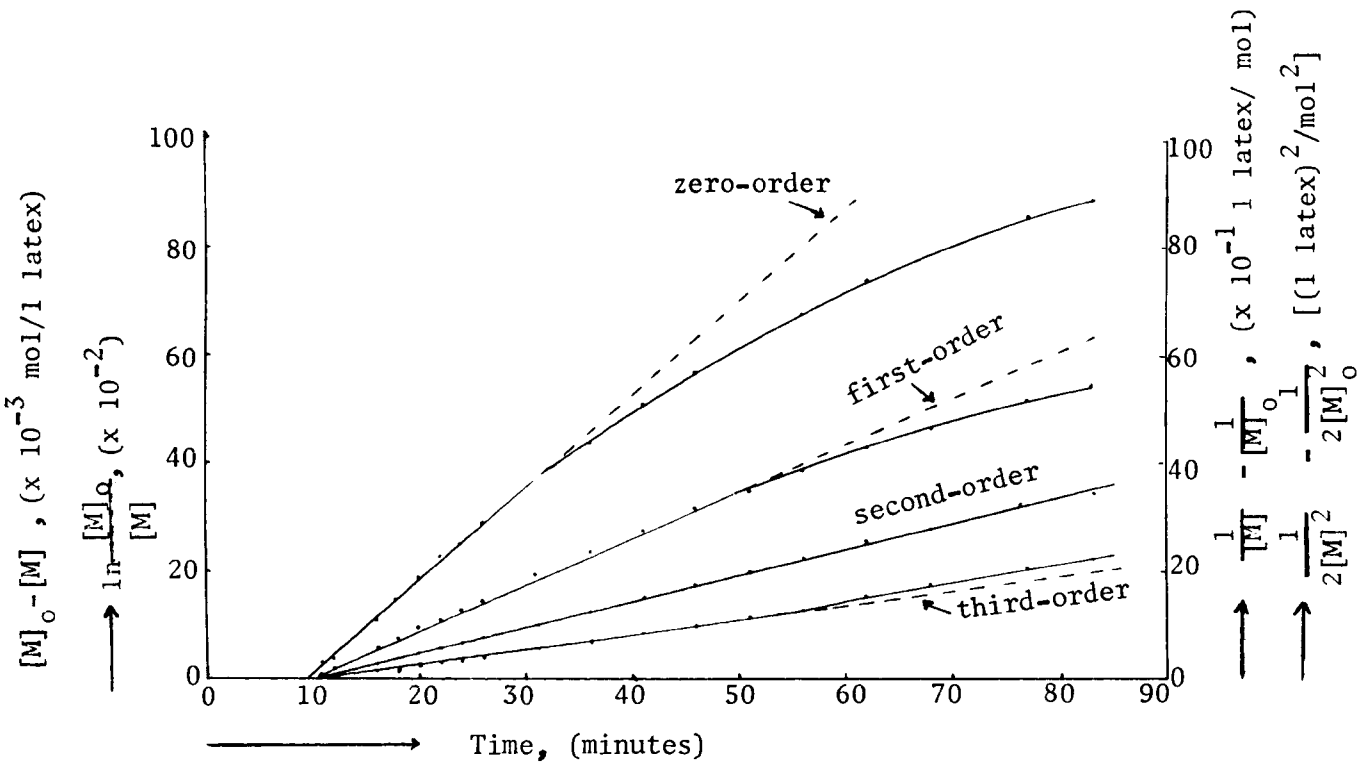
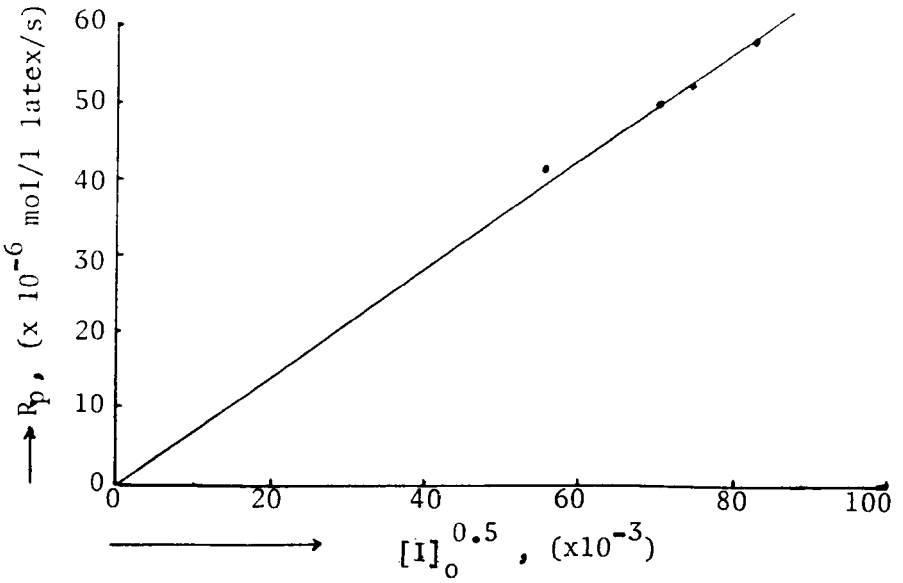


Figure 8.7D Determination of order of reaction for HPMA with respect to monomer concentration at any instant during polymerisation in NR latex at 30.00 ± 0.03°C



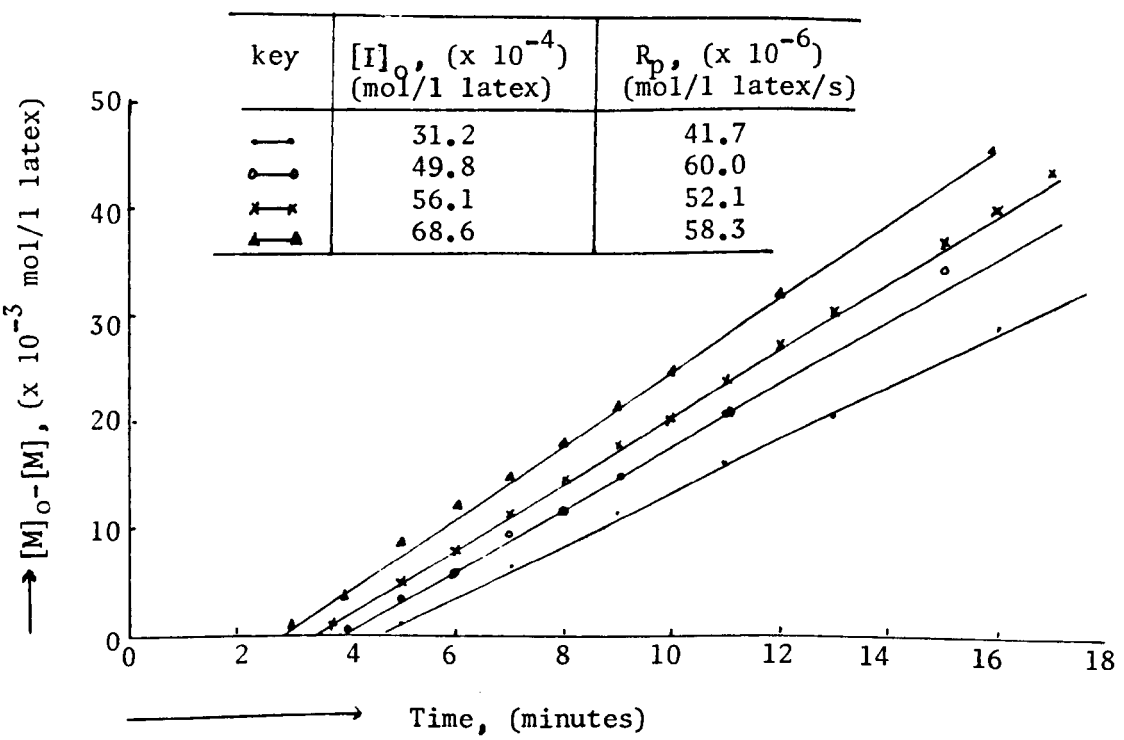
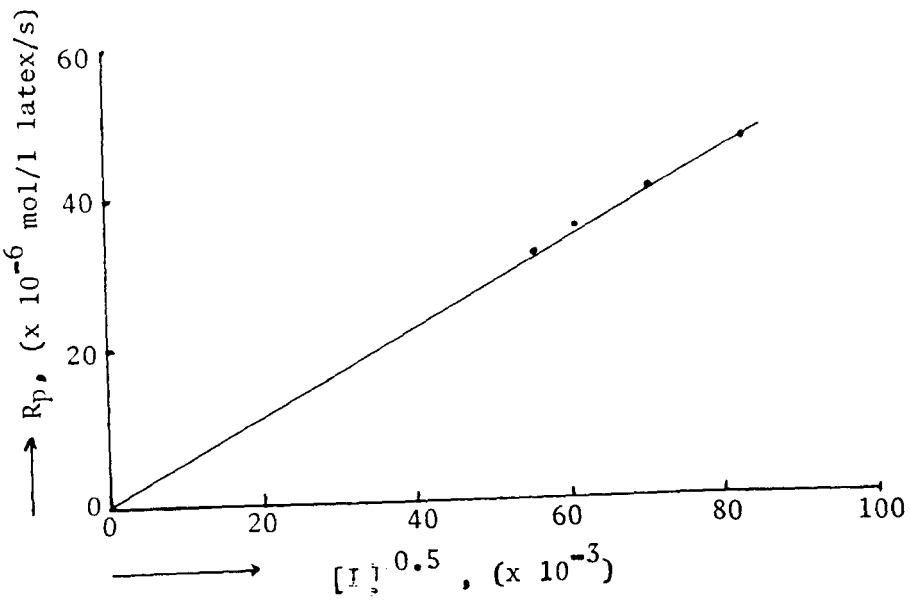
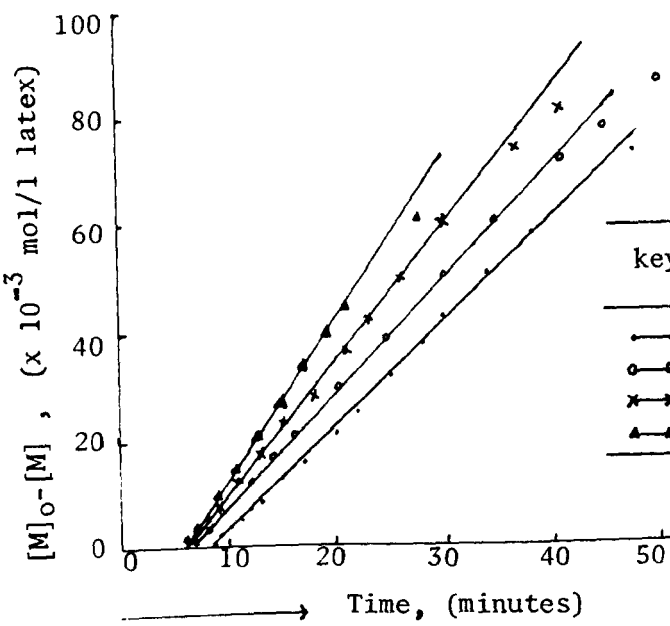


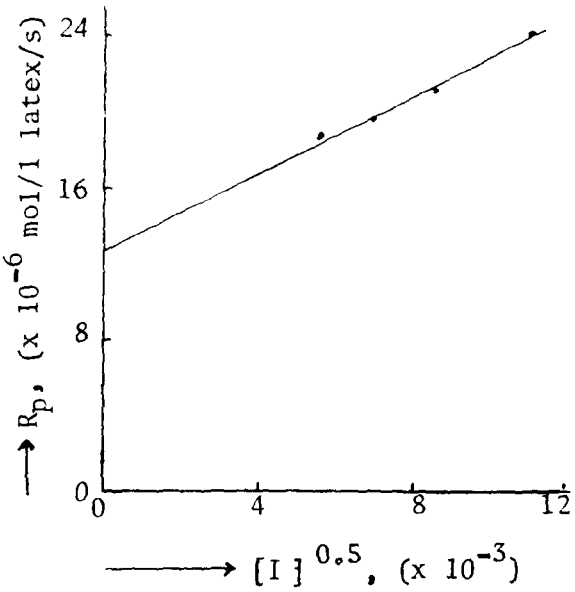
Figure 8.8A Effect of initiator concentration upon rate of polymerisation of HEA in NR latex at 30.00 ± 0.03°C

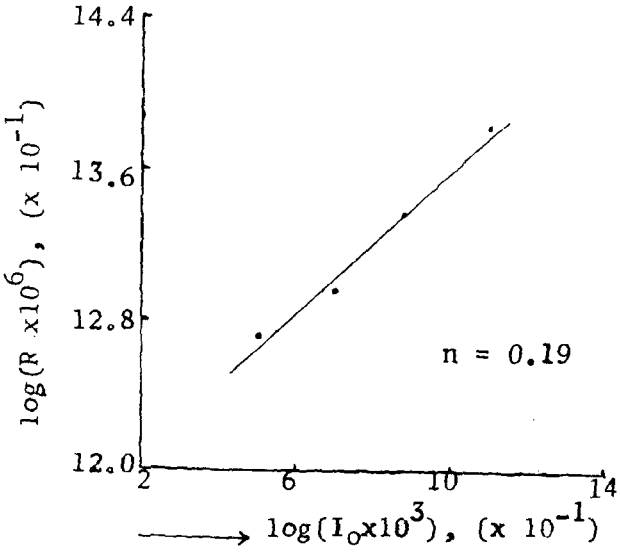


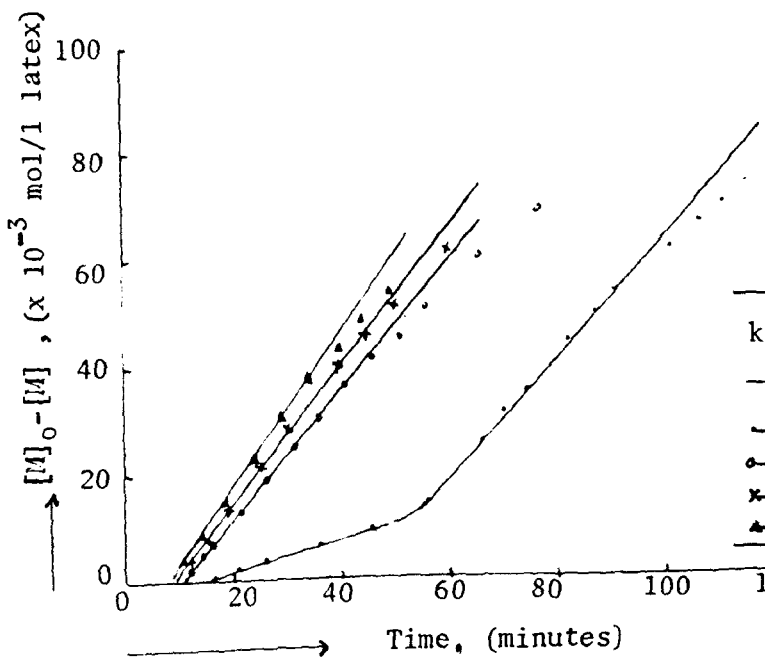


key	$[I]_o$, (x 10^{-4}) (mol/l latex)	R_p, (x 10^{-6}) (mol/l latex/s)
——	31.2	32.3
—o—o—	37.4	35.6
—x—x—	49.8	40.5
—▲—▲—	68.5	46.7

Figure 8.8B Effect of initiator concentration upon rate of polymerisation of HPA in NR latex at 30.00 ± 0.03°C

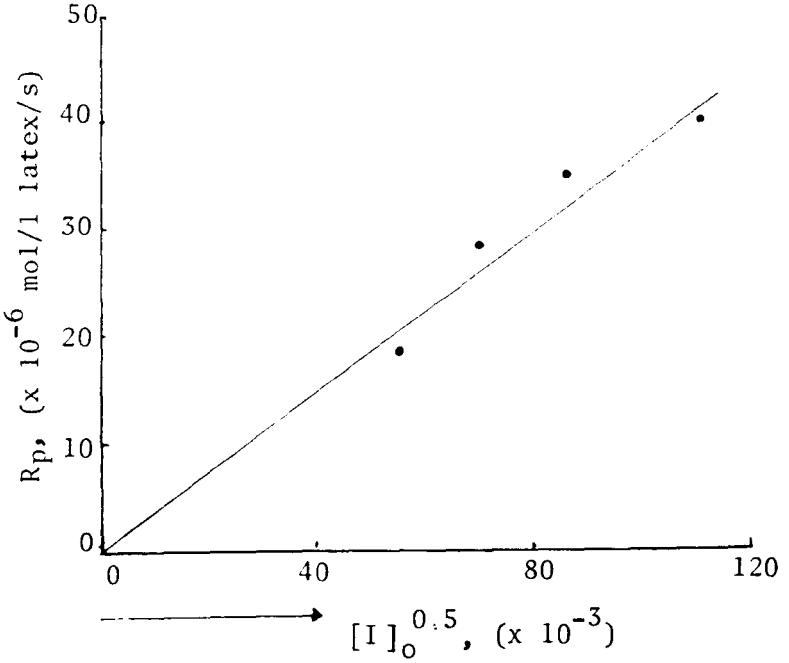






key	$[I]_o$, (x 10^{-4}) (mol/1 latex)	R_p, (x 10^{-6}) (mol/1 latex/s
——	31.0	18.6
—o—o—	49.5	19.7
—x—x—	74.7	21.7
—▲—▲—	123.5	24.1

Figure 8.8C Effect of initiator concentration upon rate of polymerisation of HEMA in NR latex at 30.00 ± 0.03°C



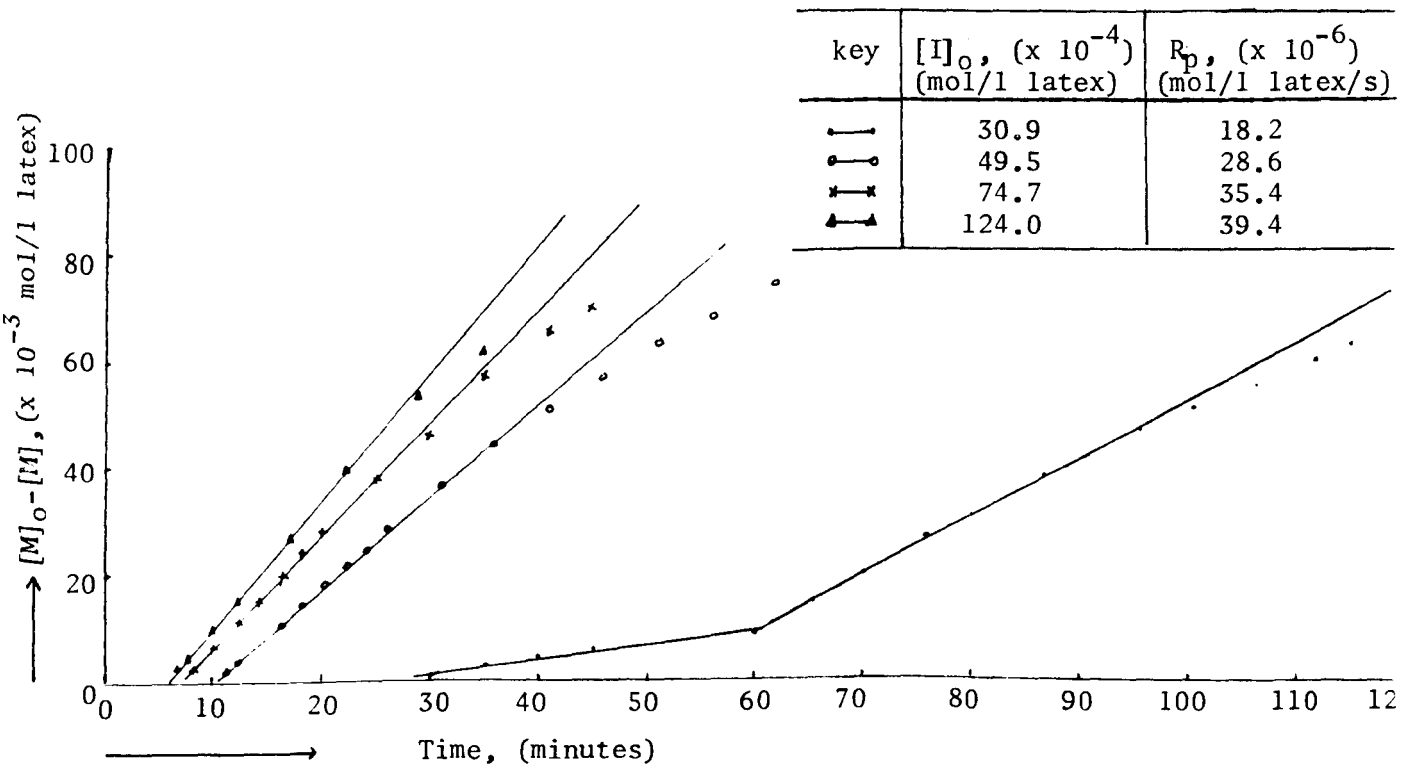


Figure 8.8D Effect of initiator concentration upon rate of polymerisation of HPMA in NR latex at 30.00 ± 0.03°C

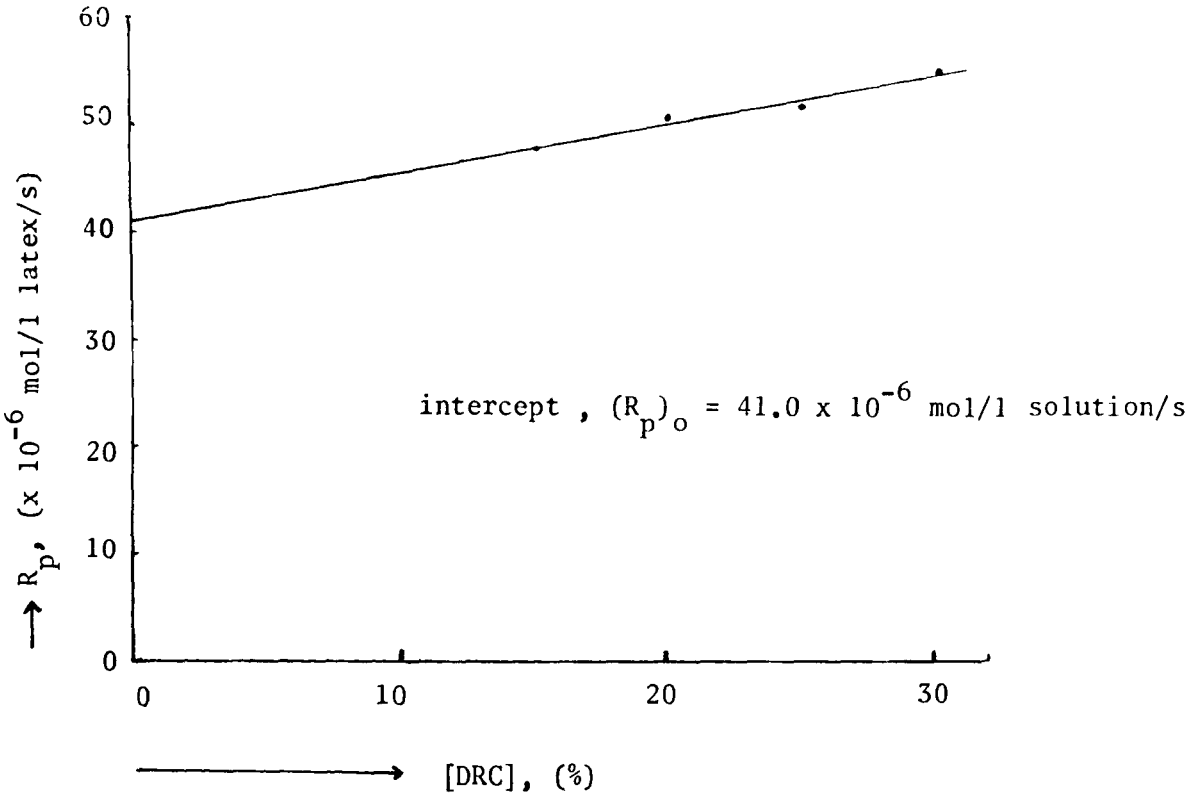


Figure 8.9A Effect of dry rubber content (DRC) upon rate of polymerisation of HEA in NR latex at 30.00 ± 0.03°C

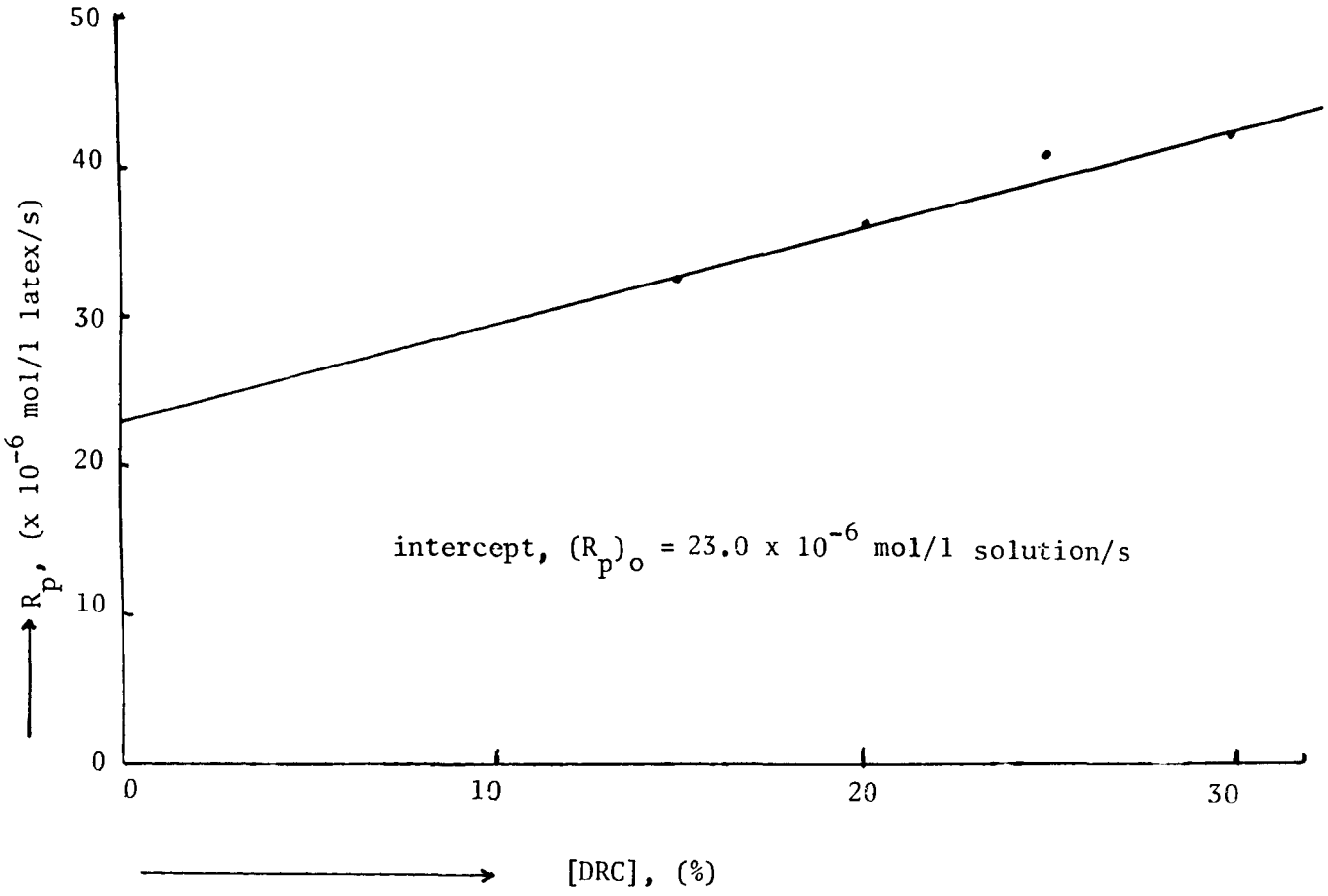


Figure 8.9B Effect of dry rubber content (DRC) upon rate of polymerisation of HPA in NR latex at 30.00 ± 0.03°C

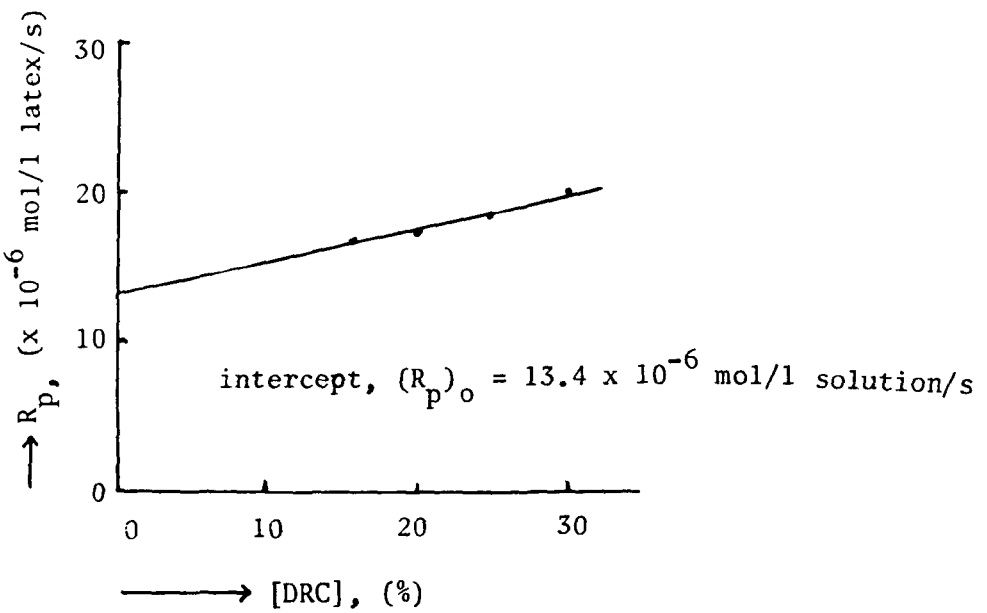


Figure 8.9C Effect of dry rubber content (DRC) upon rate of of polymerisation of HEMA in NR latex at 30.00 ± 0.03°C

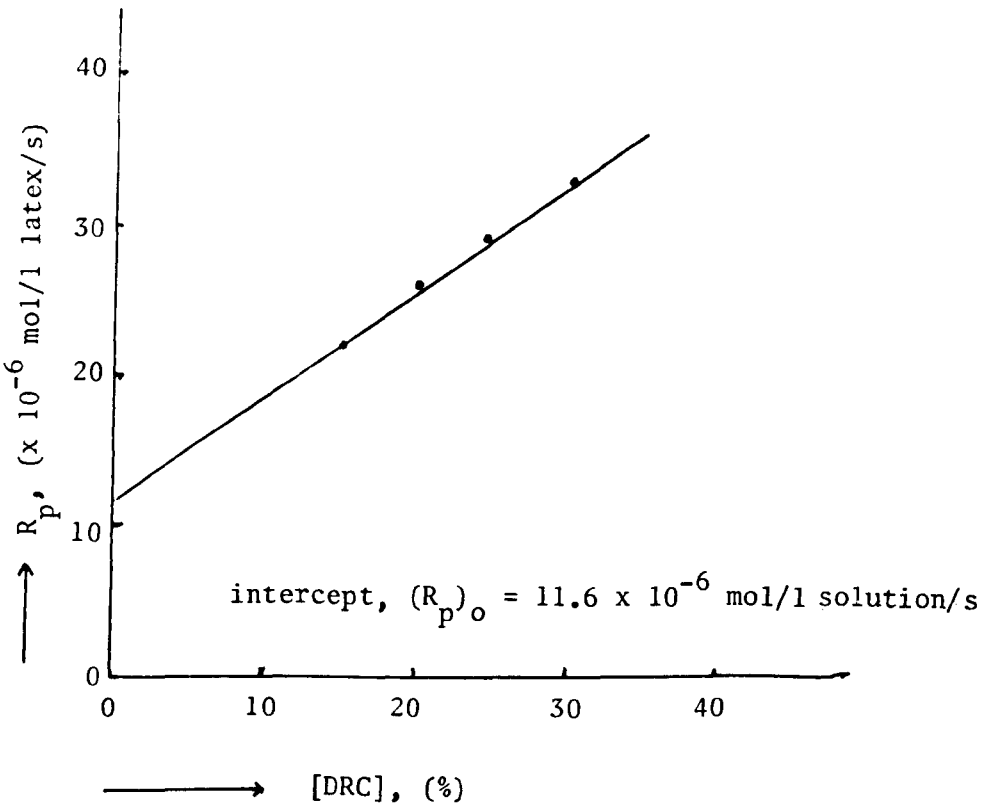
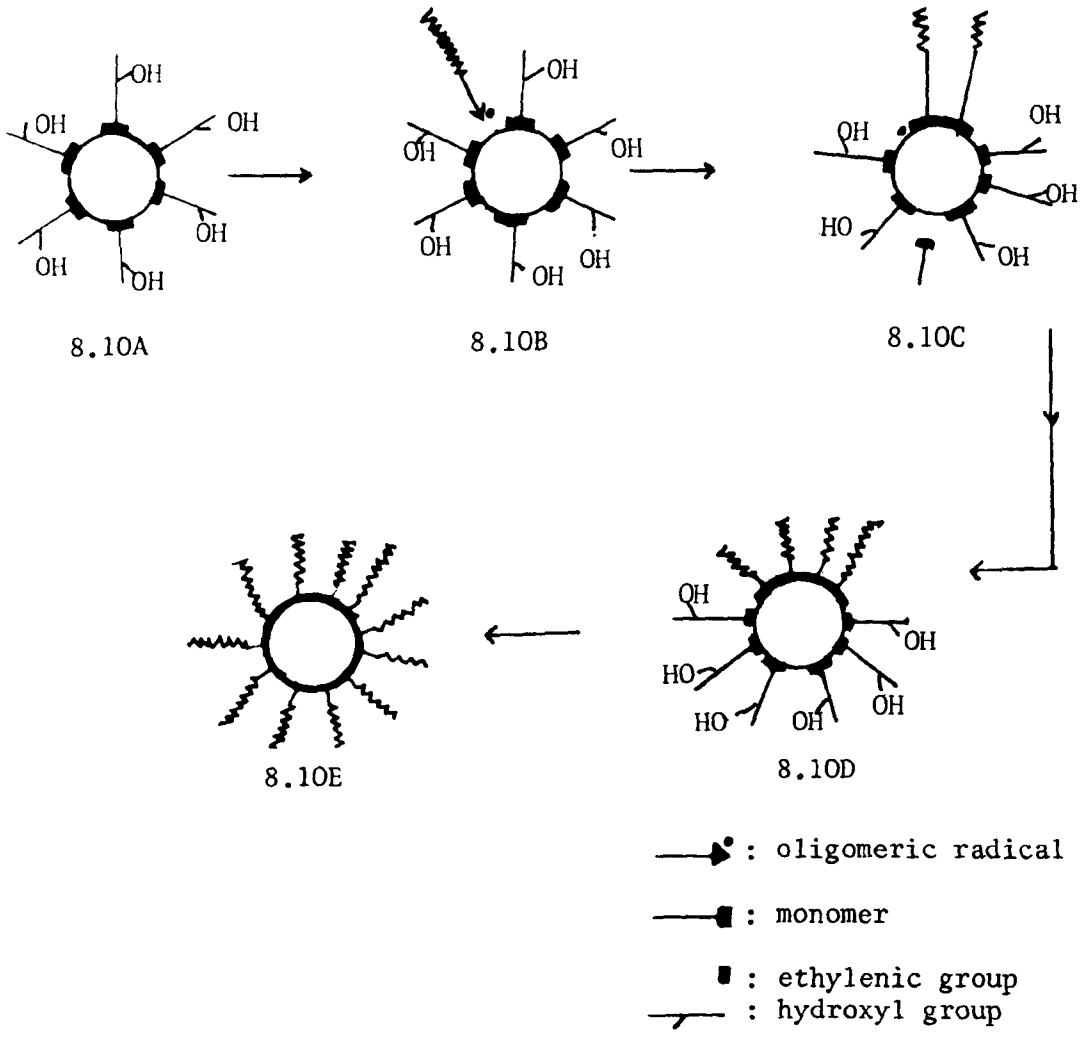


Figure 8.9D Effect of dry rubber content (DRC) upon rate of polymerisation of HPMA in NR latex at 30.00 ± 0.03°C



Figures 8.10A to 8.10E Diagram represantation of adsorption of non-ionogenic hydrophilic monomers at surface of rubber particles acting as loci of polymerisation

Chapter 9

Separation of homopolymers of non-ionogenic hydrophilic monomers and free NR from crude graft copolymers; implications for mechanism of grafting reactions to NR in NR latex

9.1 Introduction

To establish a satisfactory method for separating the homopolymers and free NR from the crude graft copolymers, preliminary studies were carried out. These are summarised in Sections 9.2 to 9.9. They include:

(i) polymerisation of the monomers under various conditions to establish whether crosslinking reactions occurred during the polymerisation;

(ii) investigation of the possibility that hydrolysis of the homopolymers occurred in acidic or in alkaline solutions;

(iii) selection of suitable solvents and conditions for dissolving the homopolymers and NR film;

(iv) justification of the efficiency of the method for separating homopolymers from NR latex.

The results of the separation experiments were used to draw conclusions concerning the mechanism of graft copolymerisation reactions in NR latex. The results are summarised in Section 9.2 to 9.10. All the results are then discussed in Section 9.11.

9.2 Solubility of homopolymers of non-ionogenic hydrophilic monomers prepared under various polymerisation conditions

The observations are summarised in Table 9.1. It was found that HEA and HPA polymerised in water to produce water-soluble PHEA and water-insoluble PHPA respectively. When the monomers where polymerised in aqueous sodium hydroxide, both polymers precipitated during polymerisation. The PHEA and PHPA were found to remain in solution when they were polymerised in 1) aqueous ammonia solution using the redox initiator, and 2) IMS using ACA as initiator. When HEMA

and HPMA were polymerised in water, sodium hydroxide solution, aqueous ammonium hydroxide or a mixture of water and non-polar solvents, the PHEMA and PHPMA precipitated. However, the PHEMA and PHPMA remained soluble when they were polymerised in IMS using ACA as initiator.

9.3 Solubility of PHEMA and PHPMA in various solvents

The observations are summarised in Table 9.2. PHEMA and PHPMA, prepared in a mixture of water and non-polar solvents in the presence or in the absence of NR latex dissolved when allowed to stand in a mixture of IMS and acetic acid (10% v/v) (IMSA) (Section 6.1.1.2.5) overnight. The polymers were also soluble in IMSA when they were polymerised in IMS using ACA as initiator. However, when prepared in water, the polymers were insoluble in water, IMSA, THF, allyl alcohol and a mixture of THF and IMSA. When the polymers were prepared in sodium hydroxide solution, the polymers were insoluble in water and in IMSA.

9.4 Justification of method used for separating PHEA and PHPA from NR latex

Table 9.3 gives the results for the recovery of PHEA and PHPA from an NR latex mixture. The PHEA and PHPA were prepared by polymerising the corresponding monomers in IMS using ACA as initiator at 62^{o}C for about 24 hours. The polymers were dried in a vacuum oven to constant mass. The dried polymers were then dissolved in distilled water prior to add to NR latex. It was found that the IMSA solution extracted successfully polymers added to the latex, by immersing in the solvent at 20 ± 2^{o}C for 6 days. The extent of recovery of the polymers was greater than 99.5%.

9.5 Investigation of hydrolysis of homopolymers of non-ionogenic hydrophilic monomers in acidic and alkaline solutions

The results are shown in Tables 9.4, 9.5 and 9.6. The titration method showed that the formation of acids from the polymers after allowing to stand in IMSA solution (pH 2.5) for 2 weeks was negligible. This results were also in accordance with the results using gravimetric method in which the recovery of the polymers after allowing to stand in IMSA for 3 weeks was in the order of 99%. In the case of the polymers which were allowed to stand in ammonia

solution (pH ca. 10) for 3 weeks, the polymers were not hydrolysed to any significant extent as the recovery of the polymers was in the order of 99%.

9.6 Insolubility of homopolymers of non-ionogenic hydrophilic monomers in non-polar solvents

The results are shown in Table 9.7. The non-ionogenic hydrophilic polymers (0.5% w/w) when added to petroleum ether (80-100°C)/toluene (1:1 by volume) were found to be insoluble, and could be recovered by filtration to an extent of 98%.

9.7 Insolubility of NR film in a polar solvent

The results are shown in Table 9.8. It was found that the NR film did not dissolve in IMSA at 20°C for 105 days nor at 40°C for 26 days. The NR film was recovered to an extent of 98 to 99%.

9.8 Solubility of NR film in non-polar solvents

The results are shown in Table 9.9. It was found that the NR films (ca. 0.5% w/w) were soluble in petroleum ether (80-100°C)/toluene (1:1 by volume) when warmed to 40°C for 39-55 days. The NR film (ca. 0.4% w/w) did not dissolve completely in the petroleum ether (60-80°C)/toluene when left at room temperature for 105 days.

9.9 Separation of free NR film from the crude graft copolymers

It was not possible to separate any free NR from the graft copolymer from which the homopolymers of the non-ionogenic hydrophilic monomers had already been removed. It is probable that only a very small amount of grafting is necessary to cause the NR to become insoluble.

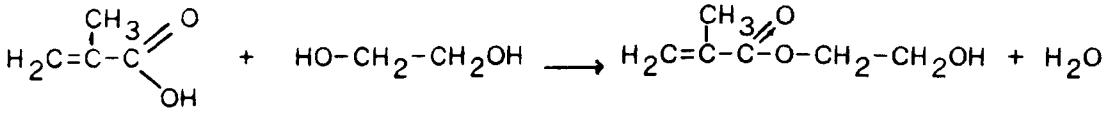
9.10 Conversion and efficiency of grafting of non-ionogenic hydrophilic monomers to NR in NR latex using ACA as initiator

The results are shown in Table 9.10. The conversions (determined gravimetrically) of the monomers polymerised in NR latex using ACA as initiator at 62-65°C were in the range 44 to 52 %. The efficiencies of the grafting were in the range 51-100%.

9.11 Discussion of results

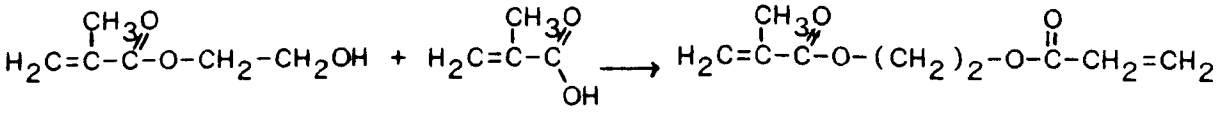
9.11.1 Investigations of possible crosslinking reactions during polymerisation of non-ionogenic hydrophilic monomers in presence of diesters

Commercial non-ionogenic hydrophilic monomers usually contains small quantity of impurities such as diesters. Details are given in Section 6.1.1.2. The presence of the diesters in the monomers are undesirable for the production of linear polymers, because the diesters could lead to branching and crosslinking reactions (132-138, 144). The diesters in the monomers are formed by side reactions during the preparation of the monomers. The most common method of preparing the monomers is the esterification of acrylic or methacrylic acid with a glycol such as ethylene glycol or propylene glycol. For example, HEMA is prepared by esterification of methacrylic acid (**a**) with ethylene glycol (**b**) to produce HEMA (**c**) (137, 138) :



(**a**) (**b**) (**c**) 9.1

At the same time, a side reaction occurs which yields a small quantity of ethylene glycol dimethacrylate (EDGMA) (**d**) :



(**c**) (**a**) (**d**) + H_2O

.....9.2

It has been reported that, if the monomer is to be used to produce linear polymers, the diester must be removed (137). Fort and Polyzoidis (137) stated that the best way of removing EDGMA is by a continuous liquid-liquid extraction method pioneered by Wichterle and Chromeck (136). However, this method is laborious and expensive. Furthermore, the method is not capable of removing all of the diester from the monomer. After purification, the diester was found to be present to extents of 0.04% to 0.3% (136, 137). Macret and Hild (138) developed an alternative method for removing

the diester from the monomers. They reported that preparative absorption chromatography on silica columns completely removed the diesters. However, this method is expensive, and is considered to be inefficient because of the low yield of monomer obtained. A classical distillation method was considered to be disadvantageous (144) because 1) the difference in boiling points between the monoesters and the corresponding diesters is small, and 2) a highly-crosslinked polymer might form in the column and distillation head, which would be difficult to remove. In addition, BP Chemicals (139-142) point out that the distillation of the monomers could lead to polymerisation. The inhibitor present in the monomers was also not removed. This is because distillation is not practical, and any attempt to remove it by washing with sodium hydroxide would result in dissolution and may also lead to partial conversion to the corresponding diester and glycol. In these circumstances, no attempt was made to purify the monomers, and they were used as received.

The diester present in the monomers might lead to the formation of a branched and crosslinked polymer. Wichterle (132) stated that the pendent vinyl group of the diester can either :

(i) form a crosslinked polymer by reaction with growing radicals of the monoester;

(ii) form a ring by reaction with its own growing radical; or

(iii) remain unreacted.

In this project, it was observed that polymerisation of HEA in aqueous solution, at pH ca. 5, caused by the slight acidity of the monomer itself, did not produce a crosslinked polymer (Table 9.1). Possible explanations of this are as follows:

(i) The diester, being insoluble in water, might not take part in the polymerisation of the HEA which is readily soluble in water.

(ii) The diester might not produce sufficient branching to bind the polymer molecules into an indefinitely large network.

However, HPA produced a crosslinked polymer when it was polymerised in water, but water-soluble PHPA was observed when it was polymerised in aqueous ammonia solution under comparable conditions to those used for HEA. The formation of crosslinked PHPA in water might be as a consequence of the acidic solution. The presence of ammonia would enhance the solubility of the monomer but not the diester impurities, and hence a comparable solubility of HPA to HEA would be obtained. Alternatively, the formation of branches to create an infinite network in the alkaline solution was less favourable than in the acidic solution. Both PHEA and PHPA are soluble in aqueous ammonia solution. Therefore it is believed that the homopolymers can be separated from NR after the monomers have been polymerised in NR latex.

Many workers have investigated the polymerisation of HEMA in water in the presence of EDGMA (133-138, 143). The HEMA can form as a crosslinked gel. There has been confusion as to whether the gel forms primarily as a consequence of crosslinking reactions or because PHEMA is insoluble in water, or both. This confusion was clarified by Duseck and Sedlacek (143). They observed that uncrosslinked PHEMA, even at low molecular mass of 1×10^4 to 2×10^4, is insoluble in water.

In this project, it was observed that PHEMA and PHPMA were insoluble when the corresponding monomers were polymerised in water, aqueous ammonia solution, serum, the mixture of water and non-polar solvents, and sodium hydroxide (Table 9.1). Further investigation of these polymers, prepared in water and sodium hydroxide, showed that they were insoluble in water, IMSA, THF, allyl alcohol, and a mixture of THF and IMSA. This strongly suggests that the polymerisation of HEMA and HPMA in these solutions produce crosslinked polymers. However, if the monomers are polymerised in water in the presence of either petroleum ether/toluene solution or petroleum ether/toluene containing NR (Appendix 20), the polymers were found to be soluble in IMSA. This indicates that the non-polar solvents absorbed the diesters during polymerisation. As a result, no crosslinked polymer was formed. It is reasonable to infer that, when polymerisations of these monomers are carried out in NR latex, the diesters are absorbed into the rubber particles, and hence removed from the polymerisation locus. Hence branching and crosslinking are minimised.

Further investigation showed that PHEMA and PHPMA were soluble if they were polymerised in IMS using ACA as initiator. These polymers, however, were insoluble when they were added to water, and soluble again when they were kept in IMSA overnight (Table 9.2). These results suggest that linear PHEMA and PHPMA are insoluble in water but soluble in IMSA. In these circumstances, IMSA was established as a solvent which was suitable for separating the homopolymers of the non-ionogenic hydrophilic monomers from the crude graft copolymers prepared in NR latex.

9.11.2 Separation of homopolymers of non-ionogenic hydrophilic monomers from NR latex using IMSA

Even though the homopolymers of the non-ionogenic monomers in NR latex were separable, it was not possible to extract the polymers directly from the latex using IMSA because, as expected, coagulation of the latex occurred. The extraction had to be carried out from wet film prepared by pressing the coagulum with a roller. The extraction of the polymers from the film using IMSA was time-dependent. It was found that PHEA and PHPA could be successfully extracted using IMSA solvent at $20\pm2^{o}C$ for 6 days. A known quantity of these polymers, added to NR latex, was recovered to extents greater than 99.5% (Table 9.3). These results also suggest that PHEA and PHPA do not hydrolyse either in aqueous ammonia (pH ca. 10) or in aqueous IMSA solution (pH ca. 2.5). If they were hydrolysed, some of the hydrolysis products would have been volatile under the drying conditions (0.16 mm Hg at $90^{o}C$ for 18 hours). However, the recovery of the polymers was approximately 99% (Tables 9.4 and 9.5). These results were confirmed by other results using the titration method as shown in Table 9.6. The titration technique showed that the extent of the hydrolysis of the polymers after allowing to stand in contact with the IMSA for 2 weeks at room temperature was negligible (Table 9.6). In addition, it was observed that the homopolymers of the non-ionogenic hydrophilic monomers did not dissolve in a mixture of petroleum-ether/toluene solvents (Table 9.7). This confirms that the use of these solvents to separate free NR from the crude graft copolymers did not not dissolve the homopolymers of the non-ionogenic hydrophilic monomers.

9.11.3 Separation of free NR from the crude graft copolymers

There is much published literature describing methods which have been established for separating the free polyisoprene from the crude graft copolymers when graft copolymerisations have been carried out using NR (124-127) (Section 5.4.2).

Basically, the methods use non-polar solvents or mixtures of non-polar solvents such as petroleum ether (60-80°), or mixtures of petroleum ether and benzene. The temperature of separation was at room temperature, with the exception of the method of of Allen and Merret (124). These workers heated the samples to 40°C for half an hour prior to separating the polymers. The time of the separation ranged from overnight to two weeks. However, these separation times might be too short to dissolve NR film.

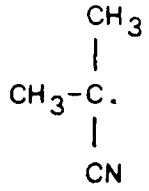
It was observed in this project that NR film when mixed with a petroleum ether (60-80°C)/toluene solvent mixture (0.35% w/w) NR in solvent) did not dissolve even after 105 days at 20°C. The NR film (0.5% w/w), however, did dissolve in a mixture of petroleum ether (80-100°)/toluene at 40°C after 39-55 days (Table 9.9). This method was used to separate the free NR from the crude graft copolymers. The NR films did not dissolve in IMSA at 20°C over a period of 105 days nor, at 40°C over 26 days (Table 9.8). This demonstrated that the use of IMSA to separate the non-ionogenic hydrophilic polymers from the crude graft copolymer would not dissolve any free NR present in the crude samples.

Unfortunately, the separation of free NR from the crude graft copolymer prepared in NR latex was unsuccessful. It was observed that, after separation of the unreacted monomers and the homopolymers using IMSA, the graft copolymers collapsed and formed pastes when they were added to the mixture of petroleum ether/toluene (1:1 by volume) and kept for 2 months. The pastes proved very difficult to separate from the free NR solution by means of filtration techniques. Therefore, the samples prepared to separate the free NR from the crude graft copolymers were abandoned. Thus the efficiency of grafting can only be reported in terms of the reaction of the polymerised monomers in NR latex. It is probable that only a very small amount of grafting is necessary to cause the NR to become insoluble.

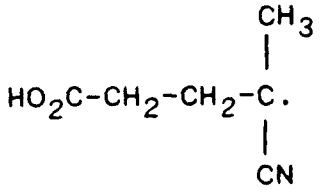
An alternative possibility is that virtually all the rubber molecules were sufficiently grafted to become insoluble in (though highly swollen by) the non-polar solvent.

9.11.4 Mechanism of grafting reactions

Allen et al. (152) reported that heating AZBN with Gutta-percha in benzene solution at 60°C leads to negligible combination of radicals from AZBN,



with the polyisoprene, that is to say, the radicals from AZBN do not attack the polyisoprene directly. Being similar to AZBN in structure, the radicals from ACA,



would be expected not to attack the NR molecule directly. Hence the ACA could be used to investigate the mechanism of grafting reactions of the non-ionogenic hydrophilic monomers to NR in NR latex. It could be argued that, if graft copolymers were obtained using this initiator, then the grafting reactions should be via either transfer reactions or addition reactions involving the NR in NR latex. It was found that graft copolymers were formed using this initiator at ca. 63°C, the efficiencies of grafting being ca. 86% for HEA, ca. 51% for HPA, ca. 65% for HEMA, and ca. 100% for HPMA (Table 9.10). This strongly suggests that transfer reactions are the dominant process by which the graft copolymers are formed in the case of HEA, HPA and HEMA. It is evidence that the transfer reactions were highly unlikely to occur in the case of HPMA because no homopolymer (PHPMA) was produced as indicated by the grafting efficiency of 100%. A possible mechanism of the grafting reactions of HPMA to NR using ACA at ca. 63°C might be via addition reactions between the growing polymer radicals and the double bond of the rubber molecules. This addition reaction mechanism would permit the possibility of

a grafting efficiency of 100%. However, if the redox initiator was used at 30°C, PHPMA was formed indicating that the transfer reactions of HPMA to NR was also occurred. This will be discussed in more details in [Section 10.15.4(i)]. Thus it is reasonable to suppose that the mechanism by which the graft copolymers form is as follows:

initiation:

$$I. \xrightarrow{k_d} 2\ R. \qquad \text{.....9.3}$$

$$R. + M \xrightarrow{k_i} RM_1. \qquad \text{.....9.4}$$

propagation:

$$RM_1. + n\ M \xrightarrow{k_p} R[M]_{n+1}. \qquad \text{.....9.5}$$

transfer (HEA, HPA and HEMA):

$$R[M]_{n+1} + -CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2- \longrightarrow -\overset{\displaystyle \cdot}{C}H-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2 + R[M]_{n+1}H \quad \text{..9.6}$$

or

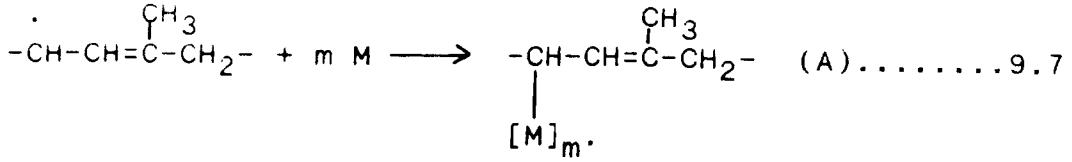
$$-CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-\overset{\displaystyle \cdot}{C}H-$$

In addition, rearrangement of the rubber radicals could take place before a further monomer addition;

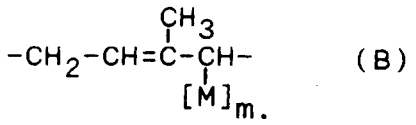
$$-\overset{\displaystyle \cdot}{C}H-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2- \rightleftharpoons -CH=CH-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle \cdot}{C}}}-CH_2-$$

grafting:

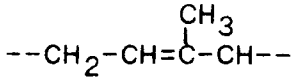
a. in case of HEA, HPA and HEMA:



or

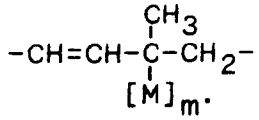


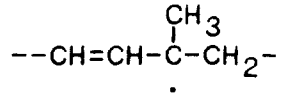
This reaction is an analogous reaction from



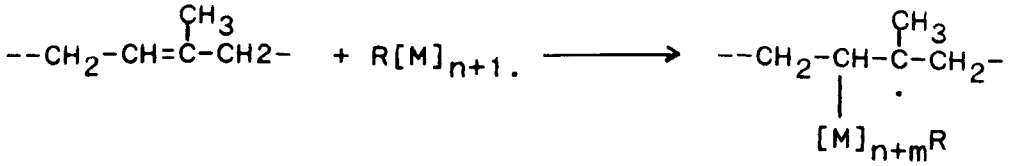
and not by rearrangement of (A)

In addition,

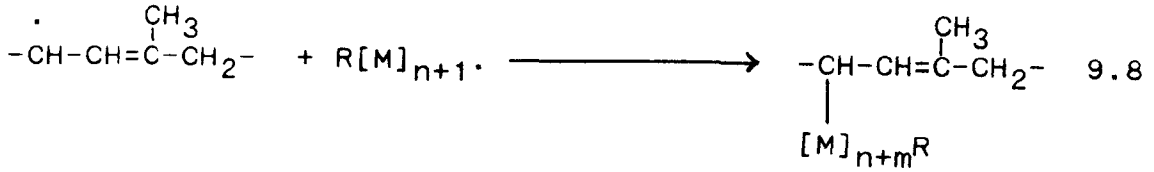


could be formed from 

b. in case of HPMA:

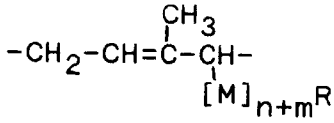


termination:

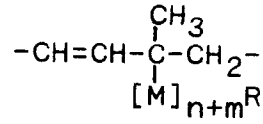


9.8

or



In addition,



could be formed from 

From table 9.10, it can be seen that the grafting efficiency for HEA is much higher than that of HPA under comparable conditions. This suggests that the formation of rubber radicals by hydrogen abstraction from the rubber molecules is faster for HEA than that for HPA. Therefore, in the presence of HEA more rubber radicals are formed. Consequently, there is more grafting with HEA than HPA. In the case of hydroxyalkyl methacrylates, it was expected that the grafting efficiency for HPMA would be higher than that of HEMA because the locus of reaction for HPMA is not only at the surface but also in the rubber phase. These conclusions are contrary to those reported by Popham et al.(57) and by Burfield and Ng who claimed that such transfer reactions did not occur (64). It is difficult to compare the present results with the results of the above authors for at least two reasons:

(i) the initiator used (ACA) was different from the that used by Popham et al., by and Burfield and Ng, who used AZBN and potassium persulphate respectively. The ACA is a water-soluble organic initiator which does not attack NR directly. AZBN is an oil-soluble organic initiator which also does not attack NR directly. However, AZBN could be absorbed into either the rubber phase or a

hydrophobic monomer. Potassium persulphate can attack NR directly. In this case, rubber radicals might be formed and attack the monomer to produce a graft copolymer prior to the transfer reactions occurring.

(ii) The method used to investigate these reactions in the present work is quite different from those used by the previous authors. Burfield and NG determined the intrinstic viscosity of the homopolymer separated from the graft copolymer, and compared the values they obtained with those for polymers produced by homopolymerisation to predict the extent of transfer reactions. They found the difference in intrinstic viscosity was negligible, and concluded that such transfer reactions did not occur. Popham et al. used a fractional precipitation titration technique, to precipitate free PMMA from a graft copolymer. The present work used an extraction technique, and the efficiency of this technique for extracting the homopolymers was established (Section 9.11.2).

Table 9.1 Observations concerning solubility of homopolymers of non-ionogenic hydrophilic monomers polymerised under various conditions[x)]

monomer	concentration (%w/w)	initiator	level (pphm)	medium	observation concerning homopolymers
HEA	7.01	redox	0.99	water	soluble
HEA	6.99	redox	0.99	1.5 % NH_4OH[a)]	soluble
HEA	7.03	ACA	0.98	0.06 % NaOH[a)]	gel
HEA	7.03	ACA	1.01	IMS	soluble
HPA	7.02	redox	0.99	water	precipitated
HPA	7.01	redox	0.99	1.5 % NH_4OH[a)]	soluble
HPA	7.08	ACA	0.97	0.06 % NaOH[a)]	precipitated
HPA	7.07	ACA	1.03	IMS	soluble
HEMA	7.01	redox	0.98	water	precipitated
HEMA	7.00	redox	0.99	1.5 % NH_4OH[a)]	precipitated
HEMA	7.02	redox	1.41	serum	precipitated
HEMA	7.04	redox	4.22[b)]	water + NR[c)]	precipitated
HEMA	7.04	redox	4.22[b)]	water + PE/T[d)]	precipitated
HEMA	7.03	ACA	0.98	0.06 % NaOH[a)]	precipitated
HEMA	8.85	ACA	0.80	1.5 % NH_4OH[a)]	gel
HEMA	7.15	ACA	0.99	IMS	soluble
HPMA	7.01	redox	0.98	water	precipitated
HPMA	7.04	redox	0.99	1.5 % NH_4OH[a)]	precipitated
HPMA	7.03	redox	1.41	serum	precipitated
HPMA	7.04	redox	4.22[b)]	water + NR[c)]	precipitated
HPMA	7.04	redox	4.22[b)]	water + PE/T[d)]	precipitated
HPMA	7.04	ACA	0.98	0.06 % NaOH[a)]	precipitated
HPMA	8.85	ACA	0.80	1.5 % NH_4OH[a)]	precipitated
HPMA	7.18	ACA	0.98	IMS	soluble

x) polymerisation conditions: a) ACA as initiator; temperature at ca. 60°C for ca. 17 hours, and b) redox initiator; temperature at 25°C for ca. 17 hours, unless otherwise stated,

a) aqueous solution ; b) equivalent to 1.43 pphh (parts by weight of monomer per hundred parts by weight of hydrocarbon; c) in petroleum ether/toluene solution; d) toluene

Table 9.2 Observation concerning solubility of PHEMA and PHPMA in various solvents

concentration of either PHEMA or PHPMA (%w/w)	solvent	temperature	time (days)	polymerisation system		observation
				initiator	medium	
0.49-0.63	water	40	23	redox	water	swelling
0.52-0.54	IMSA	40	18	redox	water	swelling
0.53	THF	40	18	redox	water	swelling
0.54	allyl alcohol	40	18	redox	water	swelling
0.54	THF+ IMSA	40	18	redox	water	swelling
0.50-0.51	water	40	23	ACA	NaOH[a)]	swelling
0.48-0.54	IMSA	40	18	ACA	NaOH[a)]	swelling
0.48-0.56	water	40	10	ACA	IMS	swelling[b)]
0.50-0.52	IMSA	40	1	ACA	IMS	soluble
1.23-2.30	IMSA	20	1	redox	water+ NR[c)]	soluble
1.64-2.30	IMSA	20	1	redox	water+ PE/T[d)]	soluble

a) aqueous solution
b) after drying in an oven (100°C) overnight, and then the vacuum oven (0.16 mm H_g at 90°C for 3.5 hours), the polymers (1 % w/w) in IMSA were soluble at 40°C overnight
c) in petroleum ether-toluene solution
d) a mixture of petroleum ether (80-100°C) and toluene (1:1 by volume)

Table 9.3 Recovery of homopolymers of non-ionogenic hydrophilic monomers which had been matured for 6 days at 20°C in NR latex

polymer	added polymer (pphr)	recovery (% w/w)
PHEA	35.95	99.51
PHPA	30.22	99.70

Table 9.4 Recovery of homopolymers of non-ionogenic hydrophilic monomers which had been allowed to stand in contact with ammonia solution (pH ca. 10) for 3 weeks at 20°C

polymer	recovery (% w/w)
PHEA	99.64
PHPA	99.04
PHEMA	99.71
PHPMA	99.12

Table 9.5 Recovery of homopolymers of non-ionogenic hydrophilic monomers which had been allowed to stand on contact with IMSA (pH ca. 2.5) for 3 weeks at 20°C

polymer	recovery (% w/w)
PHEA	99.64
PHPA	99.04
PHEMA	99.12
PHPMA	98.12

Table 9.6 Extent of hydrolysis of homopolymers of non-ionogenic hydrophilic monomers which had been allowed to stand in contact with IMSA for 2 weeks at 20°C using titration technique

polymer	extent of hydrolysis (% w/w)
PHEA	3.48
PHPA	2.80
PHEMA	2.60
PHPMA	1.54

Table 9.7 Recovery of homopolymers of non-ionogenic hydrophilic monomers from a non-polar solvent

polymer	concentration (% w/w)	solvent	maturation		recovery (% w/w)
			temperature (^{o}C)	time (days)	
PHEA	0.50	PE/T[x)]	40	66	98.0
PHPA	0.52	PE/T[x)]	40	66	98.1
PHEMA	0.52	PE/T[x)]	40	66	96.2
PHPMA	0.57	PE/T[x)]	40	66	98.3

x) a mixture of petroleum ether (80-100^{o}C) and toluene (1:1 by volume)

Table 9.8 Recovery of NR film from a polar solvent

NR film	concentration (% w/w)	solvent	maturation (days)		recovery (% w/w)
			20^{o}C	40^{o}C	
F	2.85	IMSA	105	-	99.26
G	0.53	IMSA	-	26	98.04

Table 9.9 Solubility of NR film in a non-polar solvent

NR film[x)]	concentration (% w/w)	solvent	maturation (days)		observation
			20°C	40°C	
A	0.99	PE/T[y)]	-	63	soluble
B	0.49	PE/T[y)]	-	55	soluble
C	0.35	PE/T[yy)]	105	-	swelling
D	0.52	PE/T[y)]	-	54	soluble
E	0.50	PE/T[y)]	-	39	soluble

x) The NR films (A and B) were prepared by drying the cast films at 20°C for 6-10 days and then in the vacuum oven at 30-50°C for 30 minutes prior to addition to the solvent. The NR films (C,D and E) were prepared similar to those of A and B but no vacuum drying.

y) A mixture of petroleum ether (80-100°C) and toluene (1:1 by volume).

yy) Similar to y) but petroleum ether (60-80°C).

Table 9.10 Conversion and efficiency of grafting of non-ionogenic hydrophilic monomers polymerised at 62-65°C in NR latex containing sodium lauryl sulphate (SLS) (2 pphr) using ACA as an initiator

monomer	initial monomer level (pphr)	conversion (% w/w)[x]	homopolymer (% w/w)[x)]	efficiency of grafting (%w/w)
HEA	20.19	51.9	14.6	85.4
HPA	20.35	51.5	48.3	50.8
HEMA	10.21	44.4	35.1	64.9
HPMA	11.17	51.4	0.0	100.0

x) based upon the total mass of monomer polymerised

Chapter 10

Preparation of modified NR latices and investigation of selected properties of products

10.1 Introduction

This chapter describes various aspects of the preparation of graft copolymer latices, and the investigation of selected physical properties of the products. The matters investigated include:

(i) the effect ammonia upon the hydrolysis of the monomers;
(ii) the effect of added homopolymers upon creaming of NR latex, and the creaming of the crude graft copolymer latices;
(iii) the effect sodium lauryl sulphate (SLS) upon the mechanical stability of NR latex;
(iv) the effect of pH upon the creaming of NR latex;
(v) the effect of dry rubber content (DRC) upon conversion and efficiency of grafting;
(vi) the effect of activation of NR latex upon conversion and efficiency of grafting;
(vii) the mechanical stability time (MST) of the modified NR latex;
(viii) the dipping behaviour of the modified NR latex;
(ix) the tensile stress-strain properties of films from the modified NR latex;
(x) the resistance of films from the modified NR latices to various solvents.

The results are summarised in Sections 10.2 to 10.14, and then discussed in Section 10.15. Two initiator systems were used throughout this work, i.e., a redox system at 30^{o}C, and ACA at ca. 63^{o}C. The redox system was used for the investigation of the MST of NR latex, kinetic studies, characterisation of the products and preparation of the graft copolymers. The ACA was used later as initiator for investigation of the mechanisms of grafting reaction, and preparation of the graft copolymers. The ACA at 65^{o}C produced substantial grafting, whereas the redox initiator system was later found to produce little grafting unless a high initiator concentration was used. The possible explanations for this are discussed in Sections 10.15.4, and 10.15.5. The selected physical properties of the crude graft copolymer latices using both initiators were subsequently investigated.

10.2 Effect of ammonia solution upon hydrolysis of non-ionogenic hydrophilic monomers

The monomers (16% w/w) were kept in a 2% ammonia solution at 30°C. As shown in Figure 10.1, the pH of the ammonia solutions at 30°C solution fall, and this was taken as evidence that hydrolysis of the monomers was occurring. The ease with which the monomers underwent hydrolysis was in the following order: HEA > HPA >>> HEMA > HPMA.

10.3 Effect of added homopolymers of non-ionogenic hydrophilic monomers upon creaming of NR latex

The results are shown in Table 10.1. Excessive amounts (10-50 pphr) of added polymers (PHEA and PHPA) to NR latex produced cream. The effectiveness of the polymers in enhancing the creaming process is in the following order: PHPA > PHEA. PHEMA and PHPMA are not soluble in NR latex.

10.4 Creaming of crude graft copolymer latices

The results in Table 10.2 show that extensive creaming occurred in the crude graft copolymer latices prepared by polymerising HEMA and HPMA monomers in NR latex and stored for 4 months. Little creaming was observed in crude NR/PHEA and NR/PHPA graft-copolymer latices under comparable conditions. The graft copolymer latices investigated were prepared using ACA initiator.

10.5 Maximum amount of non-ionogenic hydrophilic monomers that can be polymerised in NR latex (25% DRC)

The results are shown in Tables 10.3, 10.4, 10.5, 10.6. and 10.7. Maximum amounts of the monomers that could be polymerised in NR latex (25% DRC reaction mixture) in a 2-l reaction vessels in the presence of SLS (3.66 pphr) were found to be as follows:

HEA : 50 pphr
HPA : 50 pphr
HEMA : 20 pphr
HPMA : 20 pphr

Exceeding these monomer contents caused flocculation or coagulation.

10.6 Effect of pH upon creaming of modified NR latex

The results are shown in Table 10.8. It was observed that PHEA and PHPA are more active as creaming agents at high pH (ca. 10) than at low pH (ca. 6).

10.7 Effect of dry rubber content (DRC) upon conversion and efficiency of grafting of non-ionogenic hydrophilic monomers in NR latex

The results are shown in Table 10.9. It was observed that, by keeping the monomer concentration (0.5 mol/l latex) and redox initiator (5.1×10^{-3} mol/l latex) constant but increasing the DRC from 15% to 35%, the following changes occurred:

the conversion of HEA increased from 55 to 88%
the conversion of HPA increased from 45 to 80%
HEMA coagulated during polymerisation
HPMA produced viscous/gel products

The grafting efficiency for HEA and HPA was found to be negligible.

10.8 Effect of activation upon conversion and efficiency of grafting of non-ionogenic hydrophilic monomers in NR latex

The results are shown in Table 10.7. At low concentrations of redox initiator (0.54 pphr), the longer the activation time, i.e., the time the potassium persulphate was added prior to the sodium metabisulphite and monomer (Section 6.4), the lower was the conversion of HEA and HPA. Similar results were observed for HEMA and HPMA. When the redox initiator concentration was increased, the conversion and efficiency of grafting also increased. Thus at low redox initiator concentrations, activation failed to increase either the conversions or the grafting efficiency. Thus, in effect, deactivation occurred.

10.9 Mechanical stability time (MST) of modified NR latex

As indicated in Table 10.10, it was observed that, when the NR latex and modified NR latex were diluted (25% DRC), excessive foaming occurred when the latex was subjected to the MST test. For this reason, no MST values of the modified latices are recorded.

10.10 Effect of added coagulants upon stability of modified NR latices

As shown in Table 10.11, the coagulants (acetic acid, IMS, acetone, potassium chloride, calcium chloride, barium chloride and ferric chloride) destabilised the modified NR latices.

10.11 Vulcanisation behaviour

(i) In presence of SLS

The results are shown in Figures 10.2, 10.3, and 10.4. SLS appears to act as plasticiser, retarder and an anti-reversion agent during the sulphur-vulcanisation of NR film using CBS/TMTD accelerator system at 140^{o}C. Further investigation of the use of various accelerator systems, i.e., CBS/TMTD and ZDC at low temperature (100^{o}C) showed that the induction period of vulcanisation using ZDC was shorter (ca. 15 minutes) than when using CBS/TMTD. However, after 1.5 hours, both accelerators showed comparable increases in torque.

(ii) In presence of added PHEA and PHPA, and crude NR/PHEMA and NR/PHPMA grafts

The results are shown in Figures 10.2, 10.3, 10.5, 10.6 and 10.7. The Monsanto Rheometer 100 showed that the polymers act as plasticiser, retarders and inhibitor for the sulphur-vulcanisation of NR. Dicumyl peroxide also failed to vulcanise films from the modified NR latices. However, it was possible to vulcanise the crude NR/PHEMA graft-copolymer latex and crude NR/PHPMA graft-copolymer latex.

10.12 Tensile stress-strain properties of modified NR films

The results of the tensile stress-strain properties on both vulcanised and unvulcanised from modified NR films are shown in Tables 10.12A and 10.12B.

(i) In presence of SLS

The results are shown in Table 10.12A. The SLS increased the tensile strength, and elongation at break of films cast from NR latex. However, the SLS reduced the modulus of the vulcanised film.

(ii) **Modified NR film prepared using redox initiator**

The results are shown in Table 10.12A. It was observed that no graft copolymers were formed using HEA as monomer at 30°C (35-61% conversion). The higher was the concentration of the monomer, the lower was the tensile strength of vulcanised films. There was a tendency for the elongation at break to increase as the initial monomer concentration increased. Similar results were observed for crude NR/PHPA graft-copolymers. In the case of the crude NR/HEMA graft-copolymers and the crude NR/HPMA graft-copolymers, the tensile strengths of the products were greater than those of the control NR films. In all cases, the tensile strengths of the vulcanised films of the products were much higher than those of unvulcanised films.

(iii) **Crude graft copolymers prepared using ACA as an initiator**

The results are shown in Table 10.12B. The tensile strengths of the crude NR/PHEA graft-copolymer and the crude NR/PHPA graft-copolymer were lower than those of control NR films. However, the elongation at break increased substantially compared to that of the control NR films. In the case of crude NR/PHEMA graft-copolymer and crude NR/PHPMA graft-copolymer, their tensile strengths were much greater than those of films from the control latices, whereas the elongation at break were similar to those of films from the control NR films containing SLS (3.66 pphr).

10.13 Solvent resistance of modified NR films

(i) Effect of added PHEA and PHPA to NR

Table 10.13 shows the oil uptake of NR, and blends of PHEA and PHPA to NR. At low concentrations of added PHEA and PHPA (10 pphr), the resistances to solvent of the vulcanised blends was found to be slightly less than those of the control NR films, absorbing 1-14 % more solvent. The higher was the concentration of PHEA and PHPA, the better was the solvent resistance of the unvulcanised blends, but the poorer was the solvent resistance of the vulcanised blends.

(ii) Modified NR prepared using the redox initiator

The results are shown in Figure 10.14A. In the case of the crude NR/HEA graft-copolymers, where no grafting occurred, the vulcanised films showed that the higher was the initial monomer concentrations, the lower was the resistance to solvent, but the greater was the water absorption. However, the unvulcanised films show that the higher was the initial monomer concentrations, the more resistant to solvent and to water. Similar results were observed for the crude NR/PHPA graft-copolymers.

In the case of the vulcanised films from the crude NR/PHEMA graft-copolymers and the crude NR/PHPMA graft-copolymers, the products were more resistant to solvent than those of the control NR. Generally, these products show worse resistance to water than those of the control films. The unvulcanised films from the crude NR/PHEMA graft-copolymers were slightly more resistant to solvent, but less resistant to water than that of the control NR films. However, the unvulcanised films from the crude NR/PHPMA graft-copolymers were slightly more resistance to solvent, but similar or less resistant to water.

(iii) **Crude graft copolymers prepared using ACA as an initiator**

The results are shown in Figure 10.14B. The crude NR/PHEA and NR/PHPA graft-copolymers were much less resistant to solvent than were the control NR films. However, the crude products absorbed more water (4 to 6 times as much) than did those from the control NR films. The crude NR/PHEMA and NR/PHPMA graft-copolymers were slightly less resistant to solvent than were those of the control NR films.

10.14 Dipping behaviour of modified NR latices

As shown in Table 10.15, the modified NR latices were found to be unsuitable for dipping applications, with the exception of the crude NR/PHPMA graft-copolymer latex prepared using ACA as initiator.

10.15 Discussion of results

10.15.1 Hydrolysis of non-ionogenic hydrophilic monomers in aqueous ammonia solution

It was found that the four monomers hydrolysed in a 2% aqueous ammonia solution (pH ca. 10) at 30^{o}C. The hydroxyalkyl acrylates (HEA and HPA) hydrolysed much faster than did the hydroxyalkyl methacrylates (HEMA and HPMA). The susceptibility of the monomers to alkaline hydrolysis was in the following order: HEA > HPA >> HEMA > HPMA (Figure 10.1). The hydrolysis of the monomers produced acids and alcohols. The pH of the solutions after 23 hours decreased to 5.3, 6.5, 8.7 and 8.9 for HEA, HPA, HEMA and HPMA respectively. As mentioned in Section 7.11.2, the hydrolysis of the monomers decreased the MST of NR latex. It is not unexpected that the ester monomers undergo hydrolysis under alkaline conditions.

10.15.2 Creaming of NR latex

(i) **Effect of added homopolymers of non-ionogenic hydrophilic monomers**

A homopolymer of a hydrophilic monomer bearing hydroxyl groups would be expected to be an effective creaming agent. Possible mechanisms

for the creaming process are given in Section 3.2.5. It was found that PHEA and PHPA at large quantities act as creaming agents for NR latex. In this project, experiments using large quantities of added homopolymers were carried out in order to match the amounts of the monomers polymerised in NR latex. It was of interest to investigate the extent of creaming that occurs when large quantities of these monomers were polymerised in NR latex. The The effectiveness of the polymers as creaming agents is in the following order: HPA > PHEA. A concentration of (30 pphr) proved to be the optimum for creaming, giving a serum layer 15% (v/v) for PHEA and 53% (v/v) for PHPA. Beyond 30 pphr, the PHEA did not increase the serum layer of NR latex. In the case of PHPA (50 pphr), the serum layer was reduced to 34% (v/v) (Table 10.1). This is attributed to too high configurational stability of the aggregates. Consequently, the individual particles were less able to arrange themselves readily into a close-packed configuration.

(ii) Creaming of crude graft copolymer latices

For the purpose of this investigation, crude graft copolymers were prepared by polymerising the monomers in NR latices. The serum layers obtained from the crude graft copolymer latices were 52% v/v for crude NR/PHEMA graft-copolymer latex, and 40% v/v for crude NR/PHPMA graft-copolymer latex. These results conflict with the previous views of the present author. It was thought that the graft copolymers themselves would enhance latex stability. However, the polymers appeared to destabilise the latex in the sense that the modified NR latices were not macroscopically homogeneously stable. It is not clear how such a creaming process occurs. However, it might be attributed to the insolubility of the polymer units bound to the NR. The crude NR/PHEA graft-copolymer latex and the crude NR/PHPA graft-copolymer latex produced only small serum layers (5% in each case. The grafts themselves were unlikely to

produce the serum layers. This is because the water-soluble polymers bound to NR would be expected to self-stabilise the latex. However, such polymers could also bridge the particles, and this might be the reason for the creaming.

10.15.3 Investigation of maximum amounts of monomers which can be polymerised in NR latex

(i) Polymerisation of HEA and HPA

It was observed that the monomers (ca. 40 pphr), in the absence of SLS, coagulated the latex Tables 10.3 and 10.4). A possible explanation of this is given in Section 7.11.2. To increase the quantity of the monomers which could be mixed into the latex, attempts were made to stabilise the latex by adding SLS (1-6 pphr). It was observed that, with small quantities of samples (75.0 g) in jars, the monomers could be polymerised up to 50 pphr in the presence of 2 pphr of SLS, and up to 75 pphr in the presence of 3 pphr of SLS. Further addition of the monomers up to 100 pphr, even in the presence of 6 pphr of SLS, caused the latex to coagulate (Tables 10.3 and 10.4). The pH values of the latices containing HEA (75 pphr) and HPA (75 pphr) after polymerisation were 5.95 and 6.48 respectively. The stability of the products under acidic condition was attributed to the presence of the SLS. This soap is much less sensitive to acids than are the carboxylates (1). An explanation for this is that the sulphate ionises at a low pH and consequently it is able to stabilise the latex colloidally. However, the carboxylates do not ionise at a low pH, and they are no longer able to act as stabiliser at low pH.

In the case of HEA and HPA (ca. 50 pphr respectively), the products produced serum layers of 0 and 14% v/v respectively after 34 days maturation (Table 10.8). Attempts were made to avoid such separation by adding 35% aqueous ammonia solution to raise the pH from ca. 6 to ca. 10. Such treatment, however, only increased

the serum layer to 29% v/v for HEA and 43% v/v for HPA (Table 10.8). This suggested that the homopolymers were more active as creaming agents at higher pH than at lower pH.

It was observed that, if the monomers (75 pphr) in the presence of SLS (3 pphr) were polymerised in larger quantities (1.5 kg) in a 2-l reaction vessel with constant mechanical stirring, the latex coagulated. The maximum amounts of the monomers that could be polymerised in NR latex under such conditions were 30 pphr for HEA and 50 pphr for HPA. A possible explanation of this is as follows: To keep the reaction mixtures homogeneous, the stirring applied was more rapid for large quantity than for small quantities of reactants. Thus, the average kinetic energy of rubber particles become greater for the larger quantities than for the smaller quantities. This kinetic energy could overcome the repulsive forces between charged particles bringing about coagulation. Therefore, the amount of monomer that could be added and still keep the latex stable is less for large reaction mixtures than for a small reaction mixtures.

Another interesting aspect of the polymerisation of HEA and HPA in larger quantities (1.5 kg) is that these monomers could be polymerised at up to 50 pphr of added monomers provided that the latex was activated prior to addition of the monomers. The activation was carried out by adding the redox initiator 75 minutes prior to the monomers (Table 10.7). It was thought that this treatment would provide the most favourable conditions for polymerisation of the monomers. The activation process may increase the rate of polymerisation, thus polymerising the monomers more quickly to a form in which they do not destabilise the latex so drastically.

(ii) Polymerisation of HEMA and HPMA

Coagulation occurred during the polymerisation of HEMA and HPMA at levels greater than 20 pphr, even in the presence of SLS (3-4 pphr) (Tables 10.5 and 10.6). An explanation for this is

given in Section 7.11, where HEMA and HPMA were found to be more effective in destabilising the latex than were HEA and HPA. It is thought that reduction in the dielectric constant of the dispersion medium was unlikely to be the cause of the coagulation, as was previously suggested by the present author (6). Calculations for $1/\kappa$ in the presence of these monomers (30 to 60 pphr) showed that the value of $1/\kappa$ decreased slightly, approximately between 3.1 to 6.3%.

10.15.4 Effect of dry rubber content (DRC) upon conversion and efficiency of grafting in absence of SLS

(i) **HEA and HPA**

Keeping the concentration of the monomers (0.5 mol/l latex) and redox initiator (5×10^{-3} mol/l latex) constant in the absence of SLS, and increasing the DRC from 15 to 35%, the conversion increased from 55.0 to 88.3% for HEA and from 45.5 to 80.0% for HPA (Table 10.9). No grafting occurred except in the case of HEA (only 3.4% grafting efficiency) at 35% DRC. These results were unexpected because:

a) The initial polymerisation is believed to be predominantly at the surface of rubber particles. As mentioned in Section 7.11.2, the large increase in MST brought about by the presence of the monomers indicates that the monomers are adsorbed onto the surface of rubber particles. Thus, the growing radicals would attack the rubber molecules easily.

b) The redox initiator is a powerful oxidising agent. Thus the initiator would attack rubber molecule to produce rubber radicals, which would subsequently react with the monomers to produce graft copolymers.

However, the characterisation of the products showed that no grafting actually occurred. Possible explanations of this are as follows: At high dry rubber content, one would expect

monomer molecules to congregate at the surface of the rubber particles and polymerisation to predominate there. However, at low polymerisation temperature (30°C), the rubber molecules may not have sufficient energy to overcome the energy barrier for reaction with the growing polymer radicals. Alternatively, the activation energy for the transfer reactions between the growing polymer radicals and rubber molecules might be higher than the activation energy for the homopolymerisation. Thus the reactivity of the monomer towards the growing radicals at a comparatively low temperature (30°C) is greater than the reactivity of the rubber molecules towards the growing radicals. Flory (101) lists a table of transfer constants for various solvents with styrene, comparing the effect of increasing temperature. In each case, the transfer constant is higher at the higher temperature than at the lower temperature, indicating that the rate of transfer reaction relative to homopolymerisation is temperature-dependent. In this case, it is believed that at 30°C the rate of the transfer reactions of the growing radicals to NR was virtually zero as a consequence of the high activation energy of the transfer reactions. At a higher temperature (ca. 63°C), the rate of transfer became significant and grafting occurred (Section 9.11.4). It should be noted that different initiator systems were used at different temperatures, namely, the redox system at 30°C, which was expected to attack NR molecules directly, and ACA at ca. 63°C which does not attack NR molecule directly. In these circumstances, the difference in grafting is believed to be due to the temperature difference rather than to inherent initiator effects. Both systems achieved a reasonable conversion of monomer to polymer.

(ii) HEMA and HPMA

Unfortunately, HEMA coagulated the latex in all cases. HPMA could be polymerised to 15% DRC but the products were extremely viscous, even at low conversion, and no grafting occurred

(Table 10.5). The explanation of the coagulation brought about by the monomers and initiator is given in Sections 7.11.2 and 7.11.3.

10.15.5 Effect of activation upon conversion and efficiency of grafting

(i) HEA and HPA

The polymerisation of HEA (30 to 50 pphr) in NR latex (25% DRC of reaction mixture) using a redox initiator (0.55 pphr) at 30^{o}C produced no graft copolymer even though the latex was activated by prior addition of the redox initiator and allowing the mixture to stand for 75 minutes before adding the monomer (Table 10.7). There is a tendency that, at low concentration of the redox initiator (0.54 pphr), the longer was the activation time, the lower was the conversion (Table 10.7). This implies that, the deactivation was occurring rather than activation. This might be due to decomposition of the initiator during the activation period, leading to a lower concentration of the initiator during the polymerisation, thereby reducing the conversion. In the case of HPA, grafting (17.6%) occurred when no activation was carried out. However, no grafting occurred when a period of activation was allowed before the monomers was added. This also might be a consequence of the decomposition of the initiator. The conversion of monomer to polymer decreased from 70 to 40% when an activation time of 75 minutes was used. One might expect a corresponding decrease in transfer under these conditions, but not the complete absence of the transfer which was observed. However, it is concluded that the redox initiator radicals at low concentrations did not attack the rubber particles directly, because, if such attack had occurred, the activation time would have led to a build-up of rubber radicals at the surface, facilitating the grafting reactions when the monomers were subsequently added to the activated latices.

(ii) HEMA and HPMA

The polymerisation of HEMA (ca. 11 pphr) using the redox initiator (0.54 pphr) without activation gave 33% conversion with a 50% grafting efficiency. This was contrary to the results obtained for HEA and HPA (0% grafting efficiency). A possible explanation of this is as follows: The activation energy for transfer reactions for the methacrylate radicals and rubber molecules is lower than for the acrylates and rubber molecules, and thus the grafting efficiencies of the methacrylates are less sensitive to temperature than are those of acrylates. In this circumstance, the grafting reactions at low temperature would be more favourable for the methacrylates than for the acrylates.

When activation was carried out, the conversion of the monomer decreased to 25% with zero grafting. This was similar to the results obtained with HEA and HPA. However, further addition of the redox initiator (1.63 pphr), increased the conversion to 43.13% with 5.5% grafting. A further increase in initiator concentration (2.07 pphr) resulted in little change in the conversion (44.73%) but an increased in the grafting efficiency (23.10%). These observations suggest that the activation procedure could increase the grafting efficiency, providing that the initiator concentration was higher than 2 pphr. The efficiency of grafting at 10 pphr without activation was higher in the case of HPMA (6.3%) than in the case of HEMA (50.0%). This suggests that the activation energy for transfer reactions for the growing polymer radicals of PHEMA and rubber molecules is lower than for the polymer radicals of PHPMA and rubber molecules. Thus the grafting efficiencies of the polymer radicals of PHEMA are less sensitive to temperature than those of PHPMA. A further increase in monomer concentration (15 pphr), the conversion was increased but the grafting efficiency decreased. Finally, the latex coagulated when the monomers were increased to

28 pphr for HEMA and to 20 pphr for HPMA.

10.15.6 Investigation of colloid stability of modified NR latices

(i) Mechanical stability time of modified NR latices

The DRCs of the modified NR latices being low (25% DRC), the Klaxon apparatus failed to measure the MST because of the excessive foaming which occurred during the test (Table 10.9). Such a diluted latex would be expected to be very stable (Section 3.2.1). It was also observed that the control latex containing SLS (2-3.66 pphr) produced excessive foaming in the early stages of the test. Similar results were observed for the crude graft copolymer latices and for other modified NR latices (Table 10.10). It was reasonable that the modified latices would have very high mechanical stability, because of the low dry rubber content (25% DRC) and the presence of homopolymers of the non-ionogenic hydrophilic monomers.

(ii) effect of selected coagulants upon colloid stability of modified latices

The modified latices were greatly destabilised by adding excess coagulants (2,500 pphr) to the latices (Table 10.11). The effects of selected coagulants are discussed below:

a) Acetic acid

It appeared that acetic acid (2,500 pphr) did not coagulate NR latex containing SLS (2-3.66 pphr) and some of the modified NR latices. The obvious explanation for this is that the SLS remains ionised at low pH. Thus the SLS still acts as stabiliser, even in the presence of large quantities of the acid. In the case of the crude graft copolymer latices prepared using ACA as initiator (with high grafting efficiency), all of the latices flocculated, whereas the crude NR/PHPMA graft-copolymer latex coagulated. This suggests that these graft-copolymer latices were more sensitive to the

acid than was the control NR latex despite containing SLS (2 pphr). The modified NR latices (with zero or little grafting) produced cream. This suggests that the crude graft-copolymer latices with a higher grafting efficiency were less stable than those of the modified NR latices with a lower grafting efficiency (Table 10.11).

b) IMS and acetone

All the modified NR latices coagulated when IMS (2,500 pphr) or acetone (2,500 pphr) was added to the latices. This suggests that the dehydration processes brought about by IMS or acetone are more effective in destabilising the latices than are the processes associated with the addition of the acid coagulant (Table 10.11).

e) Ionic coagulants

The ionic coagulants sodium chloride, potassium chloride, calcium chloride, barium chloride,and ferric chloride, destabilised the modified NR latices. The most effective coagulant was barium chloride. This coagulant produced lumps of solid rubber immediately it was added. Other coagulants, such as calcium chloride and ferric chloride, coagulated the latices immediately; this was then followed by phase separation. Sodium and potassium chlorides did not coagulate the crude graft copolymers but did produce a cream. In this project, the redox initiator containing potassium and sodium might have played an important role in enhancing the formation of cream.

10.15.7 Vulcanisation behaviour, stress-strain behaviour and oil resistance of modified NR

NR is usually vulcanised with a combination of sulphur, accelerator/s, zinc oxide, and a fatty acid. The mix formulation may also contain other components, e.g., fillers, plastisers, antioxidants, etc. Vulcanisation converts the rubber from a linear plastic substance of very low strength into highly-elastic crosslinked material of

considerable strength (147). The vulcanisation process can be followed by determining the change in viscosity or stiffness of the compound using curemeters. Many curemeters do not measure a true viscosity of the compound but a shear torque or a Mooney Viscosity, which is related to the true viscosity of the compound. In this work, a commonly-used method for determining the vulcanisation behaviour of NR - the Monsanto Rheometer 100 - was used to study the vulcanisation behaviour of films obtained from the modified NR latices. To some extent, the vulcanisation behaviour could be related to the tensile stress-strain properties and the solvent-resistance of the films.

10.15.7.1 Vulcanisation behaviour of NR and modified NR

(i) Sulphur-vulcanisation behaviour of control NR

The NR film obtained from NR latex (25% DRC) using the compound-1 of Table 6.17 showed a very short optimum cure time (< 4 minutes) at 140^{o}C, this being the time required to reach a maximum torque (ca. 43 lb-in). The vulcanisate then began to revert immediately. After 90 minutes, the torque had decreased to 32 lb-in, and the reversion still continued. An interesting result was found for the NR film containing sodium lauryl sulphate (SLS) (3.66 pphr). The SLS acted not only as a plastiser by lowering the viscosity of the rubber, but also as an anti-reversion agent for NR. In the absence of SLS, the optimum torque was higher, but a somewhat higher torque was observed after longer times when SLS was present. SLS appears to retard crosslinking but to inhibit reversion. Reduction in temperature to 100^{o}C reduced the rate of the sulphur-crosslinking using both the ZDC and CBS/TMTD accelerator systems. It was observed that the main difference between the two accelerator system at 100^{o}C is that the induction period prior to crosslinking to occur was longer ca. 15 minutes in the case of CBS/TMTD than in the case of ZDC. However, after 1.5 hours both vulcanisates showed comparable increases in torque. These results were taken as evidence that both accelerator systems could be used to vulcanise NR films at 100^{o}C as they showed

comparable increases in torque after 1.5 hours vulcanisation. However, the physical properties of the two systems may not be the same because the physical properties might depend upon the type of crosslinking, rather than upon the type of the accelerators (151).

(ii) **Sulphur-vulcanisation behaviour of NR film containing added PHEA and PHPA**

The rheometric tests showed that PHEA (10 pphr) retarded the vulcanisation of NR (Figure 10.2). Further addition of the PHEA (30-50 pphr) inhibited vulcanisation altogether. In the case of PHPA (10 pphr), the torque increased slightly (ca. 5 lb-in) above the initial value. Further addition of PHPA (30-50 pphr) inhibited the vulcanisation altogether. The viscosity decreased to a level much lower than that of the control NR film (Figure 10.3). These results indicate that PHEA and PHPA act not only as effective plastisers but also as retarders and inhibitors of the vulcanisation of NR. The retardation/inhibition of vulcanisation by the polymers could have been a consequence of the acidic property of the impurities presence in the polymers. As mentioned in Section 6.1.1.2, HEA and HPA contain impurities such as acrylic acid. This acid might polymerise to produce polyacrylic acid. The presence author is unable to offer other explanations why these polymers retard the vulcanisation of NR.

Further investigation showed that vulcanised films from NR/PHEA and NR/PHPA blends showed some resistance to swelling in solvent [a mixture of isooctane:toluene (70:30) by volume] (Table 10.14). At low concentration (10 pphr) of the blends, the oil uptake was only about 1.3% for NR/PHEA blend and 14.3% for NR/PHPA blend higher than that of the control NR film containing SLS (3.66 pphr) which is almost certainly a consequence of retardation of vulcanisation. At higher concentration (50 pphr), however, the oil uptake was 94% higher for NR/PHEA blend and 63% higher for NR/PHPA blend above that of the control film. These

swelling results suggest that, at least at low concentrations of the blends (10 pphr), the polymers did not inhibit the vulcanisation as suggested by the Rheometric tests. At higher concentration of the polymers (50 pphr), the polymers might have retarded the vulcanisation. It may have been that the polymers were such effective plastisers that they softened the crosslinked NR. As a result, the soft compound was slipping when subjected to the Rheometric test, and no torque was recorded. By contrast, the swelling tests show that crosslinking has occurred.

(iii) Sulphur- and peroxide-vulcanisation of modified NR film

The sulphur-vulcanisation behaviours of the films from the crude NR/PHEA and NR/PHPA graft-copolymers (Figure 10.5) were similar to those of the blends of NR/PHEA and NR/PHPA (Figures 10.2 and 10.3). Rather surprisingly, the peroxide-vulcanisation [dicumyl peroxide (2.75 pphr) (140^{o}C)] behaviour of the films from the crude NR/PHEA and NR/PHPA graft-copolymers (Figure 10.6) was similar to sulphur-vulcanisation (Figure 10.5) in which no increase in torque occurred when measured on the Rheometer. This might be a consequence of the acidic property of the impurities presence in the polymers as mentioned earlier. It was thought that the dicumyl peroxide would be more likely to increase the torque of NR in the presence of the polymers than would the sulphur-vulcanisation. However, this is not the case. In these circumstances, the vulcanisation behaviour of NR in the presence of the polymers is apparently not affected by the nature of the vulcanisation system.

(iv) Sulphur-vulcanisation behaviour of crude graft copolymers

The sulphur-vulcanisation behaviour of the crude graft copolymers prepared using ACA as an initiator (Section 9.2) is of interest. The crude NR/PHEMA graft-copolymer and crude

NR/PHPMA graft-copolymer showed the typical vulcanisation behaviour of NR but with much lower maximum torque values (ca. 21 lb-in) (Figure 10.7). The viscosities as reflected by the minimum torque of the crude grafts were also lower than those of the controls, suggesting that the graft copolymers act as plastisers. However, the vulcanisation behaviours of the crude NR/PHEA graft-copolymer and crude NR/PHPA graft-copolymer were similar to those of the blends of NR/PHEA and NR/PHPA.

10.15.7.2 Tensile stress-strain properties of films from modified NR latices

(i) Effect of SLS

As mentioned in Section 10.11.(i), the SLS acted as plastiser, retarder and anti-reversion agent for the vulcanisation of NR. The materials containing SLS gave lower modulus but higher tensile strength and elongation at break when vulcanised, as compared with the material not containing SLS. For comparison, the modulus at 300% elongation, tensile strength and elongation at break of NR in the absence of SLS was 3.34 MPa, 4.06 MPa and 333% respectively whereas the modulus, tensile strength and elongation at break of NR in the presence of SLS (3.66 pphr) was 2.53 MPa, 8.19 MPa and 540% respectively.

(ii) Films from modified NR latex prepared using redox initiator

Using a redox initiator resulted in virtually zero grafting for HEA and HPA in NR latex. Hence the crude NR/PHEA and NR/PHPA graft-copolymers were in fact in the form of blends. To avoid confusion, the term "crude graft-copolymer" is still used throughout this discussion for those latices prepared by graft-copolymerising the monomers, rather than "blend", even though the materials were actually in the form of blends. The tensile strengths of the vulcanised NR from the crude NR/PHEA and NR/PHPA graft-copolymers increased substantially above those of the control NR film, and then decreased

progressively as the initial monomer concentrations increased. This suggests that, in the case of polymers produced using higher concentrations of the HEA and HPA, the polymers may act as retarders as well as plastisers. There was a trend for modified NRs produced using higher monomer concentrations to have the higher elongations at break. As expected, the moduli, tensile strengths and elongations at break of the modified NRs prepared using HEMA and HPMA were higher than those of the control NR (Table 10.12A). In all cases, the tensile strengths of the vulcanised films were far higher than those of unvulcanised films. This suggests that crosslinking of the NR during polymerisation of the monomers was unlikely to have occurred.

(iii) Films from modified NR latices prepared using ACA initiator

The moduli and tensile strengths of the crude NR/PHEA and NR/PHPA graft-copolymers were much lower than those of the control NR. However, the elongation at break of these grafts was far higher than that of the control NR (Table 10.12B). In the case of the crude NR/PHEMA and NR/PHPMA graft-copolymers, their tensile strengths and elongations at break were higher than those of the control NR. These results were in accordance with those for the vulcanisation behaviour of the crude graft copolymers (Figure 10.7), suggesting that the vulcanisation of NR in the presence of PHEMA and PHPMA was more favourable than in the presence of PHEA and PHPA.

10.15.7.3 Solvent-resistance

(i) Modified NR prepared using redox initiator

a. HEA and HPA

The uptake of solvent by the vulcanised films from crude NR/PHEA and NR/PHPA graft-copolymers increased as the initial monomer concentrations polymerised in NR latex increased. This is

further confirmation that the higher the concentration of homopolymers (PHEA and PHPA) formed during polymerisations of HEA and HPA in NR latex, the more the vulcanisation is retarded, thereby increasing swelling by solvent. The vulcanised films from the crude graft copolymers absorbed less water than did those of the control NR when a monomer level of 30% or less was used. When higher monomer levels were used, the modified NR films showed the same or worse resistance to water than did those of the control NR. The water-absorptions of the vulcanised films of the modified NRs ranged from 2 to 13%.

b. HEMA and HPMA

The uptakes of solvent by these modified NR films were slightly less than that of the control NR, being about 39% less than the control. All the unvulcanised and vulcanised films from the crude NR/HEMA graft-copolymers showed a worse resistance to water than did those from the control NR latex. The unvulcanised and vulcanised films from the crude NR/PHPMA graft-copolymers showed the same or worse resistance to water than did those of the control NR. The water-absorption of the vulcanised films of the modified NR ranged from 7 to 29% (Table 10.14A).

(ii) Crude graft copolymers prepared using ACA initiator

It was observed that the crude NR/PHEA and NR/PHPA graft-copolymers, with grafting efficiencies of ca. 51 and 85% respectively, were far less resistant to solvent than were the crude NR/PHEMA and NR/PHPMA graft-copolymers with grafting efficiencies of ca. 65 and 100% respectively (Table 10.14B). In fact, of the various crude graft copolymers investigated, the crude NR/PHPMA graft-copolymer was found to be the most resistant to solvent, even though its uptake of solvent was slightly higher (1.2-fold) than that of the control NR film. A major disadvantage of this graft is that the water

absorption was higher (2.4%) than that of the control NR. It might be expected that the presence of the hydrophilic polymer units in the crude grafts/blends would improve the solvent resistance of the grafts/blends compared to NR. However, the effect of the presence of these hydrophilic polymers is to retard the vulcanisation. Thus a comparison of solvent resistance is difficult without comparing materials having similar crosslink concentrations.

10.15.8 Dipping behaviour of modified NR latices

It was not possible to form deposits of rubber film on the formers either by using a dipped coagulant or by using a zinc-ammine heat sensitised system, or by using PVME heat sensitised system. It was observed that the deposits ran down the side of the formers when withdrawn from the control NR latex containing SLS (2-3.66 pphr) in all cases. Therefore a combination of either dipped coagulant and the zinc-ammine system, or dipped coagulant and the PVME system, was employed, i.e., the formers were first coated with a dried coagulant and then filled with boiling water prior to dipping in to a latex containing either SLS (2-3.66 pphr) and zinc-ammine ions, or SLS(2-3.66 pphr) and PVME. However, these methods still produced deposits that ran down the side of the formers. Satisfactory deposits could be produced in the absence of SLS by any method employed. The deposits also ran down the side of the formers when either

i) dipped coagulant, or
ii) the zinc-ammine system, or
iii) the combination of the dipped coagulant and the zinc-ammine system, or
iv) the combination of the dipped coagulant and the PVME

was employed to the crude graft copolymer latices with the exception of the crude NR/PHPMA graft-copolymer latex. A possible explanation of this is that the destabilisation brought about by either

i) the cation ions, or
ii) the zinc-ammine ions, or
iii) the heat-coagulating effect of the PVME, or

iv) the combination of either i) and ii), or i) and iii)

is not enough to compensate for the increase in colloid stability brought about by the presence of the SLS, the homopolymers, and the low DRCs (25%) of the latices. In the case of the crude NR/PHPMA graft copolymer latex, this crude graft produced deposits when the combination of the dipped coagulant and the zinc-ammine system was employed (Table 10.15). This suggests that this graft-copolymer latex was less stable than were the other modified NR latices. The thickness of the film produced from this graft-copolymer latex after 0.5 minutes dwell time was ca. 45% greater than that produced from the control NR latex.

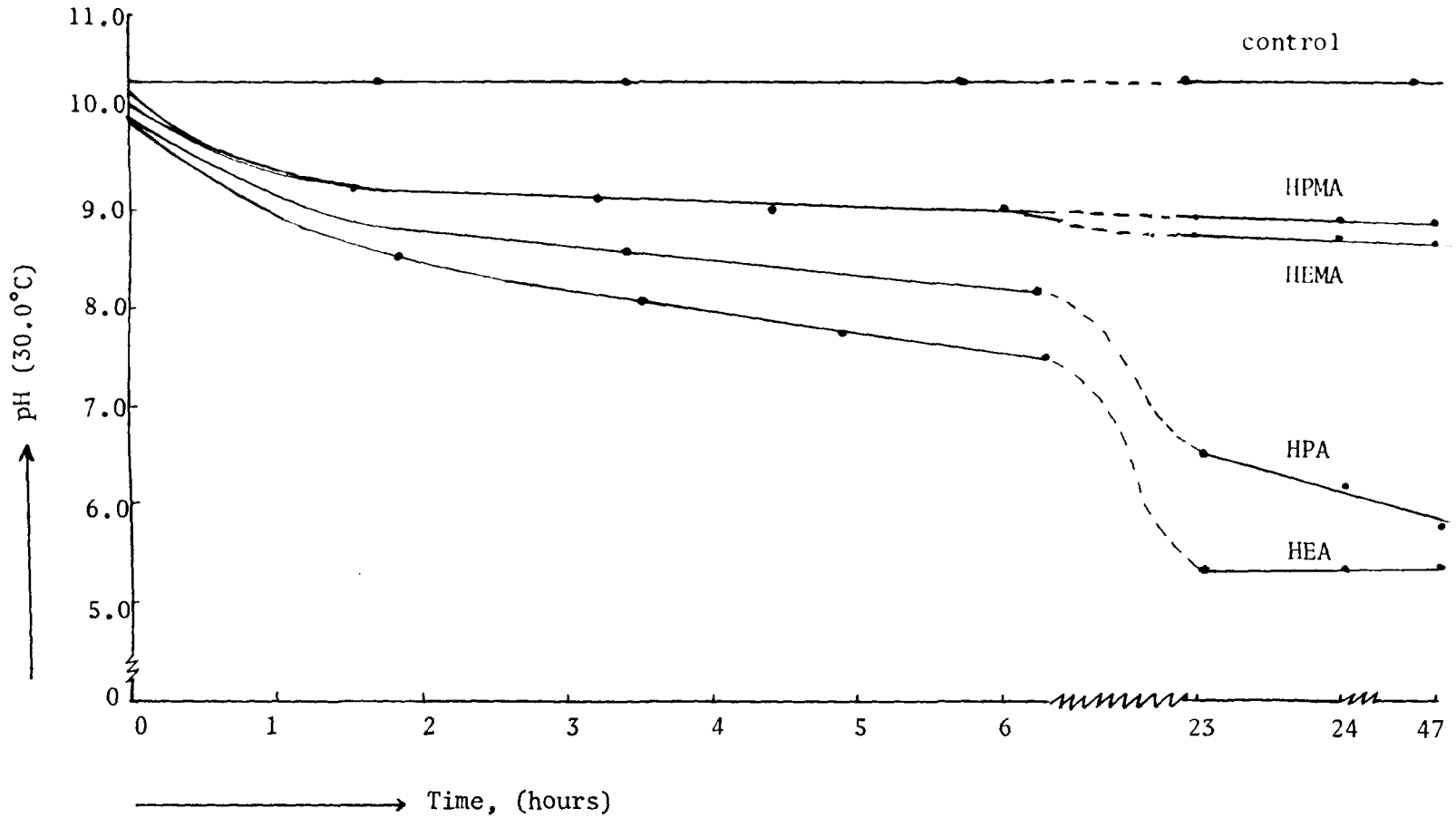


Figure 10.1 Effect of time upon pH of non-ionogenic hydrophilic monomers dissolved in 2% aqueous ammonia solution at 30.0 ± 0.1°C

Table 10.1 Effect of added homopolymers of non-ionogenic hydrophilic monomers upon creaming of NR latex for 4 months observation at 20°C

polymer	polymer level (pphr)	serum layer (% v/v)
control	0	0
PHEA	10	11
PHEA	30	15
PHEA	50	15
PHPA	10	18
PHPA	30	53
PHPA	50	34

Table 10.2 Creaming of crude graft copolymer latices after 4 months prepared using ACA as initiator

monomer	initial monomer level (pphr)	monomer conversion (% w/w)	efficiency of grafting (% w/w)	serum layer (% v/v)
control	0	0	0	0
HEA	20.19	51.9	85.4	5
HPA	20.35	51.5	50.8	5
HEMA	10.21	44.4	64.9	52
HPMA	11.17	51.4	100.0	40

Table 10.3 Polymerisation of various amounts of HEA in NR latex at 30°C

	code									
	A-0	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9
HEA, pphr	40.10	40.35	50.56	75.07	99.99	40.62	100.81	74.81	100.00	75.35
SLS, pphr	0.00	2.00	2.00	3.00	3.00	4.00	4.00	4.00	6.00	6.00
redox initiator, pphr	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.83	0.43	0.43
DRC of reaction mixture, %	25.07	25.08	25.08	24.96	24.96	24.98	24.99	25.04	24.53	24.96
pH at 30°C										
- 0 hour	10.11	10.15	10.05	10.30	10.18	9.93	10.32	9.32	9.73	10.10
- 1 hour	FLOC	-	-	9.40	-	-	9.15	-	-	-
- 3 hours		-	-	8.08	-	-	CC	-	CC	-
- 4 hours		-	-	7.65	-	-		CC		-
- 5 hours		-	-	7.50	-	-				-
- 22 hours		-	-	6.25	-	-				-
- 24 hours		6.07	6.01	5.95	CC	5.65				5.40
observation		STAB	STAB	STAB		STAB				STAB
serum, % v/v (23 days storage).....		0	0	3		0				0

FLOC = flocculation; CC = completely coagulated; STAB = stable

Table 10.4 Polymerisation of various amounts of HPA polymerised in NR latex at 30 ^{o}C

	code						
	B-0	B-1	B-2	B-3	B-4	B-5	B-6
HPA, pphr	40.11	40.35	50.56	75.07	99.91	100.80	100.36
SLS, pphr	0.00	2.00	2.00	3.00	3.00	4.00	6.00
redox initiator, pphr	0.44	0.43	0.43	0.43	0.43	0.43	0.43
DRC, %	25.01	25.08	25.08	25.08	25.08	24.90	24.99
pH at 30^{o}C							
0 hour	-	10.22	10.18	10.36	10.25	10.35	10.00
1 hour	FLOC	-	-	9.73	9.60	9.60	CC
3 hours		-	-	8.72	8.48	-	
4 hours		-	-	8.20	8.10	7.80	
5 hours		-	-	7.90	7.80	7.65	
22 hours		-	-	6.68	6.78	6.25	
24 hours		6.40	6.45	6.48	PC	CC	
observation		STAB	STAB	STAB			

FLOC = flocculation; CC = completely coagulated; PC = partly coagulated
STAB = stable

Table 10.5 Polymerisation of various amounts of HEMA in NR latex at 30°C

	code												
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13
HEMA, pphr	9.67	14.59	19.41	24.29	30.40	30.30	30.33	40.44	40.48	50.72	50.72	50.72	50.72
SLS, pphr	0.00	0.00	0.00	0.00	1.00	2.00	3.00	3.00	4.00	4.00	4.00	4.00	4.00
redox initiator, pphr	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	1.27	2.17	2.99
DRC, %	25.04	25.04	25.04	25.04	25.00	25.08	25.06	25.06	25.00	25.00	25.00	25.00	25.00
pH at 30°C:													
0 hour	10.54	10.49	10.42	10.38	10.22	10.25	10.23	10.22	10.23	10.20	10.25	10.25	10.25
1 hour	-	-	-	-	-	-	-	-	-	-	10.00	10.01	10.05
2 hours	-	-	-	-	-	-	-	-	-	-	9.63	9.70	PC
3 hours	-	-	-	-	-	-	-	-	-	-	9.43	9.43	
20 hours	-	-	-	-	-	-	-	-	-	-	8.65	8.68	
21 hours	-	-	-	-	-	-	-	-	-	-	8.50	PC	
22 hours	-	-	-	-	9.35	9.33	9.38	9.28	9.39	9.33	-		
24 hours	9.83	9.83	9.71	9.62	-	-	-	-	-	-	8.13		
stability after polymerisation								STAB	STAB	STAB	STAB		
1 day storage	STAB	STAB	STAB	STAB	STAB	STAB	STAB	STAB	STAB	STAB	PC		
2 days storage	-	-	-	-	PC	-	-	PC	PC	MC	CC		
3 days storage	-	-	-	-	MC	PC	-	MC	MC	CC			
4 days storage	-	-	-	-	CC	CC	Gel	CC	CC				
7 days storage	CR	CR	PC	CC									
(serum layer, % v/v)...	8	15	-										
41 days storage	-	-	CC										
(serum layer, % v/v)...	26	16											

PC = partly coagulated; MC = mostly coagulated; CC = completely coagulated;
STAB = stable; CR = creaming

Table 10.6 Polymerisation of various amounts of HPMA in NR latex at 30°C

	code										
	D-1	D-2	D-3	D-4	D-5	D-6	D-7	D-8	D-9	D-10	D-11
HPMA, pphr	30.39	30.30	30.33	40.44	30.40	40.53	40.57	50.64	50.64	50.63	50.21
SLS, pphr	1.00	2.00	3.00	3.00	4.00	4.00	5.00	5.00	5.00	5.00	6.00
redox initiator, pphr	0.43	0.43	0.43	0.43	0.43	0.43	1.28	1.28	1.28	0.85	0.43
DRC, %	25.00	25.08	25.06	25.06	25.00	25.00	25.04	25.04	25.04	25.04	24.99
pH at 30°C											
0 hour	10.20	10.15	10.20	10.13	10.45	10.39	9.50	9.43	9.53	9.35	9.95
1 hour	-	-	-	CC	-	-	9.50	9.22	9.30	-	-
2 hours	-	-	-		-	-	PC	CC	CC	-	CC
4 hours	-	-	-		-	-				CC	
24 hours	9.50	9.55	9.50		9.62	9.53					
stability after polymerisation											
1 day storage	PC	PC	PC		STAB	PC					
2 days storage					PC						

PC = Partly coagulated; STAB = Stable

Table 10.7 Effect of activation time, monomer and initiator level upon conversion, extent of serum layer, and efficiency of grafting of non-ionogenic hydrophilic monomers polymerised in NR latex (25% DRC) in the presence of sodium lauryl sulphate (3.66 pphr) using redox initiator

monomer	level (pphr)	activation time (minutes)		redox initiator (pphr)	conversion (% w/w)	efficiency of grafting (% w/w)	serum layer (% v/v)	appearance of serum
		$K_2S_2O_8$	$Na_2S_2O_5$					
HEA	29.86	0	0	0.55	70.09	0.0	42	clear
	29.91	25	8	0.55	46.50	0.0	38	cloudy
	40.04	25	5	0.55	51.09	0.0	56	cloudy
	49.85	75	15	0.55	35.30	0.0	39	cloudy
HPA	39.71	0	0	0.55	69.74	17.6	32	clear
	39.86	25	9	0.55	56.79	5.7	33	cloudy
	40.01	75	15	0.55	38.21	0.0	9	clear
	50.03	77	15	0.55	39.55	0.0	10	clear
HEMA	11.30	0	0	0.54	33.05	50.0	41	clear
	10.05	70	10	0.54	24.74	0.0	51	cloudy
	10.93	75	17	1.63	43.13	5.5	43	cloudy
	10.05	73	15	2.07	44.72	23.1	43	cloudy
	20.07	75	14	2.07	58.29	7.2	19	clear
	28.38	77	15	2.07	13.29	cc	-	-
HPMA	10.00	0	0	0.54	73.66	6.3	37	clear
	10.04	25	15	0.54	34.83	0.0	47	cloudy
	9.99	75	17	0.80	16.33	0.0	28	cloudy
	10.05	80	18	1.44	42.47	32.6	36	clear
	10.05	75	15	2.18	57.50	61.0	48	x)
	20.04	75	15	2.18	cc	-	-	-

x) = flocculation after 3 days

Table 10.8 Effect of pH upon creaming of modified NR latex

	code							
	A-1		A-2		B-1		B-2	
	HEA[1)]		HEA[2)]		HPA[3)]		HPA[4)]	
pH after polymerisation.....	6.07	-	6.01	-	6.40	-	6.45	-
pH after adding of ammonia.....	-	10.32	-	10.25	-	10.25	-	10.33
stability /creaming								
10 days storage.....	stable	PS	stable	PS	stable	PS	stable	PS
serum,(% v/v)..	0	50	0	22	0	19	0	14
34 days storage.....	stable	-	stable	-	PS	PS	PS	PS
serum,(% v/v)..	0	50	0	43	-	43	14	29

HEA[1)] = 40.35 pphr; HEA[2)] = 50.56 pphr
HPA[1)] = 40.35 pphr; HPA[2)] = 50.56 pphr
PS = phase separation

Table 10.9 Effect of dry rubber content (DRC) upon conversion and efficiency of grafting of non-ionogenic hydrophilic monomers (0.5 mol/l latex) in absence of sodium lauryl sulphate and using redox initiator (5.06×10^{-3} mol/l latex) at $30^{o}C$

monomer	level (pphr)	final DRC (%)	redox initiator (pphr)	pH		conversion (% w/w)	efficiency of grafting (% w/w)	serum layer[xxx] (% w/w)
				BP[x]	AP[xx]			
HEA	38.89	15.02	0.75	10.58	9.20	55.02	0.0	10
	23.31	25.06	0.45	10.52	8.94	57.16	0.0	3
	16.67	35.04	0.32	10.40	9.02	88.33	3.4	28
HPA	38.89	15.02	0.75	10.57	9.35	45.54	0.0	3
	23.34	25.02	0.45	10.48	9.25	57.51	0.0	8
	16.64	35.09	0.32	10.38	8.98	80.00	0.0	8
HEMA	44.29	15.02	0.76	10.48	CC	CC	-	-
	26.28	25.03	0.45	10.43	CC	CC	-	-
	18.76	35.02	0.32	10.38	CC	CC	-	-
HPMA	48.53	15.02	0.75	10.51	9.72	6.88	0.0	EV
	29.14	25.02	0.45	10.46	9.71	11.97	0.0	G
	21.19	34.84	0.32	10.42	CC	CC	-	

[x] BP=before polymerisation; [xx] AP= after polymerisation; [xxx] after 50 days.

CC = completely coagulated; EV = extremely viscous after one week; G = gel after one week.

Table 10.10 Mechanical stability time (MST) of the modified NR latex (25% DRC)

monomer	level (pphr)	SLS (pphr)	initiator		conversion (% w/w)	grafting efficiency (% w/w)	KCl (pphr)	NaCl (pphr)	MST
			ACA (pphr)	redox (pphr)					
control	-	-	-	-	-	-	-	-	foaming
	-	-	-	-	-	-	9	-	foaming
	-	-	-	-	-	-	-	9	foaming
	-	2.00	-	-	-	-	-	-	foaming
	-	3.66	-	--	-	-	-	foaming	
	-	3.66	-	-	-	-	9	-	foaming
	-	3.66	-	-	-	-	-	9	foaming
HEA	20.19	2.00	0.87	-	51.9	85.4	-	-	foaming
HPA	20.35	2.00	0.87	-	51.5	50.8	-	-	foaming
HEMA	10.21	2.00	0.87	-	44.4	64.9	-	-	foaming
HPMA	11.17	2.00	0.87	-	51.4	100.0	-	-	foaming
HEA	29.86	3.66	-	0.54	70.1	0.0	-	-	foaming
HPA	39.71	3.66	-	0.54	69.7	17.6	-	-	foaming
HEMA	15.08	3.66	-	2.18	62.2	17.0	-	-	foaming
HPMA	10.05	3.66	-	1.44	42.5	32.6	-	-	foaming

Table 10.11 Effect of added coagulants (2,500 pphr) upon stability of modified NR latex (25% DRC)

monomer	level (pphr)	SLS (pphr)	initiator		conversion (% w/w)	grafting efficiency (% w/w)	acetic acid	IMS	acetone	NaCl	KCl	$CaCl_2$	$BaCl_2$	$FeCl_3$
			ACA (pphr)	redox (pphr)										
control	-	-	-	-	-	-	ICL	ICL	ICL	IFS	FS	ICL	ICL	ICS
	-	2.00	-	-	-	-	CR	ICL	ICL	FS	FS	ICS	ICL	ICS
	-	3.66	-	-	-	-	CR	ICL	ICL	FS	IF	ICS	ICL	ICL
HEA	20.19	2.00	0.87	-	51.9	85.4	F	ICL	ICL	CR	CR	-	ICL	ICS
HPA	20.35	2.00	0.87	-	51.5	50.8	F	ICL	ICL	CR	CR	-	ICL	ICS
HEMA	10.21	2.00	0.87	-	44.4	64.9	F	ICL	ICL	CR	CR	-	ICL	ICS
HPMA	11.17	2.00	0.87	-	51.4	100.0	IC	ICL	ICL	CR	CR	-	ICL	ICS
HEA	9.98	3.66	-	0.55	60.9	0.5	CR	ICL	ICL	CR	IFS	ICS	ICL	ICS
	29.91	3.66	-	0.55	46.5	0.0	CR	ICL	ICL	CR	IFS	ICS	ICL	ICS
	49.85	3.66	-	0.55	35.3	0.0	CR	ICL	ICL	IFS	IFS	IFS	ICL	ICS
HPA	9.91	3.66	-	0.55	60.7	0.0	CR	ICL	ICL	IFS	IFS	ICS	ICL	ICS
	39.86	3.66	-	0.55	56.8	0.0	CR	ICL	ICL	CR	IFS	IFS	ICL	ICS
	50.03	3.66	-	0.55	39.6	0.0	CR	ICL	ICL	FS	IFS	IFS	ICL	ICS
HEMA	15.08	3.66	-	2.18	2.2	17.0	CR	IFL	ICL	FS	IFS	IFS	ICL	ICS
HPMA	15.54	3.66	-	0.80	27.7	0.0	CR	ICL	ICL	FS	IFS	IFS	ICL	ICS

ICL = immediately coagulated in the form of lump; IFS = immediately flocculated and followed by separation; ICS = immediately coagulated and followed by separation; CR = creaming; FS = flocculated and followed by separation; IF = immediately flocculated; IFL = immediately flocculated and followed by formation of lump, F = flocculation.

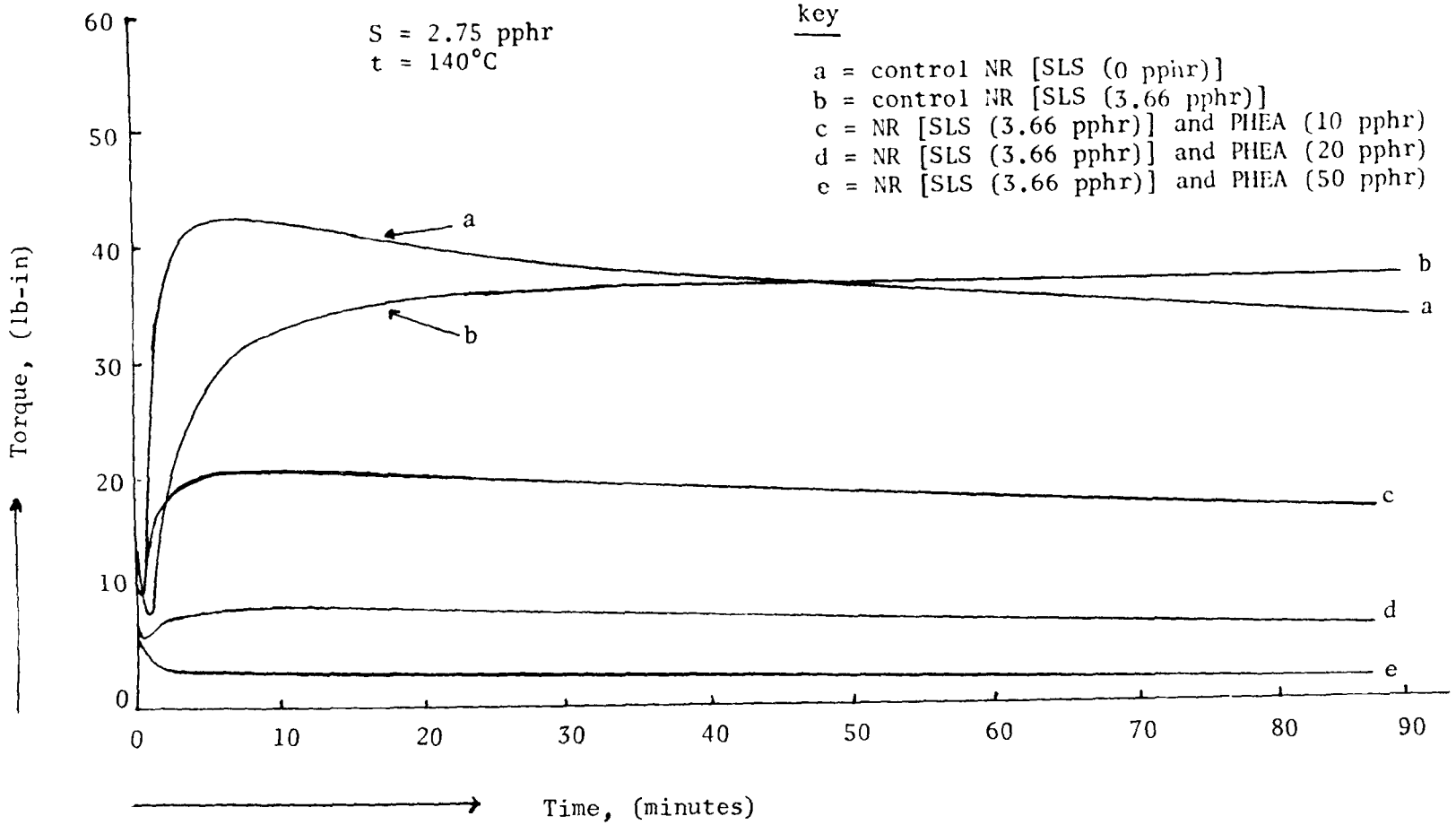


Figure 10.2 Effect of added polyhydroxyethyl acrylate (PHEA) upon sulphur-vulcanisation behaviour of NR at 140°C

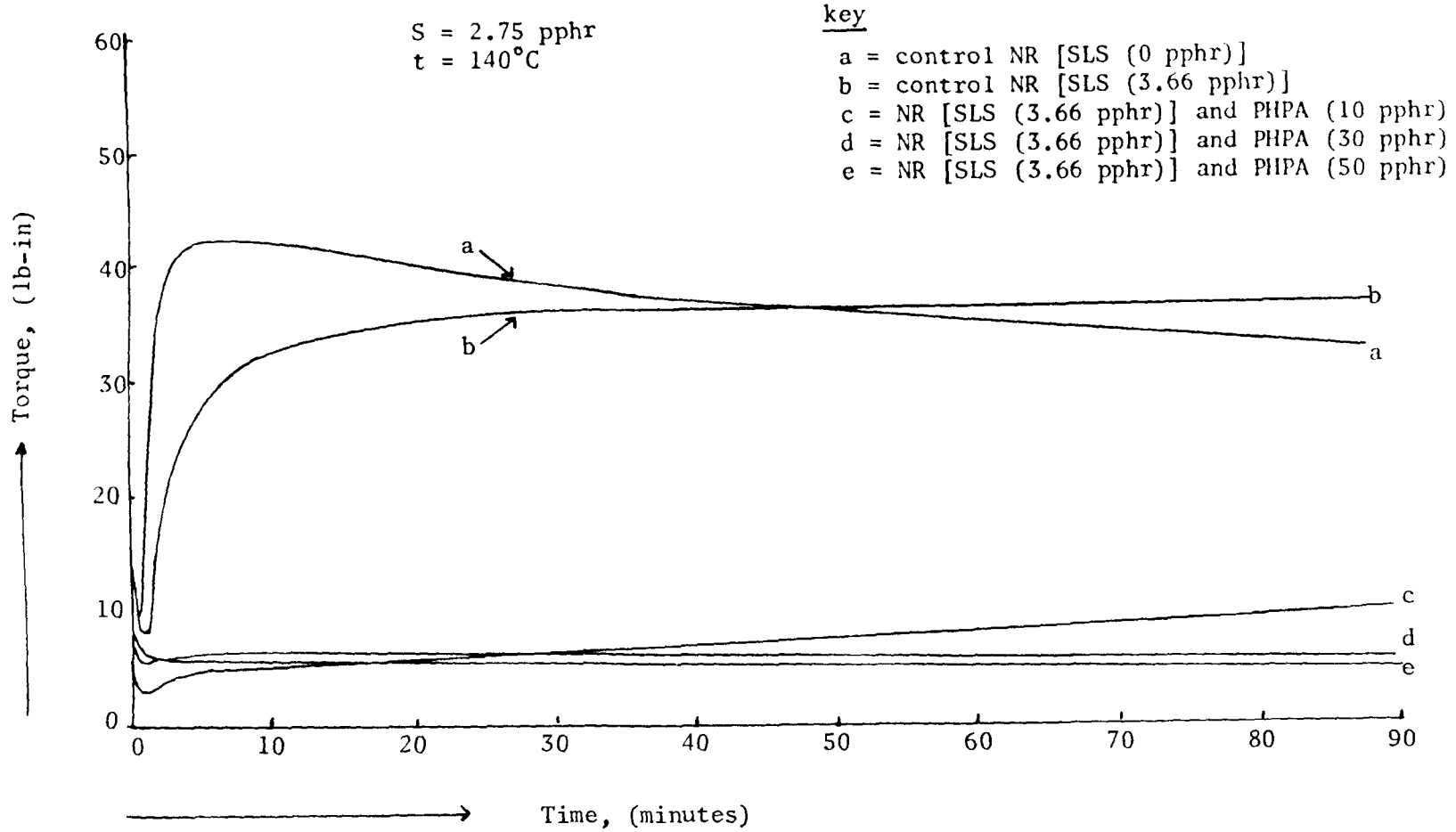
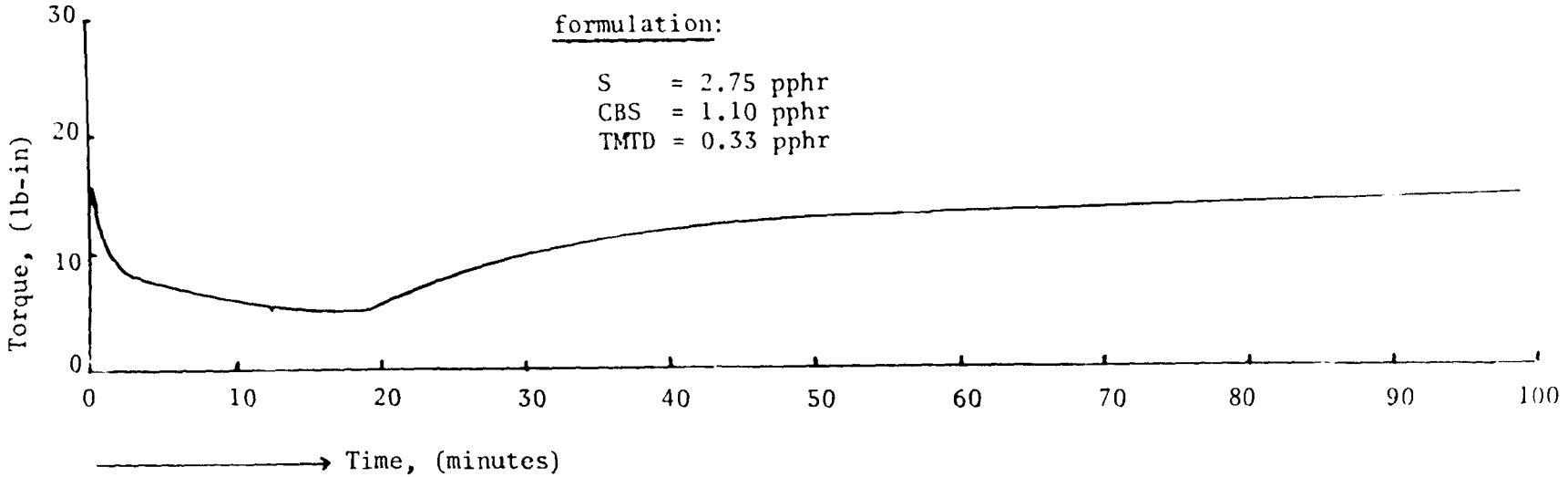


Figure 10.3 Effect of added polyhydroxypropyl acrylate (PHPA) upon sulphur-vulcanisation behaviour of NR at 140°C



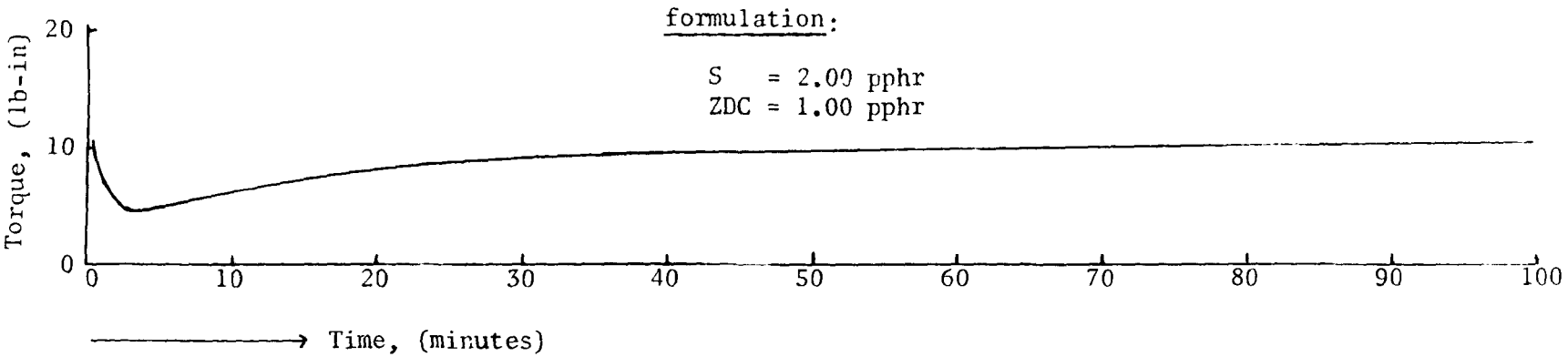


Figure 10.4 Effect of nature of accelerator upon sulphur-vulcanisation behaviour of NR at 100°C

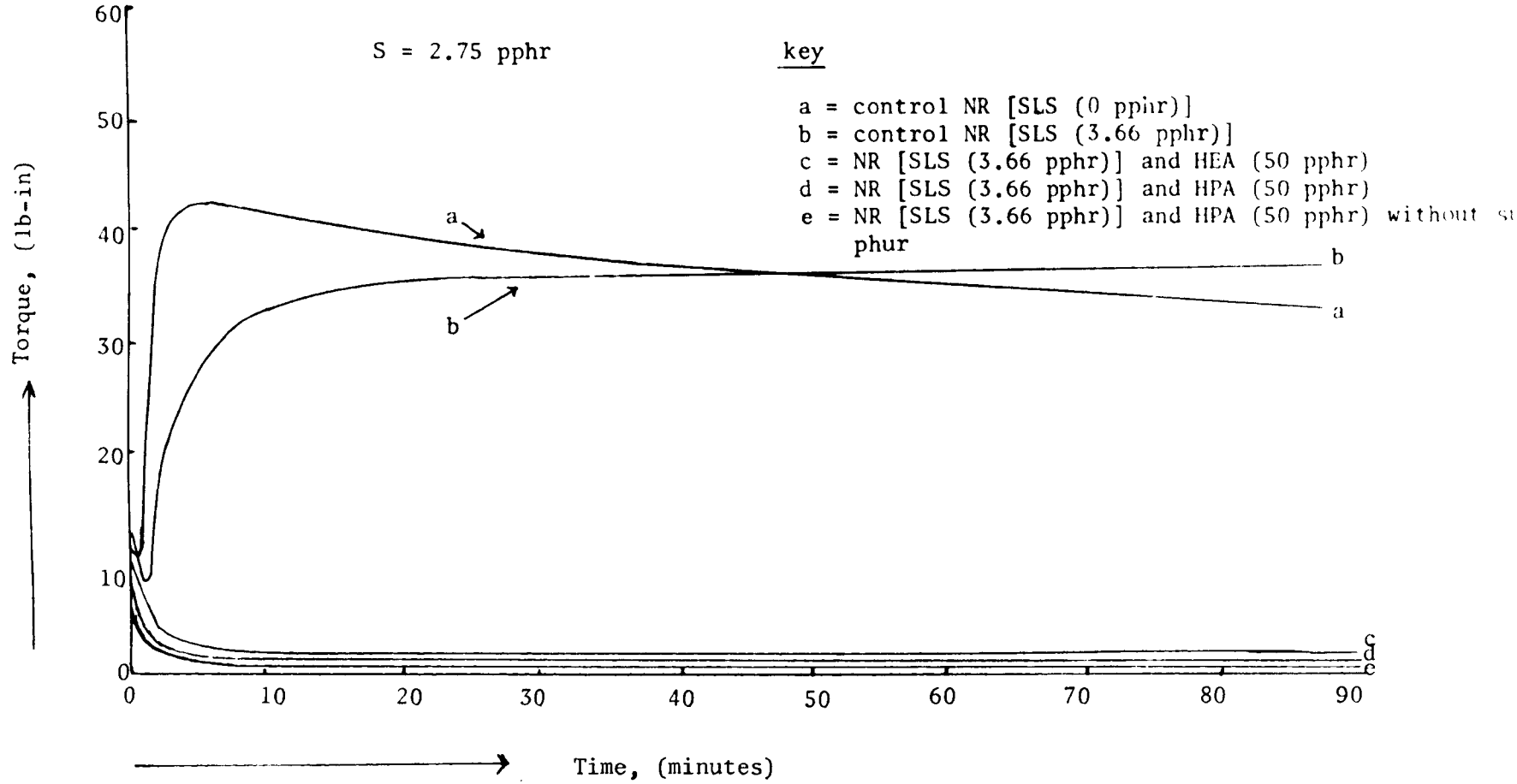


Figure 10.5 Sulphur-vulcanisation behaviour of modified NRs at 140°C

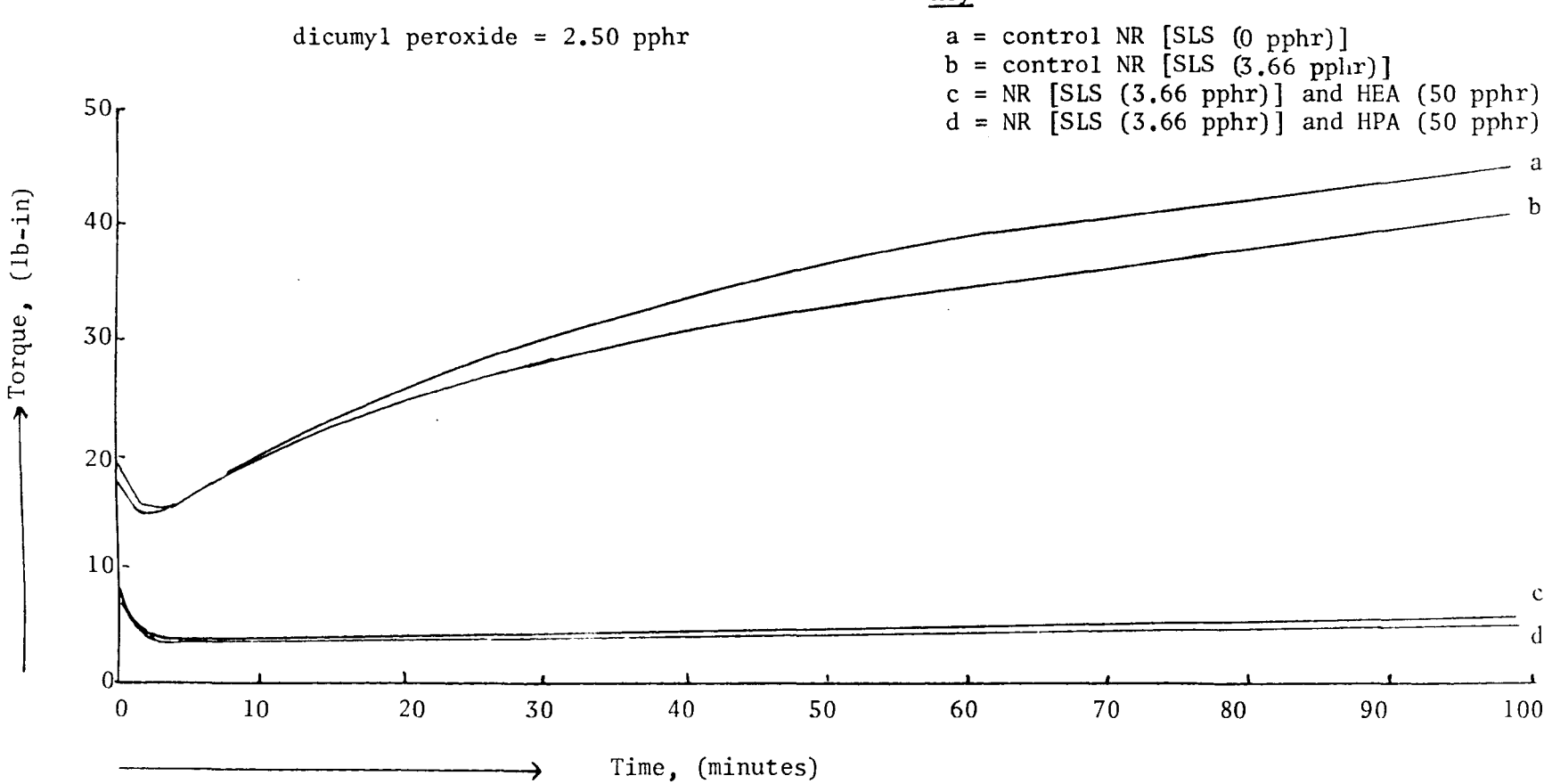


Figure 10.6 Peroxide-vulcanisation behaviour of modified NR at 140°C

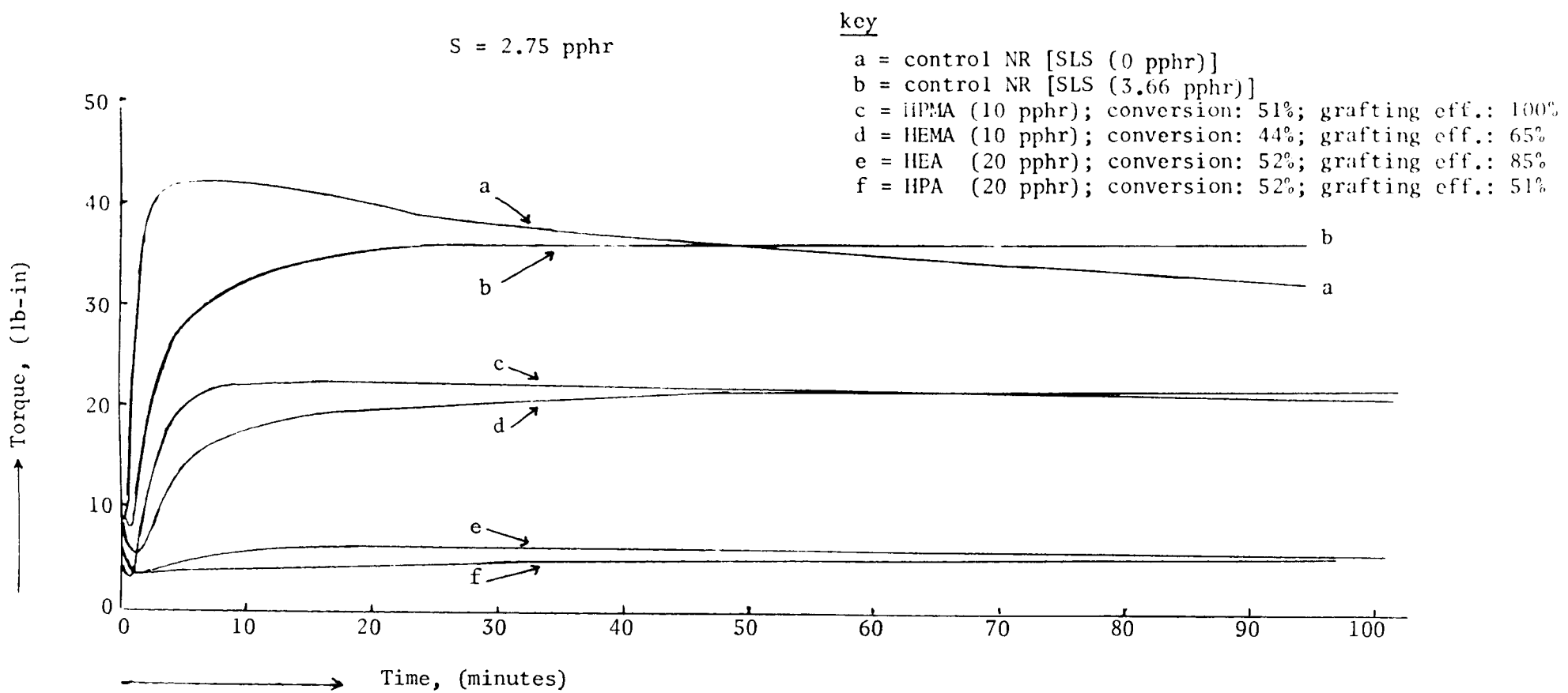


Figure 10.7 Sulphur-vulcanisation behaviour of crude graft copolymer films at 140°C

Table 10.12A Stress-strain of the modified NR prepared using the redox initiator

monomer	level (pphr)	SLS (pphr)	conversion (%)	grafting efficiency (%)	modulus at 100% (MPa)		modulus at 300% (MPa)		tensile strength (MPa)		elongation at break (%)	
					UF	VF	UF	VF	UF	VF	UF	VF
control	-	-	-	-	0.23	1.02	0.25	3.34	0.39	4.06	720	333
control	-	3.66	-	-	0.29	0.77	0.29	2.53	0.57	8.19	870	540
HEA	9.91	3.66	60.90	0.5	0.21	1.37	0.21	2.89	1.99	16.89	1013	480
-	20.01	3.66	65.73	0.0	0.37	1.35	0.41	2.79	1.76	12.89	860	520
	29.86	3.66	70.09	0.0	0.26	1.17	0.36	2.49	2.33	8.37	1000	533
-	40.04	3.66	51.09	0.0	0.23	0.35	0.28	0.65	2.09	6.04	677	940
-	49.85	3.66	35.30	0.0	0.35	0.29	0.39	0.43	2.29	4.89	940	933
HPA	9.91	3.66	60.67	0.0	0.13	1.96	0.17	4.83	0.64	17.12	1030	473
-	19.87	3.66	61.68	0.0	0.28	1.56	0.34	2.70	1.09	15.95	940	577
-	29.79	3.66	71.74	5.0	0.22	1.54	0.24	3.73	1.76	9.42	1145	493
-	39.71	3.66	69.74	17.6	0.07	1.18	0.13	2.15	1.97	10.67	1017	587
HEMA	11.30	3.66	33.05	50.0	0.32	2.09	0.39	4.65	2.22	10.03	892	415
-	10.93	3.66	43.13	5.5	0.32	2.24	0.40	5.09	1.81	9.39	897	403
-	10.04	3.66	30.76	0.0	0.45	2.06	0.51	4.72	2.76	9.39	397	977
-	10.05	3.66	24.74	0.0	0.49	1.49	0.59	3.34	2.17	7.89	430	880
HPMA	10.00	3.66	73.66	6.3	0.34	1.83	0.41	4.08	1.49	15.97	497	850
-	10.04	3.66	34.83	0.0	0.27	1.48	0.41	4.11	1.08	17.37	505	840
-	20.03	3.66	12.41	33.5	0.19	2.29	0.35	4.75	1.18	14.58	487	767
-	19.97	3.66	16.92	52.1	0.29	1.35	0.43	3.15	1.54	10.13	495	873

UF = unvulcanised film; VF = vulcanised film

Table 10.12B Tensile stress-strain properties of films from modified NR using ACA initiator

monomer	level (pphr)	SLS (pphr)	conversion (%)	grafting efficiency (%)	modulus at 100% (MPa)		modulus at 300% (MPa)		tensile strength (MPA)		elongation at break (%)	
					UF	VF	UF	VF	UF	VF	UF	VF
control	-	-	-	-	0.23	1.02	0.25	3.34	0.39	4.06	720	333
control	-	2.00	-	-	0.25	0.80	0.26	2.78	0.46	6.08	781	390
HEA	20.19	2.00	51.9	85.4	x	0.27	x	0.32	x	3.08	x	987
HPA	20.35	2.00	51.5	50.8	x	0.28	x	0.38	x	1.52	x	1067
HEMA	10.21	2.00	44.4	64.9	x	1.16	x	2.69	x	13.37	x	560
HPMA	11.17	2.00	51.4	100.0	x	1.27	x	3.19	x	14.34	x	530

x = the samples were too soft
UF = unvulcanised film
VF = vulcanised film

Table 10.13 Resistance to solvents of blends of NR/PHEA and NR/PHPA (1 week immersion at 20°C)

polymer	polymer level (pphr)	SLS (pphr)	oil uptake (g solvent/g sample) UF	VF
control	-	0.00	18.51	2.25
	-	3.66	19.16	2.38
PHEA	10	3.66	19.05	2.41
	20	3.66	15.23	2.50
	30	3.66	13.89	4.62
PHPA	10	3.66	17.45	2.72
	20	3.66	15.20	2.92
	30	3.66	14.23	3.87

UF = unvulcanised film; VF = vulcanised film

Table 10.14A Resistance to solvents of modified NR prepared using the redox initiator

monomer	level (pphr)	SLS (pphr)	conversion (% w/w)	efficiency of grafting (% w/w)	water absorption		oil uptake (g solvent /g sample)	
					UF[x)]	VF[xx)]	UF[x)]	VF[xx)]
control	-	0.00	-	-	14.48	8.66	18.51	2.25
	-	3.66	-	-	39.34	8.22	19.16	2.38
HEA	9.98	3.66	60.9	0.5	78.62	2.90	19.74	2.00
	20.01	3.66	65.7	0.0	30.42	4.15	15.10	2.06
	29.86	3.66	70.1	0.0	55.42	5.95	14.26	2.74
	40.04	3.66	51.1	0.0	22.17	12.57	12.45	3.35
	49.85	3.66	35.3	0.0	15.20	10.39	11.78	6.40
HPA	9.91	3.66	60.7	0.0	80.65	3.96	17.69	1.85
	19.87	3.66	61.7	0.0	38.99	2.26	15.33	2.03
	29.79	3.66	71.7	5.0	30.66	7.05	14.68	2.55
	39.71	3.66	69.7	17.6	23.89	7.22	15.21	2.44
HEMA	11.30	3.66	33.0	50.0	56.32	20.64	15.08	1.71
	10.93	3.66	43.1	5.5	49.89	29.57	14.78	1.65
	15.08	3.66	62.2	17.0	31.52	24.63	12.56	1.67
	10.05	3.66	24.8	0.0	56.76	16.51	12.52	1.74
	10.01	3.66	30.8	0.0	54.13	13.99	14.26	1.60
HPMA	10.00	3.66	73.7	6.3	81.08	7.37	16.00	1.67
	10.04	3.66	34.8	0.0	48.27	11.18	16.41	1.70
	10.05	3.66	42.5	32.6	38.05	16.22	17.35	1.66
	20.03	3.66	12.4	33.5	18.80	9.05	10.40	1.65
	19.97	3.66	16.9	52.1	23.24	8.28	10.17	1.85

UF[x)] = unvulcanised film
VF[xx)] = vulcanised film

Table 10.14B Resistance to solvents of modified NR prepared using ACA as initiator (0.87 pphr)

monomer	level (pphr)	SLS (pphr)	conversion (% w/w)	efficiency of grafting (% w/w)	water absorption		oil uptake (g solvent /g sample)	
					UF[x)]	VF[xx)]	UF[x)]	VF[xx)]
control	-	0.00	-	-	14.48	8.66	18.51	2.25
	-	2.00	-	-	39.30	8.40	18.74	2.29
HEA	20.19	2.00	51.9	85.4	98.55	39.77	-	10.63
HPA	20.35	2.00	51.5	50.8	115.31	54.02	-	14.79
HEMA	10.21	2.00	44.4	64.9	100.09	39.89	-	3.57
HPMA	11.17	2.00	51.4	100.0	88.98	20.72	-	2.73

UF[x)] = unvulcanised film
VF[xx)] = vulcanised film

Table 10.15 Dipping behaviour of the modified NR latex (25% DRC)

monomer	level (pphr)	SLS (pphr)	initiator system	conversion (% w/w)	efficiency of grafting (% w/w)	compound		appearance of deposit	thickness of vulcanised film (mm)		
						Z.A[x)]	PVME[xx)]		dwell time (min.)		
									0.5	1	2
control	-	0.00	-	-	-	v	-	good	0.22	0.26	0.34
	-	0.00	-	-	-	-	v	good	0.26	0.33	0.55
	-	0.00	-	-	-	v	-	RDF	-	-	-
	-	2.00	-	-	-	-	v	RDF	-	-	-
	-	3.66	-	-	-	v	-	RDF	-	-	-
	-	3.66	-	-	-	-	v	RDF	-	-	-
HEA	20.19	2.00	ACA	51.9	85.4	v	-	RDF	-	-	-
	20.19	2.00	ACA	51.9	85.4	-	v	RDF	-	-	-
HPA	20.35	2.00	ACA	51.5	50.8	v	-	RDF	-	-	-
	20.35	2.00	ACA	51.5	50.8	-	v	RDF	-	-	-
HEMA	10.21	2.00	ACA	44.4	64.9	v	-	RDF	-	-	-
	10.21	2.00	ACA	44.4	64.9	-	v	RDF	-	-	-
HPMA	11.17	2.00	ACA	51.4	100.0	v	-	good	0.32	0.38	0.39
	11.17	2.00	ACA	51.4	100.0	-	v	RDF	-	-	-
HEA	9.98	3.66	redox	60.9	0.5	v	-	RDF	-	-	-
	9.98	3.66	redox	60.9	0.5	-	v	RDF	-	-	-
	49.85	3.66	redox	35.3	0.0	v	-	RDF	-	-	-
	49.85	3.66	redox	35.3	0.0	-	v	RDF	-	-	-
HPA	9.91	3.66	redox	60.7	0.0	v	-	RDF	-	-	-
	9.91	3.66	redox	60.7	0.0	-	v	RDF	-	-	-
	39.71	3.66	redox	69.7	0.0	v	-	RDF	-	-	-
	39.71	3.66	redox	69.7	0.0	-	v	RDF	-	-	-
HEMA	10.05	3.66	redox	44.7	23.1	v	-	RDF	-	-	-
	10.05	3.66	redox	44.7	23.1	-	v	RDF	-	-	-
HPMA	10.05	3.66	redox	42.5	32.6	v	-	RDF	-	-	-
	10.05	3.66	redox	42.5	32.6	-	v	RDF	-	-	-

Z.A[x)] = using zinc-ammine system

PVME[xx)] = using PVME as sensitiser

RDF = running down the side of the formers

CHAPTER 11
Conclusions and Suggestions for Further Work

11.1 Introduction

An investigation of the graft copolymerisation of the monomers HEA, HPA, HEMA and HPMA on to NR in NR latex has been carried out. The investigation involved different areas of study, including the colloid stability of the latex, reaction kinetics, characterisation of the products, mechanism of grafting reactions, preparation of the modified NR latices, and selected physical properties of the products.

11.1.1 Effect of the monomers, their homopolymers and redox initiator upon mechanical stability time (MST) of NR latex

11.1.1.1 Without maturation, the MST of the latex increased progressively as the monomer concentrations increased, until it reached a maximum MST. The differences between the MST values of the latices and the MST values of the control were 1,650 seconds for HEA; 2,295 seconds for HPA; 3,998 seconds for HEMA; and 3,948 seconds for HPMA. The increase in MST was attributed to rapid adsorption of the monomers onto the surface of the rubber particles, bringing about hydration stabilisation and possibly also steric stabilisation. The MST of the latex decreased progressively as the monomer concentration increased further. The fall of the MST was attributed to 1) dehydration of the of the hydration layer, 2) possible interactions of the monomers with the indigenous stabilisers of NR latex. On the basis of calculation, the compression of the double layer ($1/\kappa$) surrounding the rubber particles with increasing monomer concentrations due to effects upon the dielectric constant was negligible, and that the MST of NR latex was not affected by reduction of dielectric constant at the monomer concentrations studied. The effectiveness of the monomers in increasing, and subsequently decreasing, the MST is in the following order: HPMA > HEMA > HPA > HEA.

11.1.1.2 The MST of the latex in the presence of the monomers decreased substantially over a short period of maturation, and the decrease then slowed with time. This was attributed to hydrolysis of the monomers, as well as to the occurrence of dehydration. The hydrolysis of the adsorbed monomers produced acids and alcohols which

eventually desorb from the surface of the rubber particles to the aqueous phase, thereby reducing the MST. Also, the acids would be expected to reduce the MST by pH effect.

11.1.1.3 The MST of the latex decreased progressively as the concentration of the redox initiator [potassium persulphate-sodium metabisulphite (1:1 by weight)] increased, until a concentration of 1.50 pphr, at which the latex flocculated. This decrease in MST was attributed to the increase in ionic strength of the dispersion medium of the latex.

11.1.1.4 The MST of the latex in the presence of the redox initiator and monomers increased progressively as the TSC of the latices decreased. This was attributed to increasing solvation stabilisation, the desorption of cations present at the surface, and increasing the distance between the rubber particles.

11.1.1.5 The presence of homopolymers of the non-ionogenic hydrophilic monomers (PHEA, PHPA and PHPMA) (ca. 0.2 pphr) in NR latex increased the MST. This was attributed to steric stabilisation and the formation of a hydration layer by the polymers. These stabilisation processes were counteracted by any displacement of the indigenous stabilisers by the added polymers. In the case of PHEMA, the stabilisation processes were insufficient to return the MST to the value of the control.

11.1.2 Reaction kinetics of polymerisation of non-ionogenic hydrophilic monomers in NR latex

11.1.2.1 The gravimetric method for determining the conversion of the monomers to polymers during polymerisation in NR latex was found to be impractical, because the method showed polymer formation at the beginning of the polymerisation even when the most effective inhibitor (Nonox DPPD) was added to the samples prior to the addition of monomers and initiator. Possible reasons for this are 1) the propagation rate coefficient for the polymerisation of the monomers might be higher than that of the rate coefficient for the reaction of the inhibitor with growing polymer radicals present, 2) the water-insoluble inhibitor might suppress the polymerisation at the surface of rubber particles but not in the aqueous phase, and 3) the rate of reaction between the initiator and the monomers might be faster than the rate of reaction

between the inhibitor and the radicals present, i.e., initiator radicals and monomer radicals.

11.1.2.2 The gravimetric method , however, could be used to determine the conversion of the monomers after polymerisation had ceased and the reaction was completed. The inhibitor added to the sample was then able to stop any subsequent polymerisation during the prolonged drying in the vacuum oven (0.16 mm Hg for 18 hours at 90^{o}C).

11.1.2.3 The polymerisation of the monomers in aqueous solution (pH ca. 5) and aqueous ammonia solution (pH ca. 10) gave "complex" conversion-time curves. However, the curves became "simple" when the monomers were polymerised in NR latex. A possible reason for these differences in behaviour is that the water-soluble inhibitor present in the monomers did not interfere with the polymerisation taking place at the surface of the rubber particles, whereas it did interfere with the solution polymerisations.

11.1.2.4 The rates of polymerisation of the four monomers were found to be first-order with respect to initial monomer concentration in all cases. The first-order kinetics indicated that the polymerisations behave as if they were true solution polymerisations. Hence one might assume that the locus of polymerisation occurred mainly in the aqueous phase of the NR latex. Instead, the kinetics were found to conform to zero-order for HEA and HPA, to first-order for HEMA, and to second-order for HPMA when zero-, first-, and second-order curves were plotted for conversion-time data for individual polymerisations. This apparent contradiction is difficult to explain. However, it might be attributed to the heterogeneous nature of NR latex, the solubility of the monomers in the aqueous phase, and the adsorptivity of the monomers and homopolymers of the non-ionogenic hydrophilic monomers towards the rubber particles. Thus the polymerisation might occur at the surface of the rubber particles as well as in the aqueous phase. Polymerisation at the surface would be expected to take place during the initial stage of the polymerisation, i.e., when the monomer concentration was highest.

11.1.2.5 The rate of polymerisation of all of the monomers, with the exception for HEMA, was half-order with respect to initiator concentration. This indicates that the

termination was dominated by a bimolecular reaction between propagating radicals. In the case of HEMA, the order of reaction with respect to initiator was 0.20. It is difficult to offer an explanation for this.

11.1.2.6 The rates of polymerisation of the four monomers were found to be first-order dependence with respect to the dry rubber content (DRC). The first-order dependence with respect to the DRC is also difficult to explain because the presence of hydroperoxide group on the rubber molecule would give rise to half-order. However, the presence of non-rubber in the latex, such as an amine, might bring about termination reactions that are first-order with respect to radical concentration to produce homopolymers. In fact, the characterisation of the products of the polymerisations using the redox initiator at $30^{o}C$ proved that most of the monomers were converted to homopolymers rather than graft copolymers. The increase of rate with increase of the DRC might be attributed to the combination of the two following factors:

1) The proportion of monomer adsorbed at the surface would increase although the actual concentration of adsorbed monomer might decrease as a consequence of the increase of surface area of the rubber particles,

2) A corresponding reduction of volume of the aqueous phase with increase of the DRC.

Therefore, the presence of rubber in NR latex would accelerate rather than retard the polymerisation.

11.1.3 Separation of homopolymers of non-ionogenic hydrophilic monomers and free NR from crude graft copolymers

11.1.3.1 Separation of PHEA and PHPA from NR latex

It was found that the polymerisation of HEA and HPA in aqueous ammonia solution (pH ca. 10) produced no crosslinked polymers, despite the probable presence of crosslinking impurities. These are diesters formed by side-reactions during the preparation of the monomers. The absence of crosslinking was attributed to the presence of ammonia enhancing the solubilities of the monomers and homopolymers of the monomers but not the diesters. It

appears very unlikely that crosslinking occurs between the growing polymer radicals and the diesters. Alternatively, the diesters produced insufficient branching to bind the polymer molecules into an indefinitely large network. The polymers added to NR latex were successfully separated by extraction using IMSA for 6 days at 20°C, recovery being ca. 99.5%.

11.1.3.2 Separation of PHEMA and PHPMA from NR latex

The polymerisation of HEMA and HPMA using a redox initiator at 30°C in aqueous solution containing a non-polar phase such as an NR/petroleum ether-toluene solution or a petroleum ether solution produced precipitated but uncrosslinked polymers, despite the probable presence of crosslinking impurities. These polymers dissolved in IMSA when left overnight at 20°C. The obvious reason for this is that the non-polar crosslinking impurities dissolved readily in the non-polar solvents. It was possible that the crosslinking impurities polymerised in the non-polar solvents, but, if they did, did not interfere with the polymerisation of the monomers in the aqueous solution. When the monomers were polymerised in NR latex (ca. 35% conversion), up to 100% of the homopolymers could be separated implying 0% efficiency of grafting.

11.1.3.3 Separation of free NR

The NR film (ca. 0.5% w/w) dissolved completely in a mixture of petroleum ether (80-100°C) and toluene when allowed to stand at 40°C for 39-55 days. However, the separation of the free NR from the graft copolymers, freed from homopolymers, was unsuccessful because of the collapse of the graft copolymers to form pastes. A possible reason for this is that virtually all the rubber molecules were sufficiently grafted to became insoluble in (though highly swollen by) the non-polar solvent. The polymerisation of the monomers in NR latex was therefore considered in terms of the efficiency of grafting, excluding the degree of grafting and percentage of grafting.

11.1.4 Mechanism of grafting reactions

11.1.4.1 Introduction

In this project, the mechanism of the grafting reactions was investigated by polymerising different types of

monomers and initiators, and by varying the polymerisation temperature.

11.1.4.2 HEA and HPA

The polymerisation of HEA and HPA in NR latex (80-88% conversions) using the redox initiator (0.5 pphr) at a low temperature (30°C) produced zero grafting for HEA. This strongly suggests that 1) no transfer of hydrogen from the rubber molecules to the growing radicals to produce the graft copolymer occurred, and 2) no oxidation of the rubber molecules to produce rubber radicals occurred which could cross-terminate with the growing polymer radicals to form the graft copolymer. In the case of HPA, only a little grafting occurred (up to 17.6% grafting efficiency), presumably by transfer reactions involving NR in NR latex. The transfer reactions were believed to be temperature-dependent, that is to say, the activation energy of the transfer reactions between the growing radicals and rubber molecules is higher than the activation energy of homopolymerisation reactions. When ACA (0.87 pphr) at 62-65°C, which does not attack NR directly, was employed as initiator, the grafting efficiency of the monomers (ca. 52% conversion for each monomer) was approximately for HEA and 51% for HPA. This strongly suggests that the grafting reactions were dominated by transfer reactions to the NR. In addition the mobility of the growing polymer chain radicals will be greater at higher temperatures. At low temperature the reaction may depend upon the monomers moving to the growing radicals.

11.1.4.3 HEMA and HPMA

The polymerisation of HEMA and HPMA in NR latex (33% and 74% conversion respectively) using the redox initiator (0.54 pphr) at 30°C produced a 50% grafting efficiency for HEMA but only a little grafting (6.3%) for HPMA. This was attributed to the lower activation energy for the transfer reactions between the growing polymer radicals of PHEMA and rubber molecules than the activation energy for the transfer reactions between the growing polymer radicals of PHPMA and rubber molecules. However, when the ACA initiator (0.87 pphr) was employed at 62-65°C, the efficiency of the grafting was up to ca. 65% for HEMA and 100% for HPMA. This indicates that the grafting reactions for HPMA at ca. 63°C were not via transfer reactions but via addition reactions between the growing radicals and the

double bonds of the rubber molecules. This strongly suggests that the grafting reactions by which the graft copolymers formed are temperature-dependent.

11.1.5 Preparation of modified NR latices

11.1.5.1 Preparation of crude NR/PHEA and NR/PHPA graft-copolymer latices

The crude graft-copolymer latices could be easily prepared by polymerising the monomers in NR latex (ca. 20 pphr) using ACA as initiator (0.87 pphr) at 62-65^{o}C for about 24 hours. The conversions were ca. 52% for HEA and HPA, and the grafting efficiencies were ca. 85% for HEA and ca. 51% for HPA. The products contained a serum layer (ca. 5% v/v) which could be easily re-mixed by stirring. However, the preparation of the graft-copolymer latices using a low concentration of the redox initiator (0.54 pphr) and at a low temperature (30^{o}C) was unattractive because of reluctance to form graft copolymers.

11.1.5.2 Preparation of crude NR/PHEMA and NR/PHPMA graft-copolymer latices

The crude graft-copolymer latices could easily be prepared by polymerising the monomers in NR latex (ca. 10 pphr) using ACA as initiator (0.87 pphr) at 62-65^{o}C for about 24 hours. The conversions were ca. 44% for HEMA and ca. 52% for HPMA, and the grafting efficiencies were ca. 65% for HEMA and ca. 100% for HPMA. The products contained a serum layer (ca. 52% v/v for HEMA, ca. 40% v/v for HPMA). The serum could be easily re-mixed by stirring. Alternatively, crude NR/PHEMA graft copolymer could be prepared by polymerising HEMA in NR latex (ca. 11 pphr) using the redox initiator (0.54 pphr) at 30^{o}C for about 24 hours. The conversion was 33% and the grafting efficiency ca. 50%. In the case of the crude NR/PHPMA graft, this graft could also be produced by polymerising HPMA (10 pphr) using the redox initiator (0.54 pphr) at 30^{o}C with an activation time of 1.5 hours. The conversion was ca. 42% and the grafting efficiency ca. 33%.

11.1.6 Effect of added PHEA and PHPA upon creaming of NR latex, and creaming of crude graft copolymers

It was found that large quantities of PHEA and PHPA act as creaming agents for NR latex. PHEA and PHPA (20 pphr)

produced serum layers of 15% v/v and 53% v/v respectively. It was observed that creaming of the crude NR/PHEA and NR/PHPA graft-copolymer latices was unlikely to occur because the graft-copolymers would enhance the stability of the latex. In contrast, the creaming of the crude NR/PHEMA and NR/PHPMA graft-copolymer latices did occur. The serum layers were found to be 52% v/v for the crude NR/PHEMA graft-copolymer latex and 40% v/v for the crude NR/PHPMA graft-copolymer latex. It is not clear how such a creaming process occurred. However, it might be attributable to the insolubility of the polymer units bound to the NR particles.

11.1.7 Selected properties of modified NR latices and NR

11.1.7.1 Coagulation of modified NR latices

The mechanical stability of the modified NR latices was difficult to assess because of the excessive foaming which occurred when the MST tests were carried out. However, the latices were easily coagulated using IMS, acetone, IMSA, barium chloride and ferric chloride. Acetic acid is not an effective coagulant for the latices because of the presence of the SLS (3.66 pphr) which acts as stabiliser even at low pH.

11.1.7.2 Vulcanisation behaviour

(i) **Effect of PHEA, PHPA, and SLS upon vulcanisation behaviour**

It was found that PHEA and PHPA act as plastisers and retarder/inhibitor during the vulcanisation of NR. The retardation/inhibition might have been a consequence of the acidic property of the impurities presence in the polymers. No crosslinking was detected using the Monsanto Rheometer 100 in the presence of PHEA (20 - 30 pphr) or PHPA (10-30 pphr). As a matter of fact, some vulcanisation of the blends did occur. This was confirmed by the results for swelling in solvent. The rubber did not dissolve and the swelling was less than for the corresponding unvulcanised films. Failure to observe vulcanisation in the Monsanto Rheometer was attributed to the too powerful plasticising effect of the homopolymers, causing slippage

when the samples were subjected to the Rheometer test. Interestingly, the SLS (3.66 pphr) acts not only as a plasticiser, an anti-reversion, but also as a retarder during vulcanisation of NR.

(ii) **Effect of type of accelerators upon vulcanisation of NR at 100°C**

It was found that the induction period for the CBS/TMTD accelerator combination was longer ca. 15 minutes than that for ZDC when vulcanisation was carried out at 100°C. However, after 1.5 hours vulcanisation, both vulcanisates showed comparable increases in torque.

(iii) **Effect of crude NR grafts upon vulcanisation behaviour of NR**

The rheometric tests showed that the crude NR/PHEA and NR/PHPA graft-copolymers were more difficult to vulcanise than were the crude NR/PHEMA and NR/PHPMA graft-copolymers. This was attributed to the fact that PHEA and PHPA were more effective as plasticisers than were PHEMA and PHPMA.

11.1.7.3 **Tensile stress-strain properties of vulcanised and vulcanised films from modified NR latices**

(i) **Effect of SLS**

SLS (3.66 pphr) doubled the tensile strength and increased by some 50% elongation at break of the NR film. However, the SLS decreased the moduli of the NR.

(ii) **Effect of modified NR prepared using the redox initiator**

Generally, the tensile strengths and moduli of the vulcanised films from the crude NR/PHEA and NR/PHPA graft-copolymers decreased as the initial monomer concentrations increased. This was probably a consequence of the greater retarding effect of PHEA and PHPA upon vulcanisation at high concentrations. The

tensile strengths and moduli of the crude NR/PHEMA and NR/PHPMA graft-copolymers were the same or higher than those of the control. In all cases, the tensile strengths of the vulcanised films were far higher than those of the unvulcanised films. This suggested that crosslinking reaction of the NR during the graft-copolymerisation of the monomers was unlikely to have occurred.

(iii) **Crude graft copolymers prepared using ACA as initiator**

The tensile strengths of the crude NR/PHEMA graft-copolymers and NR/PPMA graft-copolymers were far greater than those of the crude NR/PHEA and NR/PHPA graft-copolymers. This was probably as consequences of i) the crosslinking reaction was more favourable in the presence of the methacrylates than in the presence of the acrylates, ii) the enhancement of strength brought about by the methacrylates is higher than that brought about by the acrylates.

11.1.7.4 Solvent resistance

(i) **Swelling in hydrocarbon solvent**

Unexpectedly, the presence of the hydrophilic polymer units in the graft-copolymers decreased the resistance to swelling in solvent. This was thought to be due to lower crosslink concentrations in the vulcanisates, brought about by the retarding effect of the hydrophilic polymer during vulcanisation. The solvent uptake of the vulcanised films of the crude NR/PHEA and NR/PHPA graft-copolymers increased as the monomer concentrations increased. The solvent uptake of the crude NR/PHEA and NR/PHPA graft-copolymers (10.6 and 14.79 g/g sample respectively) were much higher than those of the crude NR/PHPMA and NR/PHEMA graft-copolymers (2.73 and 3.57 g/g sample respectively), whereas the uptake of the control NR was 2.25 g/g sample.

(ii) **Water absorption**

The vulcanised films from the crude NR/PHEA graft-copolymers absorbed less water than did the controls when a monomer level of 30% or less was used. When higher monomer levels were used, the modified latices showed the same or worse resistance to water. The vulcanised films from the crude NR/PHPA graft-copolymer absorbed less water than those of the control in all cases. However, all the vulcanised films from the crude NR/PHEMA graft-copolymer showed a worse resistance to water than did those of the control, whereas the vulcanised films from the crude NR/PHPMA showed the same or worse resistance to water.

11.1.7.5 Dipping behaviour of the modified NR latices

All the modified NR latices, with the exception of the crude NR/PHPMA graft-copolymer latex, were unsuitable for dipping because the deposits ran down the side of the formers. This was attributed to the increased stability brought about by the SLS (2-3.66 pphr) and perhaps also by the presence of the homopolymers and the low DRCs (25%) of the latices. It was not possible to overcome the stability problem by using a dipping coagulant in combination with a latex heat sensitised using the zinc-ammine system or PVME as sensitiser.

11.2 Suggestions for further work

The investigation of the modification of NR in NR latex using non-ionogenic hydrophilic monomers has yielded many interesting results concerning matters such as:

(i) conditions which decrease and increase the colloid stability of the latex;

(ii) factors which enhance the transfer reactions during graft copolymerisations;

(iii) the prediction of the principal locus for the polymerisation of the monomers in NR latex - if known, this could perhaps be used to increase the grafting efficiency;

(iv) the effect of homopolymers and graft copolymers upon the creaming, vulcanisation behaviour, and selected physical properties of the products,

(v) the effect of SLS added to NR latex as stabiliser upon the dipping behaviour, vulcanisation behaviour, and selected physical properties of NR.

The following are clearly areas where further work is desirable:

(i) Investigation of the kinetics of latex polymerisation using ACA as initiator at different temperatures. The results might be used to draw inferences concerning the activation energies of transfer reactions for the various monomers and NR.

(ii) Experiments using a "cleaner" latex than conventional ammonia-preserved NR latex, e.g., purified NR latex, SBR latex, artificial PI latex, etc. The purpose would be to eliminate or minimise any perturbing effect of the non-rubber constituents in conventional ammonia-preserved NR latex.

(iii) Experiments using more dilute NR latex (lower than 15% DRC) to find out how transition from the "simple" polymerisation behaviour to the "complex" polymerisation behaviour in aqueous media occurs. This may throw some light on polymerisation mechanisms, especially if attempts were made to elucidate the polymerisation mechanism for the monomers in aqueous media.

Appendix 1A Details of addition of stabilisers and monomers to separate portions of NR latex (85.00 g) for preliminary investigation of monomer effect upon stability (Section 6.1.3.1)

material	mass (g)	concentration (% w/w)	level (pphr)
Texofor A-60	0.00 - 10.16	20.0	0.00 - 3.99
Texofor FP-300	0.00 - 11.63	35.0	0.00 - 8.00
SLS	0.00 - 13.56	30.0	0.00 - 7.99
HEA	0.00 - 1.03	undiluted	0.00 - 2.02
HPA	0.00 - 1.03	undiluted	0.00 - 2.02
HEMA	0.00 - 2.00	undiluted	0.00 - 3.93
HPMA	0.00 - 2.00	undiluted	0.00 - 3.93

Appendix 1B. Preparation of stabiliser solutions of high concentration (Section 6.1.3.1)

(i) Texofor A-60 (20% w/w)

An aqueous solution of Texofor A-60 (20% w/w) was prepared by heating to 60^{o}C. The solution precipitated once the temperature reduced to 20^{o}C. The solution was heated to about 35^{o}C prior to use to ensure complete dissolution.

(ii) Texofor FP-300 (35% w/w)

Texofor FP-300 (25.0 g) was added to distilled water (25.0 g), and the mixture stirred thoroughly and kept at 20 $\pm$ 2^{o}C. The stabiliser almost dissolved overnight. To the mixture was added water (21.4 g) to give a 35% w/w solution. The mixture was stirred and kept for few days at 20 $\pm$ 2^{o}C prior to use.

(iii) Sodium lauryl sulphate (30% w/w)

SLS (25.0 g) was added to distilled water (25.0 g) and kept overnight at 20^{o}C. The soap did not dissolve completely. The mixture was then diluted with water (33.3 g) to give a 30% w/w solution, and stirred thoroughly using a clean glass rod. The solution was kept for several days at 20^{o}C. The solution was heated to about 30^{o}C until it was completely dissolved. The sample was then heated to about 25^{o}C prior to use.

Appendix 2 Details of additions of monomers to separate portions of NR latex (85.00 g) for investigation of effects of monomers upon mechanical stability (Section 6.1.3.3)

monomer	mass (g)	concentration[x] (% w/w)	level (pphr)
HEA	8.16	0.00 - 85.78	0.00 - 13.87
HPA	8.17	0.00 - 67.47	0.00 - 10.92
HEMA	8.16	0.00 - 73.53	0.00 - 11.89
HPMA[xx]	8.00	0.00 - 50.00	0.00 - 7.92

x) aqueous solution
xx) as a mixture

Appendix 3 Details of additions of monomers to separate portions of NR latex (800.00 g) for investigation of effect of maturation upon mechanical stability (Section 6.1.3.4)

monomer	mass (g)	concentration[x] (% w/w)	level (pphr)
HEA	74.62	56.75	8.91
HPA	74.77	18.88	2.97
HEMA	74.62	12.73	1.99
HPMA[xx]	74.62	12.74	1.99

x) aqueous solution
xx) as a mixture

Appendix 4 Details of additions of monomers to separate portions of NR latex (1,020 g) for investigation of effect of maturation upon mechanical stability of NR latex containing a having low level of the monomers (Section 6.1.3.5)

monomer	mass (g)	concentration[x)] (% w/w)	level (pphr)
HEA	97.92	6.13	0.99
HPA	97.93	6.12	0.99
HEMA	97.91	6.14	0.99
HPMA	97.92	6.13	0.99

x) aqueous solution

Appendix 5 Details of addition of redox initiator to separate portions of NR latex (85.00 g) for investigation of effect of redox initiator upon mechanical stability (Section 6.1.3.6)

initiator	mass (g)	concentration[a)] (% w/w)	level (pphr)	total (pphr)
$K_2S_2O_8$[b)]	0.00-5.32	0.00-5.94	0.00-0.63	0.00-1.27
$Na_2S_2O_5$	0.00-4.01	0.00-8.10	0.00-0.64	

a) aqueous solution
b) as a mixture

Appendix 6 Details of addition of both redox initiator and monomers to separate portions of NR latex [85.00 g for (i), (ii), and 1,020 g for (iii)] for investigation of effect of both redox initiator and monomer upon mechanical stability (Sections 6.1.3.7.1 to 6.1.3.7.3)

(i) initiator

initiator	mass (g)	concentration[x] (%w/w)	level (pphr)
$K_2S_2O_8$	5.19	3.74	0.38
$Na_2S_2O_5$	3.67	5.31	0.39

(ii) monomer

monomer	mass (g)	concentration[x] (% w/w)	level (pphr)
HEA	8.16	12.25	1.98
HPA	8.16	12.25	1.98
HEMA	8.16	12.25	1.98
HPMA[xx]	8.16	12.25	1.98

(iii) mixtures of initiator and monomer

material	mass (g)	concentration[x] (% w/w)	level (pphr)
$K_2S_2O_8$[xx]	32.32	7.15	0.38
$Na_2S_2O_5$	26.12	9.18	0.39
HEA	48.01	25.02	1.98
HPA	48.00	25.00	1.98
HEMA	48.01	25.02	1.98
HPMA[xx]	48.03	25.05	1.99

[x] aqueous solution
[xx] as a mixture

Appendix 7 Details of addition of redox initiator and monomers to separate portions of NR latex (85.00 g) for investigation of effect of dilution in presence of initiator and monomer upon mechanical stability (Section 6.1.3.8)

final TSC (% w/w)	material	mass (g)	concentration[x] (% w/w)	level (pphr)
55.0	$K_2S_2O_8$[xx]	3.19	6.05	0.38
	$Na_2S_2O_5$	2.70	7.41	0.39
	HEA	4.02	25.37	2.00
	HPA	3.89	26.22	2.00
	HEMA	3.89	26.22	2.00
	HPMA[xx]	3.89	26.22	2.00
	Water	0.00	-	-
50.0	$K_2S_2O_8$	4.19	4.61	0.38
	$Na_2S_2O_5$	4.20	4.76	0.39
	HEA	5.02	20.32	2.00
	HPA	5.02	20.32	2.00
	HEMA	5.02	20.32	2.00
	HPMA[xx]	5.02	20.32	2.00
	Water	5.82	-	-
40.0	$K_2S_2O_8$	4.19	4.61	0.38
	$Na_2S_2O_5$	4.20	4.76	0.39
	HEA	5.02	20.32	2.00
	HPA	5.02	20.32	2.00
	HEMA	5.02	20.32	2.00
	HPMA[xx]	5.02	20.32	2.00
	Water	17.35	-	-

[x] aqueous solution
[xx] as a mixture

Appendix 8 Calculation of effect of redox initiator upon thickness of double layer surrounding particles in NR latex

As mentioned in Section 7.11.3, the thickness of double layer surrounding rubber particles in NR latex is related to the ionic strength (I) by

$$1/K = 744.47\sqrt{\frac{1}{I}}$$

$$\text{where} \quad = 0.5\sum m_i . z_i^2$$

where m_i is the concentration of each ionic species, [ions/cm^3], and z_i is the valency of each ionic species. It was assumed that the contribution of ionic strength of the initial latex could be calculated from the VFA No., the latter being ca. 0.02 g/100 g rubber. The VFA No. of NR latex is mainly acetic acid,

$$CH_3COOH \longrightarrow CH_3COO^- + H^+$$

The ionic species derived from the redox initiator which were taken into account for the calculation were as follows:

$$K_2S_2O_8 \longrightarrow 2\,K^+ + .S_2O_8^{2-}$$

$$Na_2S_2O_5 + H_2O \longrightarrow 2\,Na^+ + 2\,HSO_3^-$$

For the purpose of the calculation, the mass of the latex sample was taken as ca. 100 g and their final DRC as ca. 55%. The variation of ionic strength and $1/K$ for the latex with concentrations of the relevant electrolytes is as follows:

redox initiator (pphr)	concentration of acid and electrolytes, m_i, ($\times 10^{17}$ ions/cm^3)x)			contribution to ionic strength, $m_i . z_i^2$, ($\times 10^{17}$ ions/cm^3)x)						ionic strength (I)	$1/K$	
	CH_3COOH	$K_2S_2O_8$	$Na_2S_2O_5$	CH_3COO^-	H^+	K^+	$S_2O_8^{2-}$	Na^+	HSO_3^-	$0.5\sum m_i . z_i^2$	cm$\times 10^{-8}$	Å
0.00	24.50	-	-	24.50	24.50	-	-	-	-	24.50	47.6	47.6
0.26	24.50	70.79	50.32	24.50	24.50	70.79	141.58	100.64	100.64	231.33	15.5	15.5
0.50	24.50	136.13	96.77	24.50	24.50	136.13	272.26	193.54	193.54	422.24	11.5	11.5
0.80	24.50	217.82	154.83	24.50	24.50	217.82	435.64	309.66	309.66	660.89	9.2	9.2
1.00	24.50	272.28	193.54	24.50	24.50	272.28	544.56	387.08	387.08	820.00	8.2	8.2
1.30	24.50	353.95	251.60	24.50	24.50	353.95	707.90	503.20	503.20	1058.63	7.2	7.2

x) in aqueous phase

Appendix 9A Determination of density of non-ionogenic hydrophilic monomers and their polymers

1. Non-ionogenic hydrophilic monomers

A weighed 25-ml clean pycnometer ($30^{o}C$) was filled with distilled water. The pycnometer was then closed, and the water overflow from the pycnometer was removed carefully by means of tissue paper. The pycnometer containing distilled water was then weighed accurately. The volume of the pycnometer was calculated as follows:

$$V\ (30^{o}C) = \frac{m_2 - m_1}{\rho_w} \quad \text{.....A.8.1}$$

where m_1 is the mass of pycnometer, m_2 is the mass of pycnometer containing water, and ρ_w is the density of water at $30^{o}C$, being 0.9957 g/cm^3. The respective monomer ($30^{o}C$) was added to the calibrated pycnometer ($30^{o}C$). The monomer overflow from the pycnometer was removed carefully by means of tissue paper. The pycnometer containing monomer was weighed accurately. The density of monomer was calculated as follows:

$$\rho_m = \frac{m_3 - m_1}{V} \quad \text{.....A.8.2}$$

where ρ_m is the density of monomer, m_3 is the mass of pycnometer containing polymer, m_1 is the mass of pycnometer, and V is the volume of the pycnometer. The determination of the density of each of the monomers was carried out in duplicate. The results of the determinations are given in Appendix 9B.

2. Polymers of non-ionogenic hydrophilic monomers

A 25-ml clean pycnometer was almost filled with distilled water ($30^{o}C$). The pycnometer was closed gently. The water overflow from the pycnometer was removed as previously. The pycnometer was weighed accurately. An accurate weighed mass of polymer was then gently added to the water in the pycnometer. The water overflow from the pycnometer was removed as previously. The pycnometer containing water and polymer was weighed immediately. The volume of water displaced, which corresponded to the volume of the polymer,

was calculated as follows:

$$V_p = \frac{m_4 - m_2}{\rho_w} \quad \text{.....A.8.3}$$

where V_p is the volume of polymer, m_4 is the mass of pycnometer containing water, ρ_w is the density of water (30°C). The density of polymer was then calculated as follows:

$$\rho_p = \frac{m_p}{V_p} \quad \text{.....A.8.4}$$

where m_p is the mass of polymer, V_p is the volume of polymer, and ρ_p is the density of polymer. The determination of the density of each of the polymers was carried out in duplicate. The results of the determinations are given in Appendix 9B.

Appendix 9B Densities of non-ionogenic hydrophilic monomers and their polymers at 30°C

monomer	polymer	density at 30°C (g/cm^3)	
		monomer	polymer
HEA	-	1.0980	-
-	PHEA	-	1.3330
HPA	-	1.0440	-
-	PHPA	-	1.2598
HEMA	-	1.0632	-
-	PHEMA	-	1.2961
HPMA	-	1.0206	-
-	PHPMA	-	1.2391

Appendix 10 Derivation of equation used for calculating of conversion of monomer using the dilatometer

The volume of a monomer in a capillary is as follows:

$$V_m = \pi r^2.h \quad \text{.....A.9.1}$$

where V_m is the volume of monomer in the capillary, r is the radius of the capillary, and h is the height of monomer in the capillary. If the monomer is polymerised to 100% conversion, the volume contraction of monomer (ΔV_{100}) is as follows:

$$\Delta V_{100} = V_m - V_p = \pi r^2 (h_{100} - h_0) = \pi r^2 . \Delta h_{100} \text{....A.9.2}$$

$$\text{also} \quad \Delta V_{100} = \frac{M_m}{\rho_m} - \frac{M_p}{\rho_p} \text{.....A.9.3}$$

where h_0 is the original height of monomer in the capillary (cm) at time = 0, h_{100} is the height of monomer in the capillary (cm) after complete polymerisation, and Δh_{100} is the maximum value of Δh (Figure A.9), i.e., at 100% conversion (cm). In equation A.9.3, M_m is the initial mass of monomer (g), ρ_m is the density of monomer (g/cm^3), M_p is the mass of polymer (g) in which at 100% conversion, $M_p = M_m$, and ρ_p is the density of polymer (g/cm^3).

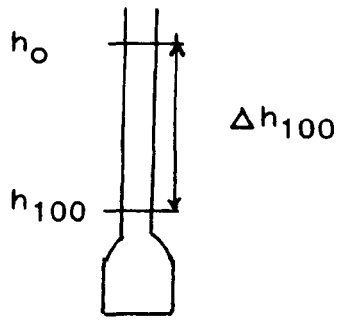


Figure A.9 Volume contraction of a monomer in a capillary

Equation A.9.3 can be transformed to

$$\Delta h_{100} = \frac{M_m (\rho_p - \rho_m)}{\rho_m . \rho_p . \pi r^2} \text{.....A.9.4}$$

Assuming that the conversion is proportional to the volume contraction of monomer, the conversion at time t is the ratio of drop in height of meniscus in the dilatometer (Δh) to the drop in height corresponding to 100% conversion, i.e.,

$$\text{conversion (\%) at time t} = \frac{\Delta h}{\Delta h_{100}} \times 100 \quad \text{.....A.9.5}$$

Substituting Equation A.9.4 into Equation A.9.5 yields,

$$\text{conversion (\%) at time t} = \frac{\pi r^2 . \rho_m . \rho_p (\Delta h)}{M_m(\rho_p - \rho_m)} \times 100 \quad \text{.....A.9.6}$$

In this work, r was constant at 1.50 mm. Hence Equation A.9.6 can be simplified as follows:

$$\text{conversion (\%) at time t} = \frac{7.069\, \rho_m . \rho_p (\Delta h)}{M_m(\rho_p - \rho_m)} \quad \text{A.9.7}$$

Appendix 11A Details of additions of monomers to water for investigation of rate conversion of non-ionogenic hydrophilic monomers in the water (Section 6.2.3.2.2)

material	concentration (% w/w)[x]	mass (g)				level (mol/l solution)	pH (27.5°C)
water	-	40.96	39.24	39.27	37.34	-	7.03
$K_2S_2O_8$	4.00	0.78	0.78	0.78	0.78	2.04×10^{-3}	3.60
$Na_2S_2O_5$	4.00	0.78	0.78	0.78	0.78	2.90×10^{-3}	4.55
HEA	10.00	14.31	-	-	-	21.56×10^{-2}	4.00
HPA	10.00	-	15.95	-	-	21.57×10^{-2}	4.20
HEMA	10.00	-	-	15.96	-	21.59×10^{-2}	4.65
HPMA	10.00	-	-	-	17.79	21.54×10^{-2}	5.00
total,(g)	-	56.83	56.75	56.79	56.69	-	-
pH (30°C)	-	5.05	5.00	5.45	5.40	-	-
product	-	L	SP	lump	P	-	-

L = liquid; SP = slightly precipitated; P = precipitated

Appendix 11B Details of additions of monomers and initiator to aqueous ammonia solution for investigating effect of rate of conversion of non-ionogenic hydrophilic monomers in the aqueous ammonia solution (Section 6.2.3.2.2)

material	concentration (% w/w)	mass (g)				level (mol/l solution)	pH (27.5°C)
NH_4OH	1.50	40.86	39.23	39.11	37.21	-	11.15
$K_2S_2O_8$	4.00	0.78	0.78	0.78	0.78	2.04×10^{-3}	11.35
$Na_2S_2O_5$	4.00	0.78	0.78	0.78	0.78	2.90×10^{-3}	10.00
HEA	10.00	14.27	-	-	-	21.56×10^{-2}	10.30
HPA	10.00	-	15.95	-	-	21.57×10^{-2}	10.38
HEMA	10.00	-	-	15.89	-	21.37×10^{-2}	10.40
HPMA	10.00	-	-	-	17.73	21.54×10^{-2}	10.45
total (g)	-	56.70	56.74	56.56	56.50	-	-
pH (30°C)	-	10.15	10.25	10.40	10.40	-	-
product	-	L	L	P	P		

L = liquid; P = precipitated (white)

Appendix 12 Details of additions of monomers to NR latex for investigating effect of water as diluent upon rate of conversion of monomers (Section 6.2.3.2.3)

material	concen-tration (% w/w)	mass (g)				level (mol/l latex)			
NR latex (Batch C)	-	15.25	15.24	15.29	15.22	-	-	-	-
water	-	28.78	28.32	28.39	28.31	-	-	-	-
$K_2S_2O_8$	4.00	3.99	3.64	3.65	3.63	8.77×10^{-3}	8.84×10^{-3}	8.85×10^{-3}	8.83×10^{-3}
$Na_2S_2O_5$	4.00	3.99	3.64	3.65	3.63	12.47×10^{-3}	12.57×10^{-3}	12.58×10^{-3}	12.55×10^{-3}
HEA	10.00	9.86	-	-	-	13.81×10^{-2}	-	-	-
HPA	9.09	-	9.83	-	-	-	11.29×10^{-2}	-	-
HEMA	10.03	-	-	9.86	-	-	-	12.36×10^{-2}	
HPMA	9.09	-	-	-	9.86	-	-	-	10.25×10^{-2}
pH (30°C)	-	9.00	9.02	9.60	9.60	-	-	-	-
DRC, %	-	15.06	15.07	15.07	15.06	-	-	-	-

Appendix 13 Details of additions of monomers and initiator to NR latex for investigating effect of nature of diluent upon rate of polymerisation of hydroxypropyl acrylate (HPA) in NR latex (Section 6.2.3.2.4)

material	concen-tration (% w/w)	mass (g)			level (mol/l latex)		
		pH 9.00	pH 9.30	pH 10.12			
NR latex (Batch C)	-	22.98	22.89	22.97	-	-	-
water	-	14.66	-	-	-	-	-
NH_4OH	0.50	-	14.59	-	-	-	-
NH_4OH	1.50	-	-	14.73	-	-	-
$K_2S_2O_8$	4.00	1.19	1.18	1.16	3.09×10^{-3}	3.16×10^{-3}	3.14×10^{-3}
$Na_2S_2O_5$	4.00	1.19	1.18	1.16	4.32×10^{-3}	4.42×10^{-3}	4.39×10^{-3}
HPA	10.00	15.65	15.59	15.69	21.51×10^{-2}	21.51×10^{-3}	21.61×10^{-3}
DRC, %	-	24.76	24.76	24.72	-	-	-

Appendix 14 Details of additions of monomers and initiator to NR latex for investigating effect of type of monomers upon rate of conversion using aqueous ammonia solution as diluent (Section 6.2.3.2.5)

material	concentration (% w/w)	mass (g)				level (mol/l latex)			
NR latex									
(Batch C)	-	22.88	23.11	23.06	23.04	-	-	-	-
NH_4OH [x)]	1.50	16.52	14.81	14.78	12.99	-	-	-	-
$K_2S_2O_8$	4.00	1.17	1.19	1.18	1.18	3.13×10^{-3}	3.15×10^{-3}	3.15×10^{-3}	3.14×10^{-3}
$Na_2S_2O_5$	4.00	1.17	1.19	1.18	1.18	4.32×10^{-3}	4.34×10^{-3}	4.33×10^{-3}	4.33×10^{-3}
HEA [x)]	10.00	13.87	-	-	-	21.27×10^{-2}	-	-	-
HPA [x)]	10.00	-	15.41	-	-	-	21.22×10^{-2}	-	-
HEMA [x)]	10.00	-	-	15.47	-	-	-	21.13×10^{-2}	-
HPMA [x)]	10.00	-	-	-	17.13	-	-	-	21.18×10^{-2}
pH (30^0C)	-	9.85	9.45	10.25	10.10	-	-	-	-
DRC, %	-	24.71	24.88	24.84	24.88	-	-	-	-

x) in a 1.5% aqueous ammonia solution

Appendix 15 Details of additions of monomers and initiator to NR latex for investigating effect of sodium lauryl sulphate (SLS) upon rate of polymerisation of HPMA (Section 6.2.3.2.6)

material	concentration (% w/w)	mass (g)		level (mol/l latex)	
		SLS (0 pphr)	SLS (1 pphr)	SLS (0 pphr)	SLS (1 pphr)
NR latex	-	23.04	23.75	-	-
NH_4OH	1.50	12.99	12.32	-	-
$K_2S_2O_8$	4.00	1.18	1.18	3.14×10^{-3}	3.14×10^{-3}
$Na_2S_2O_8$	4.00	1.18	1.18	4.33×10^{-3}	4.33×10^{-3}
HPMA	10.00	17.13	17.15	21.18×10^{-3}	21.18×10^{-3}
pH (30^0C)	-	10.60	10.60	-	-
DRC, %	-	24.98	24.98	-	-

Appendix 16 Details of additions of monomers and initiator to NR latex for investigation of order of reaction with respect to initial monomer concentration (Section 6.2.3.2.7)

material	concen-tration (% w/w)	mass (g)	level (mol/l latex)	DRC (%)
NR latex	-	23.40	-	-
$K_2S_2O_8$	4.00	0.80	2.09×10^{-3}	
$Na_2S_2O_5$	4.00	0.80	2.89×10^{-3}	
HEA	10.00-15.00	14.20-23.80	$(21.53-54.13) \times 10^{-2}$	24.83
NH_4OH	1.50	7.70-17.30		
HPA	10.00-15.00	15.90-26.60	$(21.59-54.18) \times 10^{-2}$	24.83
NH_4OH	1.50	4.90-15.60		
HEMA	10.00	13.50-23.30	$(18.08-31.19) \times 10^{-2}$	24.71
NH_4OH	1.50	8.50-16.10		
HPMA	10.00	15.00-26.30	$(18.13-31.79) \times 10^{-2}$	24.71

Appendix 17 Details of additions of monomers and initiator to NR latex for investigation of order of reaction with respect to monomer concentration during course of polymerisation occurring (Section 6.2.3.2.8)

material	concen-tration (% w/w)	mass (g)				level (mol/l latex)			
NR latex	-	23.04	23.16	22.87	22.89				
NH_4OH	1.50	17.03	14.85	15.74	13.99				
$K_2S_2O_8$	4.00	0.79	0.79	0.78	0.78	2.10×10^{-3}	2.08×10^{-3}	2.08×10^{-3}	2.08×10^{-3}
$Na_2S_2O_5$	4.00	0.79	0.79	0.78	0.78	2.89×10^{-3}	2.87×10^{-3}	2.87×10^{-3}	2.87×10^{-3}
HEA	10.00	13.98	-	-	-	21.53×10^{-3}	-	-	-
HPA	15.00	-	26.33	-	-	-	54.18×10^{-3}	-	-
HEMA	10.00	-	-	15.35	-	-	-	21.18×10^{-3}	
HPMA	10.00	-	-	-	17.11	-	-	-	21.15×10^{-3}
pH (30°C)	-	10.05	9.95	10.25	10.45	-	-	-	-
DRC, %	-	24.83	24.83	24.71	24.69	-	-	-	-

Appendix 18 Details of additions of monomers and initiators to NR latex for investigating effect of initial initiator concentration upon rate of polymerisation (Section 6.2.3.2.9)

material	concen-tration (% w/w)	mass (g)				concentration (mol/l latex)			
NR latex	-	23.40	23.40	23.40	23.40	-	-	-	-
NH_4OH	1.5	15.20-16.80	15.20-16.40	13.70-16.70	11.90-14.90	-	-	-	-
HEA	10.0	14.10	-	-	-	21.26×10^{-2}			
HPA	10.0	-	15.70	-	-		21.32×10^{-2}		
HEMA	10.0	-	-	15.70	-			21.13×10^{-2}	
HPMA	10.0	-	-	-	17.50				21.15×10^{-2}
$K_2S_2O_8$	4.0	0.50 - 1.10	0.50 - 1.10	0.50 - 2.00	0.50 - 2.00	$(1.31-2.88)\times10^{-3}$	$(1.31-2.88)\times10^{-3}$	$(1.31-5.23)\times10^{-3}$	$(1.31-5.23)\times10^{-3}$
$Na_2S_2O_5$	4.0	0.50 - 1.10	0.50 - 1.10	0.50 - 2.00	0.50 - 2.00	$(1.81-3.98)\times10^{-3}$	$(1.81-3.98)\times10^{-3}$	$(1.81-7.22)\times10^{-3}$	$(1.81-7.22)\times10^{-3}$
pH (30°C)	-	10.01-10.10	10.00-10.05	10.45-10.48	10.53-10.55	-	-	-	-
DRC, %	-	24.84	24.71	24.69	24.69				

Appendix 19 Details of additions of monomers and initiator to NR latex for investigating effect of dry rubber content upon rate of polymerisation (Section 6.2.3.2.10)

material	concen-tration (%)	mass (g)				concentration (mol/l latex)			
NR latex	-	14.30-28.50	14.30-28.50	14.30-28.50	14.30-28.50	-	-	-	-
NH_4OH	1.5	12.20-26.40	10.50-24.70	11.00-25.20	9.20-14.30	-	-	-	-
$K_2S_2O_8$	4.0	0.80	0.80	0.80	0.80	2.08×10^{-3}	2.08×10^{-3}	2.08×10^{-3}	2.08×10^{-3}
$Na_2S_2O_5$	4.0	0.80	0.80	0.80	0.80	2.87×10^{-3}	2.87×10^{-3}	2.87×10^{-3}	2.87×10^{-3}
HEA	10.0	14.20	-	-	-	21.53×10^{-2}	-	-	-
HPA	10.0	-	15.90	-	-	-	21.59×10^{-2}	-	-
HEMA	10.0	-	-	15.70	-	-	-	21.02×10^{-2}	-
HPMA	10.0	-	-	-	17.50	-	-	-	21.15×10^{-2}
DRC, %	-	14.30-28.50	15.18-30.25	15.18-30.25	15.09-30.09	-	-	-	-
pH (30^0C)	-	9.91-10.18	9.90-10.08	10.25-10.35	10.40-10.50	-	-	-	-

Appendix 20 Preparation of NR petroleum ether-toluene solution (1.42% w/w)

NR films were prepared by casting NR latex on to separate ceramic plates. The films were then dried at 20^{o}C for about 2 weeks and then in a vacuum oven (0.16 m Hg) at 50^{o}C for 30 minutes. The films (ca. 1 g) were each added to the petroleum ether-toluene (1:1 by volume) (ca. 50 g). The samples were kept in an oven at 40^{o}C until a clear solution was obtained (63 days). The solutions were then allowed to stand in a fume cupboard at 20^{o}C until a concentration of 1.42% w/w was achieved.

Appendix 21 Preparation of 20% vulcanising dispersion for investigating selected physical properties of modified NR

The method used for the preparating of this dispersion was as follows: The requisite amounts of water, sodium hydroxide solution, Vulcastab LW and Dispersol LN were added to a 2-l ball mill in that order. To these were then added the requisite amounts of the vulcanising agents: sulphur, zinc oxide, stearic acid, CBS, TMTD in that order. The composition was as shown in Table A.21. The ingredients were then ball-milled for 6 days to ensure a good dispersion.

Table A.21 Composition of 20% vulcanising dispersion for investigating selected physical properties of modified NR

ingredient	parts by weight
sulphur	64.0
zinc oxide	128.0
stearic acid	25.0
CBS	25.0
TMTD	8.0
potassium hydroxide (as 10% aqueous solution)	1.5
Vulcastab LW (as 20% aqueous solution)	0.5
Dispersol LN	10.0
water	988.0
	1250.0

Appendix 22 Preparation of 50% vulcanising dispersion containing ZDC accelerator

The method used for the preparation of this dispersion was similar to that given in Appendix 21 with the exception that the composition differed. The composition was as shown in Table A.22. The ingredients were then ball-milled for at least 3 days to ensure good dispersion.

Table A.22 Composition of 50% vulcanising dispersion for investigating effect of ZDC accelerator upon vulcanisation behaviour of NR at 100°C

ingredient	parts by weight
sulphur	33.3
zinc oxide	50.0
ZDC	16.7
potassium hydroxide (as 10% aqueous solution)	0.2
vulcastab LW (as 20% aqueous solution)	0.2
methyl cellulose	0.2
Dispersol LN (10%)	4.0
water	95.4
	200.0

Appendix 23 Preparation of 18% vulcanising dispersion for dipping investigation

The requisite amounts of water, sodium hydroxide solution, Vulcastab LW and Dispersol LN were added to a 2-l ball mill in that order. To these were then added the requisite amounts of the vulcanising agents : sulphur, zinc oxide, CBS, TMTD in that order. The ingredients were then ball-milled as previously (Appendices 21, and 22). The composition is as shown in Table A.23.

Table A.23 Composition of 18% vulcanising dispersion for investigating dipping behaviour of modified NR latices

ingredient	parts by weight
sulphur	90.6
zinc oxide	90.6
CBS	32.9
TMTD	10.9
potassium hydroxide (as 10% aqueous solution)	1.5
Vulcastab LW (as 20% aqueous solution)	0.5
Dispersol LN	10.0
water	1013.0
	1250.0

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