EFFECTS OF WATER-SOLUBLE POLYMERS UPON SOME PROPERTIES OF NATURAL RUBBER LATEX

A thesis submitted to the
COUNCIL FOR NATIONAL ACADEMIC AWARDS, ENGLAND
in partial fulfilment of the
requirements for the degree of
DOCTOR OF PHILOSOPHY

by

N.M.V.Kalyani

London School of Polymer Technology
The Polytechnic of North London
Holloway Road
London N7 8DB

January 1988

To my parents

ABSTRACT

EFFECTS OF WATER-SOLUBLE POLYMERS UPON SOME PROPERTIES OF NATURAL RUBBER LATEX

by

N.M.V.KALYANI

An investigation of the effects of various water-soluble polymers upon some properties of natural rubber latex has been carried out. All the polymers, which were of two principal types, distinguished according to the rate of addition of polymerisation reactants, were prepared by free-radical initiated solution polymerisation. Two types of monomers, namely, ionisable hydrophilic monomers and hydrophobic monomers were used in the preparation of polymers.

Both types of polymers, referred to as Type 1 and Type 2, were principally characterised by viscometry, hydrophilicity assessment and infra-red analyses. It has been found that such characteristics of these polymers as molecular weight, composition distribution and hydrophilicity are dependent upon the method used for their preparation. Explanations which have been suggested for this dependence accord with theoretical predictions.

It has also been found that certain properties of natural rubber (NR) latex such as mechanical stability (MST), viscosity, zinc-oxide thickening, heat-sensitivity and creaming can be modified with the addition of water-soluble polymers and that the extent to which each of these properties is modified depends upon the characteristics of the added polymer. The extent of the modification of MST and viscosity of NR latex greatly depended upon both the molecular weight and composition of the added polymer. The influence of composition of the added polymer in modifying zinc-oxide thickening was found to be more important than that of molecular weight. Even though the effects of polymers of Type 1 and Type 2 upon the properties of NR latex were generally similar it has not been able to make proper comparisons between the effects of these two types of polymers as their characteristics were different.

Advanced studies undertaken in connection with the programme of research in partial fulfilment of the requirements of the degree:

1. A course of postgraduate lectures and tutorials on the theory of the stability of lyophobic colloids and surface chemistry.

2. A course of postgraduate lectures and tutorials on the theories of emulsion polymerisation.

3. A course of guided study on the theory of free-radical initiated homopolymerisation and copolymerisation in solution.

4. A conference held at the Malaysian Rubber Producers Research Association, Brickendonbury, Hertfordshire, in May 1984, entitled "Developments in Natural Rubber Science and Technology".

5. A conference organised by Plastics and Rubber Institute in May, 1985 at the Scientific Societies' Lecture Theatre, Savile Row, London.

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to Dr. D.C. Blackley, Director of studies, for his guidance, encouragement and patience during the tenure of this work. I also wish to express my gratitude to Mr. D.M. Hill, Industrial supervisor, for his interest and useful suggestions during the tenure of this work.

I would also like to thank Dr. O.S. Peries, former Director of Rubber Research Institute of Sri Lanka, who made this opportunity for me and Dr. A.de.S. Liyanage, Director of Rubber Research Institute of Sri Lanka, for approving my leave enabling me to complete this degree.

I am very grateful to Dr. A.C. Haynes, who gave me the benefit of his time and his skill at all times.

I wish to thank Dr. S. Holding of RAPRA, who carried out molecular weight determination on my behalf.

I am also grateful to the British Council, Rubber Research Institute of Sri Lanka, and Food and Agriculture Organisation of the United States for providing the financial support during the tenure of this work.

Finally, the assistance extended to me by the staff of the library and the technicians of the London School of Polymer Technology is gratefully acknowledged.

CONTENTS

CHAPTER ONE

INTRODUCTION

1.1 Definition of a latex

A latex is a stable dispersion of a hydrophobic polymeric material in an aqueous medium. Hence it is an essentially two-phase system, consisting of a disperse phase and a dispersion medium . The disperse phase may be a polymer of single olefinic organic compound or a copolymer of two or more such compounds. The polymer particles, which constitute the disperse phase, are usually spherical in shape, are of colloidal dimensions, say between 30 and 500nm in diameter and are composed of a large number of polymer chains having molecular weights in the range 10^5-10^7. A latex, and more generally any colloidal dispersion, in which the dispersed phase remains essentially as discrete, single particles is said to be stable, although not in the absolute thermodynamic sense but in the kinetic sense.

1.2 Types of rubber latices

Apart from any classification based on the chemical nature of the disperse phase, rubber latices are classified generally in to three groups as follows:

1. Natural rubber latices: these are concentrated

and purified forms of the latex obtained from the botanical source, Heavea brasiliensis, one of the members of the family Euphorbiaceae, which is cultivated in tropical regions.

2. Synthetic rubber latices: these are produced from the corresponding monomers by the process known as emulsion polymerisation, using an aqueous dispersion medium.

3. Artificial rubber latices: these are produced by dispersing the bulk polymers in an aqueous medium.

1.3 Natural rubber latex

Fresh natural rubber (NR) latex contains sugars, proteins, lipids, carotenoids, mineral salts, enzymes and numerous other nitrogenous substances, in addition to water and rubber hydrocarbon. Many of these non-rubber constituents are dissolved in the aqueous phase of the latex, some are adsorbed at the surface of the rubber particles, and others are suspended in the latex. It has been shown that in fresh NR latex the non-rubber constituents which are adsorbed on the rubber particles are mainly proteins and lipid materials, possibly in the form of a complex. At least some of these proteins are phosphoproteins(1), and at least some of the lipids are phospholipids(2). The rubber hydrocarbon is linear cis-1,4-polyisoprene of high molecular weight, and occurs as molecular aggregates in the form of discrete particles which are usually spherical in shape with diameters ranging from 15nm to 3 μm(3). However, in latex from certain mature clones, those particles of medium and large size may be pear-shaped.

1.4 Preservation of NR latex

NR latex becomes contaminated by micro-organisms on tapping and during collection. Under tropical conditions, these micro-organisms multiply rapidly by utilising some of the non-rubber constituents in latex, with the production of certain acids. This is followed by the disintegration of the protective protein-lipid layer surrounding the latex particles leading to the destabilisation of latex. Thus it is necessary to add a preservative in order to keep the latex as a fluid until it is ready for processing. Preservation is normally achieved by adding up to 1.0% (w/w on the aqueous phase) of ammonia. Ammonia being a good biocide has several advantages; it controls the proliferation of bacteria, neutralises the free acids formed in the latex, helps in the precipitation of heavy metals such as magnesium, and hydrolyses the interfacial proteins and phospholipids, thereby making the latex more stable. The hydrolysis of phospholipids occurs more rapidly than does that of the proteins, so that by the time ammoniated and concentrated latex has reached the industrial user, the phospholipids have become converted to fatty-acid soaps, among other products, whilst much of the protein remains unhydrolysed. The interfacial film at this stage consists essentially of a soap-protein mixture, the composition of which changes as the latex ages.

1.5 Colloidal instability of latices

In latices, as in colloidal dispersions in general, frequent encounters between particles occur due to the Brownian movement, to gravity (creaming and sedimentation), and to convection. Whether such encounters result in permanent contact, or whether the particles rebound and remain free, is determined by the forces which are operative between the particles. If the attractive forces, which are assumed to be of the London-Van der Waals type, are larger than the repulsive forces, interaction between two or more particles may first cause the particles to cohere to give a loose aggregate and then subsequently to coalesce to give a single larger particle. The repulsive forces, which confer colloid stability upon the latex, are a consequence of one or more of the following factors:

1. the presence of electric charges at the particle surface.

2. the presence of adsorbed macromolecules at the particle surface.

3. the presence of bound water molecules at

the particle surface.

4. the presence of macromolecular substances dissolved in the dispersion medium.

The types of stabilisation conferred by these four factors are known as electrostatic, steric, solvation and exclusion stabilisation respectively. The stability imparted by macromolecules is of particular importance of this work, and so is reviewed in Chapter 2. The theories which have been developed for the stability of lyophobic colloids are discussed in Chapter 3.

1.6 Origin of the present investigation

Water-soluble polymers, such as proteins, cellulose derivatives and polyacrylates, are widely used as colloid stabilisers, viscosity enhancers and creaming agents for polymer latices. Reports concerning the effects of added macromolecules on the colloid stability of both aqueous and non-aqueous lyophobic colloids have been published in the literature. However, it appears that little attention has been given to possible correlations between the characteristics of the added water-soluble polymer and its influence upon such properties of rubber latices as mechanical stability,viscosity, and tendency to cream. It was thought that a systematic investigation of the effects of water-soluble polymers of various characteristics upon the properties of rubber latices would usefully extend our knowledge in this area, as well as being academically challenging.

1.7 Objectives of the present investigation

In this research programme, it was intended to investigate the effects various water-soluble polymers upon some selected properties of NR latices. In all cases, the water-soluble polymers have been prepared by solution polymerisation. The polymers were of two principal types, distinguished according to the rate of addition of polymerisation reactants, *i.e*, the monomers and the initiator, to the reaction system used for their preparation. The polymers of the first type were prepared by adding the polymerisation reactants over a rather short period of time, *i.e*, 20 minutes. In the preparation of polymers of the second type, the addition polymerisation reactants was made over a long period, *i.e*, about 6 hours. This second method was employed in order to overcome the problem of compositional heterogeneity which is bound to occur if monomers of widely differing monomer reactivity ratios are copolymerised by a conventional batch process.

It was expected that these polymers would adsorb to varying extents at the rubber-water interface, and that they affect properties of the latex such as colloid stability and viscosity. It is reasonable to suppose that the effects of a water-soluble polymer upon the properties of a latex will depend on such characteristics of the polymer as

1. the molecular weight

2. the composition, in particular, the balance between hydrophilic and hydrophobic units in the polymer

3. the composition distribution within the polymer

4. the degree of branching of the polymer molecule

The intention was to carry out a broad survey to obtain general information concerning the correlations between these polymer variables and effects upon some properties of NR latex, using the polymers of the first type, and secondly, to carry out a more detailed investigation to seek correlations between more important polymer characteristics, and selected properties of latex using polymers of the second type.

The molecular weight of the polymer was varied by controlling the rate of polymerisation, and by varying the monomer:solvent ratio. The rate of polymerisation was controlled by using various levels of initiator in the initial reaction mixture. The composition of the polymer was varied by using different types of monomers in various molar ratios in the initial reaction mixture. The composition distribution within the polymer was altered by using various molar ratios of comonomer pairs of noticeably different reactivity ratios. Branched polymers were prepared by using a small amount of a tetrafunctional monomer such as ethylene glycol dimethacrylate, and the degree of branching of the polymer was varied by varying the level of this monomer. The use of this branching agent was also expected to cause the molecular weight of the polymer to increase. Therefore it was in principle also possible to study how the effects of linear polymers of high molecular weight upon the properties of NR latex differ from those of branched polymers of similar molecular weight.

The polymers were principally characterised by viscometry, hydrophilicity tests, and infra-red spectroscopy.

It was intended to carry out a broad survey on the effects of polymers prepared by the first method upon such properties of NR latex as

1. mechanical stability
2. viscosity
3. zinc-oxide thickening
4. heat sensitivity
5. creaming

and then to restrict the more detailed investigation to certain selected properties only.

It was also expected these water-soluble polymers would modify the properties of NR latex either by dissolving in the aqueous phase or by adsorbing at the rubber-water interface, or perhaps by both. The ability of the polymer to dissolve or adsorb is dependent on the polymer characteristics. The possible effects of each of the polymer characteristics upon its adsorption at the rubber-water interface, and hence upon the properties of latex can be outlined as follows:

1. The molecular weight of the polymer plays an important role in determining its adsorption tendency at the rubber-water interface. For a given type of polymer the higher the molecular weight, the greater would be the adsorption tendency. The adsorbed polymer would enhance the colloid stability either by a steric mechanism alone or by a combined steric and electrostatic mechanism, depending upon its composition. It would also enhance the hydration stabilisation of latex, if the adsorbed polymer facilitates the hydration of the particle surface. The adsorption would also affect the viscosity of the latex because of the increase in the effective hydrodynamic size of the particles. If the polymer does not adsorb at all, the dissolved polymer would still be expected to affect the viscosity of the latex by

increasing the viscosity of the dispersion medium. The magnitude of this effect would be expected to increase with increasing molecular weight of the polymer.

2. The composition of the polymer would also affect its adsorption tendency. The adsorption tendency of more hydrophobic polymers would be expected to be higher than that of less hydrophobic polymers. However, there should be an optimum hydrophobicity of the polymer at which the maximum enhancement of the colloid stability would be observed. Beyond this, the efficiency of the polymer as a steric stabiliser would decrease because of the absence of sufficient hydrophilic groups, which act as stabilising moieties through their tendency to mix with the molecules of the dispersion medium.

3. The composition distribution of the polymer would also be important, because the adsorption of a polymer having a wide compositional distribution would be different from that of a polymer having a narrow compositional distribution. This is because, if the compositional distribution of the polymer is narrow, the composition of the polymer making up the polymer is approximately uniform. So the adsorption tendency of these polymer chains would be expected to be the same. In contrast, if the compositional distribution of the polymer is wide, the composition of the polymer chains making up the polymer is far from uniform. Therefore the adsorption

tendency of these polymer chains would not be expected to be the same.

4. The degree of branching would also be expected to affects its adsorption tendency at the rubber-water interface. Assuming that the branched polymers are of high molecular weight, they are expected to show a high tendency to adsorb at the rubber-water interface. The tendency of a branched polymer to adsorb at the rubber-water interface would be expected to increase with increasing the degree of branching. However, the ability of a branched polymer to enhance the colloid stability of a latex would be expected to be lower than that of a linear polymer of similar molecular weight, because of differences in conformations of these two types of polymers at the rubber-water interface, as shown in Fig. 1.1. Therefore

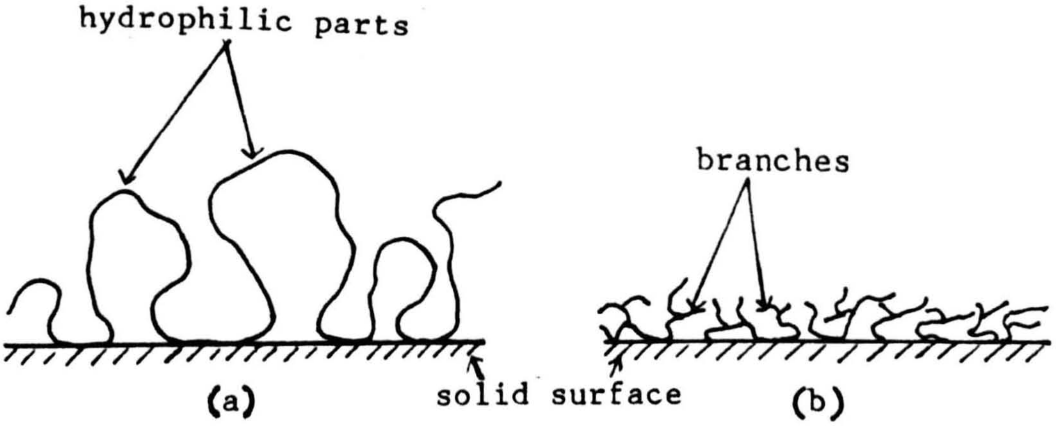


Fig. 1.1 : Schematic representation of conformations of (a) unbranched and (b) branched polymers of high molecular weight at a solid/liquid interface

the effects of branching itself would be expected to be as follows:

1. to enhance the adsorption tendency because multipoint adsorption is facilitated;

2. to reduce the enhancement of stability because extension of hydrophilic moieties into aqueous phase is discouraged.

This research programme was designed to explore and test some of these predictions in a systematic way.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In this chapter, the literature pertaining to the behaviour of water-soluble polymers such as cellulose derivatives, polyacrylates, and proteins in aqueous polymer latices is reviewed. In particular, those publications concerned with technological investigations of the effects of added water-soluble polymers upon such properties of latices as stability, heat-sensitivity, thickening and creaming are reviewed. Reference is also made to relevant fundamental investigations. This latter aspect includes the literature concerned with the stability/flocculation behaviour of aqueous polymer latices containing adsorbed polymers.

2.2 Previous technological investigations of the effects of added water-soluble polymers upon the properties of latices

Although it has long been known that hydrophilic polymers can be used to modify the interparticle interactions and hence the stability characteristics of aqueous hydrophilic colloidal dispersions, little appears to have been published concerning the correlations between the characteristics of the added polymer and its influence upon the properties of latex. Furthermore, there appear to be no previous publications concerning the effects of water-soluble polymers upon some more important technological properties such as zinc-oxide thickening. Unfortunately, what is available also seems to be rather empirical and unsystematic. A review of such investigations is given in this section.

2.2.1 Effects upon colloid stability

Saunders and Sanders(4) have investigated the effects of added methylcellulose upon the electrolyte stability of various dilute anionically-stabilised synthetic latices. A sensitising effect was observed at low concentrations of methylcellulose and, at higher concentrations, a protective action was observed where the susceptibility of the latex to coagulation by electrolytes was reduced. Some of the results published by Saunders and Sanders are illustrated in Fig. 2.1, where the stability has been defined as the percentage of the latex remaining in suspension at a given electrolyte concentration. The general shape of the curve was found to be the same for three different concentrations of electrolyte, and the increase in stability after initial sensitising effect was observed at approximately constant methylcellulose concentration. The sensitising effect was attributed to the formation of aggregates of the latex particles, held together by methylcellulose molecules. The protective action, which was observed when sufficient methylcellulose was present to cover the surface of the latex particles, was attributed to the hydrophilic nature of methylcellulose. Furthermore, these workers found that the molecular weight of the methylcellulose did not appreciably affect the amount necessary to produce a protective action.

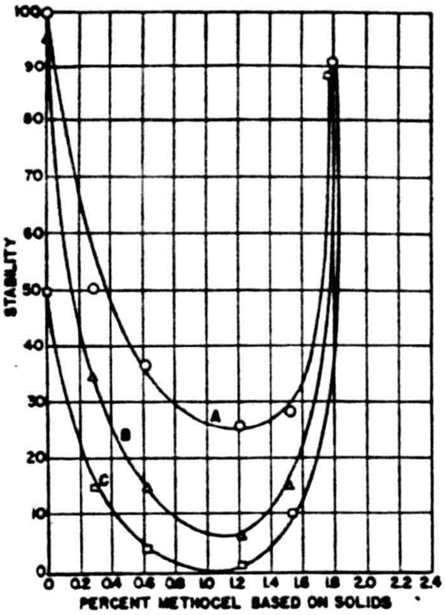


Fig. 2.1 : Dependence of latex stability upon concentrations of methylcellulose and inorganic electrolyte (calcium chloride)(4)

concentration of electrolyte A - 1 mM/l
B - 5 mM/l
C - 10 mM/l

Saunders and Sanders also found that the addition of an emulsifier (an alkylaryl sulphate) to the diluted latex reduced the amount of methylcellulose required for the protective action.

Similar observations have been reported by Frantz _et al._(5) for the effects of added methylcellulose and protein upon the agglomeration of a monodisperse anionically-stabilised polyvinyltoluene latex. Small additions of methylcellulose caused the agglomeration of the particles, whereas the larger concentrations resulted in redispersion and restabilisation of the particles. The protein, however, produced agglomeration with no subsequent stabilising effect when the particle surfaces were not completely covered with the emulsifier. But when sufficient additional emulsifier was present,no agglomeration was observed. Similar results were observed for the effects of protein addition on the electrolyte stability of anionically-stabilised polyvinyltoluene latex.

Gillespe(6) has investigated the flocculation of an anionically-stabilised styrene-butadiene copolymer latex by methylcellulose by direct measurement of the particle concentration as a function of time. He found that the apparent particle concentration decreased to a steady value corresponding to limited or partial flocculation. He attributed this equilibrium to the competition between flocculation and deflocculation. The net effect of the competition between flocculation and deflocculation was assessed by calculation of the degree of flocculation of the latex, defined as the fractional number of particles aggregated. It was calculated as follows:

$$\text{degree of flocculation} = (N - n_f)/N$$

where N = initial number of primary particles per cubic centimetre, and

n_f = apparent number of particles at equilibrium per cubic centimetre of latex

The variation of degree of flocculation with methylcellulose concentration is illustrated in Fig. 2.2.

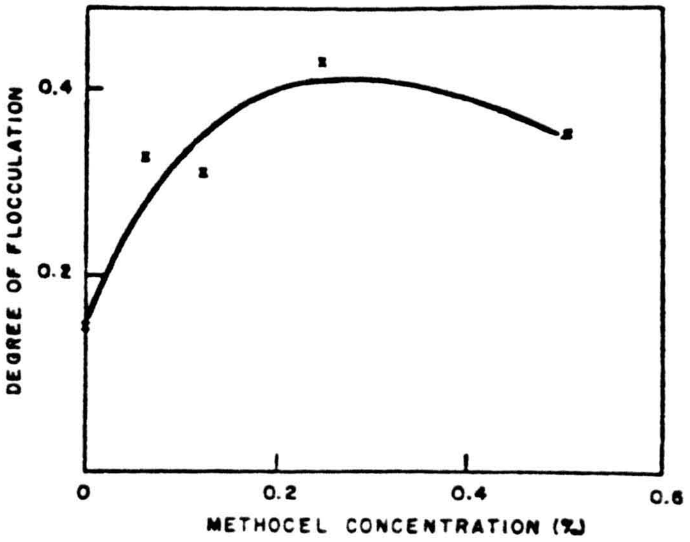


Fig. 2.2 : Variation of degree of flocculation of anionically-stabilised styrene-butadiene latex with methylcellulose concentration(6)

These results provide further evidence for the sensitisation-stabilisation effect of hydrophilic polymers upon hydrophobic colloids as aqueous latices.

The reversible flocculation of an anionically-stabilised acrylic copolymer latex and an anionically-stabilised polystyrene latex by hydroxyethylcelluloses(HEC) of various molecular weights had been investigated by Sperry _et al_.(7) They determined the weight percentage of HEC in the aqueous phase required to induce flocculation, _i.e_, the critical flocculation concentration, C_f. Latex solids content, latex polymer composition, molecular weight of soluble polymer, and serum composition were treated as independent variables. C_f was found to be strongly dependent upon the solids content of the latex when the solids content was adjusted by the addition of water alone. For a variety of serum conditions, C_f decreased with increasing molecular weight. This is illustrated in Fig. 2.3. The decrease in C_f with

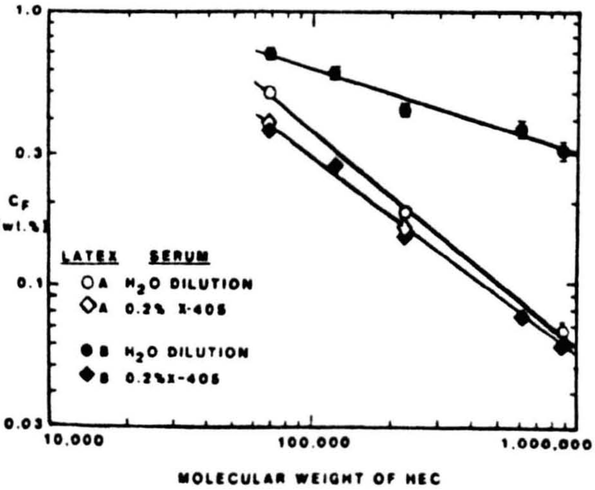


Fig. 2.3 : Dependence of C_f on molecular weight of HEC(7)

increasing molecular weight of HEC was attributed to increase in the interparticle restricted volume which facilitates operation of the attractive forces over a large interparticle area at larger separations.

Tan(8) has investigated the effects of two different grades of water-soluble methylcellulose upon the mechanical stability of ammonia-preserved natural rubber latex. His results are illustrated in Fig. 2.4. These

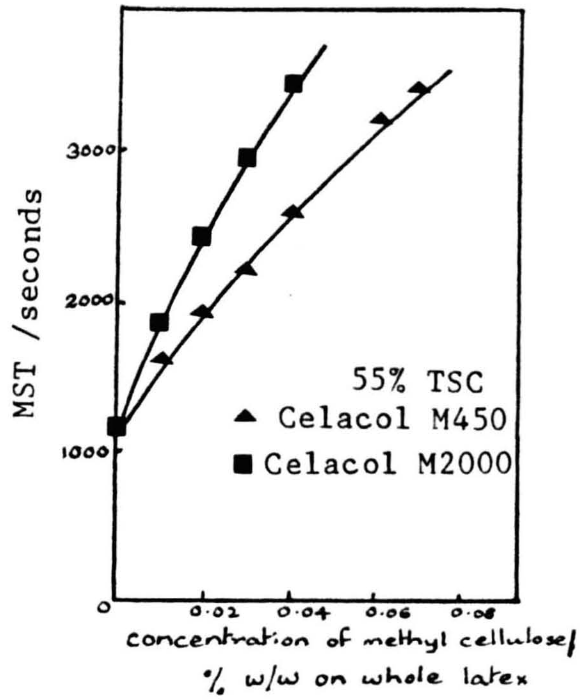


Fig. 2.4 : Effect of methylcellulose upon mechanical stability of ammonia-preserved natural rubber latex(8)

results suggest that the grade of higher viscosity, which presumably had the higher molecular weight, is more effective in enhancing mechanical stability. It is also apparent from Fig. 2.4 that a smaller quantity of the grade of higher viscosity is as effective in enhancing the mechanical stability as is a larger quantity of the grade of lower viscosity. This was attributed to the higher tendency of the high-viscosity grade of methylcellulose to adsorb at the rubber/water interface, thereby imparting loops and tails of larger average sizes and inducing a greater stabilising effect, as compared to the low-viscosity grade of methylcellulose.

Ash and Clayfield(9) have investigated the dependence of the electrolyte stability of an anionically-stabilised polystyrene latex containing non-ionic polymers upon the various parameters such as polymer composition, electrolyte concentration, polymer molecular weight and polymer concentration. The non-ionic polymers employed were polyethylene oxides and ethylene oxide/propylene oxide random copolymers of different molecular weights. The relationship between the flocculation rate and polymer concentration generally showed a characteristic maximum which shifted to a lower polymer concentration with increasing polymer molecular weight. As regards the effects of polymer composition, the results for flocculation by several random copolymers of ethylene oxide and propylene oxide in the presence of electrolyte were not found to depend in any systematic way upon the ethylene oxide/propylene oxide ratio in the copolymer. At any given concentration of polymer, an increase in electrolyte concentration was found to increase the rate of flocculation.

Blackley *et al.*(10) have investigated the effects of various C_{16-18} fatty-alcohol ethoxylates upon the mechanical and chemical stability of natural rubber latex, and have found that all the ethoxylates studied reduced the mechanical and chemical stability when present in small amounts. These same ethoxylates caused the mechanical and chemical stability to be enhanced when present in larger amounts, although the enhancements did not necessarily increase the mechanical and chemical stability to the level of the initial latex, at least over the range of additions investigated. Furthermore, they found that, for ethoxylates containing between six and thirty moles of ethylene oxide per mole of fatty alcohol, the effect of the ethoxylate upon the mechanical stability was determined primarily by the total number of ethylene oxide units which had been added to the latex as ethoxylate.

Blackley and Chua(11) have reported the effects upon the mechanical and chemical stability of natural rubber latex of four ethoxylates having different hydrophobe bases, but the same mole ratio of ethylene oxide to hydrophobe base. They found that, of the ethoxylates investigated, the cetyl/oleyl alcohol ethoxylate caused the highest reduction in mechanical and chemical stability when present in small amounts, and that the ability of the ethoxylate to enhance mechanical and chemical stability at higher levels of addition depended greatly upon the hydrophobe base of the ethoxylate.

Kronberg et al.(12) have studied the effects of polymethylmethacrylate-g-polyethylene oxide (PMMA-g-PEO) and ethoxylated nonylphenol ethers (NP-EO_n) upon the mechanical stability and freeze-thaw stability of anionically-stabilised polyvinyl chloride latex. They found that both types of polymers gave the same stabilisation behaviour. They proposed that both types of polymers may adsorb flat on the latex particles at low concentrations, whereas when the latex particles are fully covered by adsorbed polymers, the extension of water-soluble ethylene oxide units of the polymer chains into the water phase occurs, thereby conferring steric stability upon the latex.

A method for the mechanical and chemical destabilisation of natural rubber latex by the addition of nonionic polyol block copolymers such as polyethylene oxide-b-polyoxypropylene has been reported by Oldack.(13) He used four types of commercially-available polyols and demonstrated their ability to reduce mechanical and chemical stability, the latter being determined by the Dawson's zinc-oxide viscosity (zov) test.

The effects of polyethylene oxide and polyvinyl pyrolidine of various molecular weights upon the stability of an acrylic latex of polymethacrylate/polybutyl serylate (stearate ?) stabilised by grafted polyethylene oxide chains, have been studied by Belbin et al.(14) The critical flocculation concentration of polymer, C_f, defined as the smallest amount of soluble polymer needed to give a detectable sediment, was determined by mixing latex and soluble polymer at different concentrations in measuring cylinders and leaving undisturbed for two weeks at 20±1 °C. C_f was found decrease with increasing the molecular weight of the added polymer.

Gregory(15) has investigated the effects of variation of surface charge density upon the flocculation behaviour of a carboxylated polystyrene latex by two cationic polyelectrolytes of low and high molecular weight, using a simple turbidimetric procedure. The two cationic polyelectrolytes employed were commercially-available polyamines, named as Primafloc C-3 and Primafloc C-7. The surface charge density of the particles was reduced by lowering the pH and increased by adding an anionic surfactant, (sodium lauryl sulphate). The colloid stability of the latex was quantified by the turbidity of the supernant liquid obtained after allowing the flocculated latex to stand for one hour. The effect of polymer of lower molecular weight, Primafloc C-3 , upon the stability of the latex is shown in Fig. 2.5. As the surface charge was reduced, the amount of polyelectrolyte required for both flocculation and restabilisation was decreased. The electrophoretic mobility data indicated that the concentration of polymer of lower molecular weight required to give zero mobility was nearly the optimum concentration for flocculation both at pH 4.4 and 5.8.

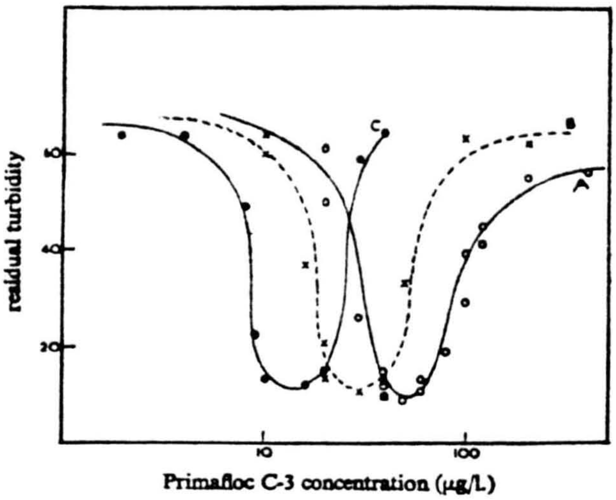


Fig. 2.5 : Flocculation of an anionically-stabilised polystyrene latex with Primafloc-3 at three different values of pH(15)

A - pH 5.8

B - pH 5.3

C - pH 4.4

The flocculation region, the range of polymer concentration at which the flocculation of latex occur, for the polymer of higher molecular weight was considerably greater than that for the polymer of lower molecular weight. This is illustrated in Fig. 2.6, where the critical values for flocculation and stabilisation were obtained from turbidity curves as the polyelectrolyte concentration required to give a residual turbidity of 30 units.

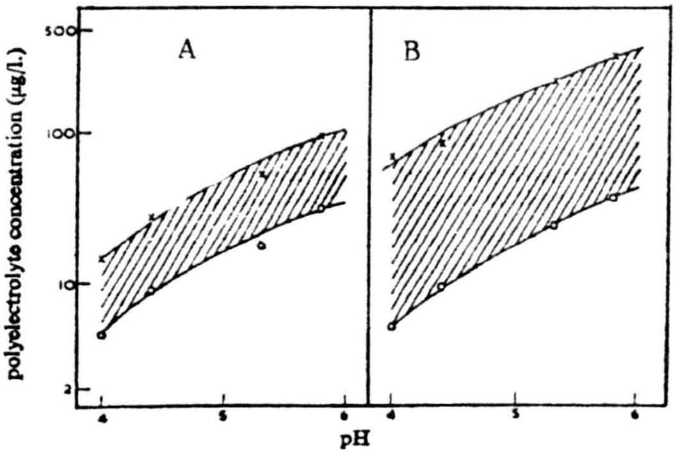


Fig. 2.6 : Flocculation of an anionically-stabilised polystyrene latex with Primafloc C-3 (A) and Primafloc C-7 (B) as a function of pH(15)

o critical flocculation concentration

x critical stabilisation concentration

Furthermore, flocculation with polymer of higher molecular weight was observed to occur well before the surface charge of the particles had been neutralised. These results led to the conclusion that interparticle bridging by polymer molecules was a significant mechanism for the flocculation of latex by the polymer of higher molecular weight, and that the polymer of lower molecular weight was effective mainly through charge neutralisation.

Gregory(16) extended his studies to investigate the rates of flocculation of a carboxylated polystyrene latex by three cationic polyelectrolytes of different molecular weights, which were based on dimethylaminoethyl methacrylate. The rates of flocculation were observed using a light-scattering technique, and they were compared with those obtained by the addition of an acid or sodium nitrate. The rates of flocculation with cationic polyelectrolytes were found to increase with decreasing ionic strength of the dispersion medium. The maximum rate observed, which appeared to be independent of the molecular weight of the polyelectrolyte, was about twice that given by high concentrations of sodium nitrate or by acid. In the absence of sodium nitrate, flocculation occurred over a rather limited range of polyelectrolyte concentration, but this range broadened considerably with increasing sodium nitrate concentration. For a fixed ionic strength, the optimum flocculant concentration was about the same for all three electrolytes, although the range became slightly broader with increasing molecular weight. In seeking to explain these effects, interparticle bridging by polymers of high molecular weight was not postulated. The nature of the charge distribution on the particles containing adsorbed polyelectrolyte was considered instead. Gregory suggested that the possible uneven distribution of negative and positive charges on the particles would provide an extra attractive contribution to the interaction energy between the particles. Further experimental evidence for this mechanism, which was referred as the "electrostatic patch" model, has been obtained by studying the flocculation rates of a carboxylated polystyrene latex by three cationic polymers and a cationic surfactant, using a turbidimetric procedure.(17)

Gregory and Sheiham(18) investigated the effect of latex particle concentration upon the flocculation of a carboxylated polystyrene latex by similar cationic polyelectrolytes. The results indicated, that at low particle concentration, the charge neutralisation was a significant mechanism for flocculation by polymers of both high and low molecular weight. But at high particle concentrations, flocculation by interparticle bridging was considered as a possible mechanism.

Ries and Mayers(19) have investigated the flocculation and stabilisation of an anionically-stabilised polystyrene latex with various cationic polyelectrolytes and also with an anionic polyelectrolyte using microelectrophoresis measurements and electron-microscope observations. The behaviour of cationic flocculants was found to be similar to that observed by Gregory. The anionic polyelectrolyte was found to enhance the negative surface potential and no flocculation was observed. However, the sequential addition of a cationic and an anionic polymer gave rather different results. When sufficient amount of a cationic polymer of low molecular weight was added to bring the latex to the point of incipient charge reversal and then an anionic polymer of high molecular weight was added, unusually large flocs were found to form. Two different explanations were given for this behaviour. The first explanation invoked bridging of latex particles by the adsorbed anionic polymer of high molecular weight; the second invoked the formation of a complex between the anionic and cationic polyelectrolytes which facilitated flocculation.

The coagulation of an anionically-stabilised carboxylated styrene-butadiene copolymer latex by polyethylenimine (PEI) has been investigated by Lauzon and Schmidt.(20) They found that there was a considerable increase in the pH of PEI solutions as the concentration of PEI was increased over a large concentration range. Two coagulation-stabilisation regions were found to occur as the concentration of PEI in the latex was increased from 10^{-4}% to 1% by weight. Furthermore, the pH of the latex was increased from its initial value, i.e., pH=8.5, to pH=11 as the concentration of PEI was increased up to 1% by weight. The first coagulation was attributed to neutralisation of surface charge of the latex particles by adsorbed protonated PEI. Further additions of PEI restabilised the latex as the surface charge was reversed. The second coagulation of the restabilised latex, which was observed at much higher concentrations of PEI, was attributed to enhancement of surface negative charge as a consequence of ionisation of surface carboxyl groups and to deprotonation of the PEI brought about by the increase in pH of the latex/PEI mixture. Subsequent restabilisation of the latex occurred when the latex particles regained their original negative charge. This explanation was confirmed by adding varying amounts of hydrochloric acid to the PEI and observing the coagulation phenomena. They found that the addition of the acid eliminated the second coagulation region. This was attributed to the increase in negative surface charge density of the particles.

The flocculation of anionically-stabilised polystyrene latices by a series of 2-vinyl pyridine/acrylamide copolymers and homopolymers has been studied by Ho and Howard.(21) The polymer molecular weight, polymer composition and charge density at the surface of the latex particles were varied. The extent of flocculation was quantified as "relative turbidity", i.e., as the ratio of the optical density of the supernant of the test system to that of a corresponding blank, where the blank being the optical density of the supernant of a latex sample containing no added polymer. Therefore relative turbidity as defined here is an inverse measure of extent of flocculation. The effects of polymer concentration and polymer molecular weight upon the extent of flocculation so defined are shown in Fig. 2.7. These experiments revealed, again, the stabilisation-flocculation-stabilisation phenomenon as the concentration of polymer was increased. This then leads immediately to the concept of optimum flocculation concentration (OFC). The OFC was independent of polymer molecular weight, but the flocculation range was broadened with increasing the polymer molecular weight. In the absence of electrolyte the polymer of low molecular weight imparted zero electrophoretic mobility at the OFC, but when 10^{-2}M sodium chloride was present, flocculation was observed over a broad range of polymer concentrations at negative particle mobilities. However, in both cases, the OFC when flocculation was brought about by the polymer of high molecular weight, the particles had a distinctly negative zeta potential. The OFC was increased as the

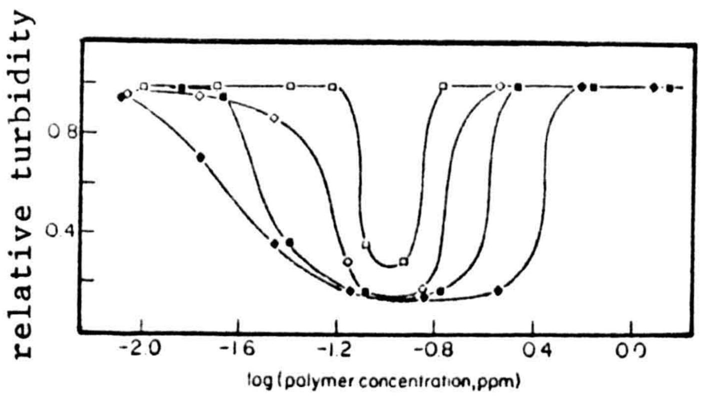


Fig. 2.7 : Effects of concentration and molecular weight of poly-2-vinyl pyridine upon flocculation of an anionically-stabilised polystyrene latex(21)

□ low molecular weight, salt free

■ low molecular weight, 10^{-2}M sodium chloride

◇ high molecular weight, salt free

◆ high molecular weight, 10^{-2}M sodium chloride

2-vinylpyridine content of the polymer was decreased.

2.2.2 Effects upon heat-sensitivity

One considers a latex compound is "heat sensitive" if it undergoes rapid destabilisation and gelation at elevated temperatures. Agents which cause the latex to destabilise rapidly at elevated temperatures are called heat-sensitising agents. The use of water-soluble polymers as heat-sensitising agents has been known for many years.(22,23) The best-known heat-sensitising agent of this type is polyvinyl methyl ether (PVME).(24,25)

The use of other water-soluble polymers such as, polyacetals,(26) polymethoxyacetals,(27) polyalkoxy alkanols(28) and polyetherthioethers (29) have also been reported. Woods(30) has reported on the use of ethylene oxide adducts as heat-sensitising agents. Gorton and Pendle(31) have reported on the use of PVME, polypropylene glycol(PPG), ethylene oxide adducts and propylene oxide/ethylene oxide adducts as heat-sensitising agents.

The mechanism of heat-sensitisation by water-soluble polymers such as PVME and PPG is believed to involve their adsorption at latex particle interfaces at room temperature and a subsequent loss of stabilising power at higher temperatures.(31) Loss of stabilising ability occurs due to dehydration of the water-soluble polymer at its cloud point, i.e., the temperature at which the water-soluble polymer precipitates out from aqueous solution.

2.2.3 Effects upon viscosity

Brown and Garrett(32) have investigated the flow behaviour of a number of combinations of latices and thickeners in order to obtain information for analysis of the processes involved in latex thickening. Amongst the thickeners investigated methylcellulose thickeners were found to increase the viscosity of latex with increasing the concentration of thickener. For sodium polyacrylate thickener, the increase in viscosity was linear with thickener concentration. Acrysol G110 (the ammonium salt of an acid-acrylic copolymer) increased viscosity both faster or slower than thickener concentration depending upon the latex indicating, a marked specificity in its tendency to interact with polymer particles. In an attempt to clarify the various specific interactions, Brown and Garrett performed a number of additional experiments using six dispersions prepared by emulsion polymerisation of styrene or methyl methacrylate with three different surfactants. Three water-soluble polymers, sodium polyacrylate, a sodium salt of a styrene-maleic acid copolymer of low molecular weight, and hydroxyethylcellulose were employed as thickeners. They found that, as the concentration of thickener was increased, the viscosity of anionically-stabilised polymethyl methacrylate latex thickened with the styrene-maleic acid copolymer first increased, passed through a maximum, then decreased passed through a minimum, and then again increased. This behaviour was not common for all the latex/thickener combinations employed. Some of their results are illustrated in Fig. 2.8. Brown and Garrett also noted that, as both the polymer and the emulsifier are varied there was no constancy in the order of thickening efficiency of the various water-soluble polymers investigated. On the basis of the results of this investigation, Brown and Garrett proposed that the

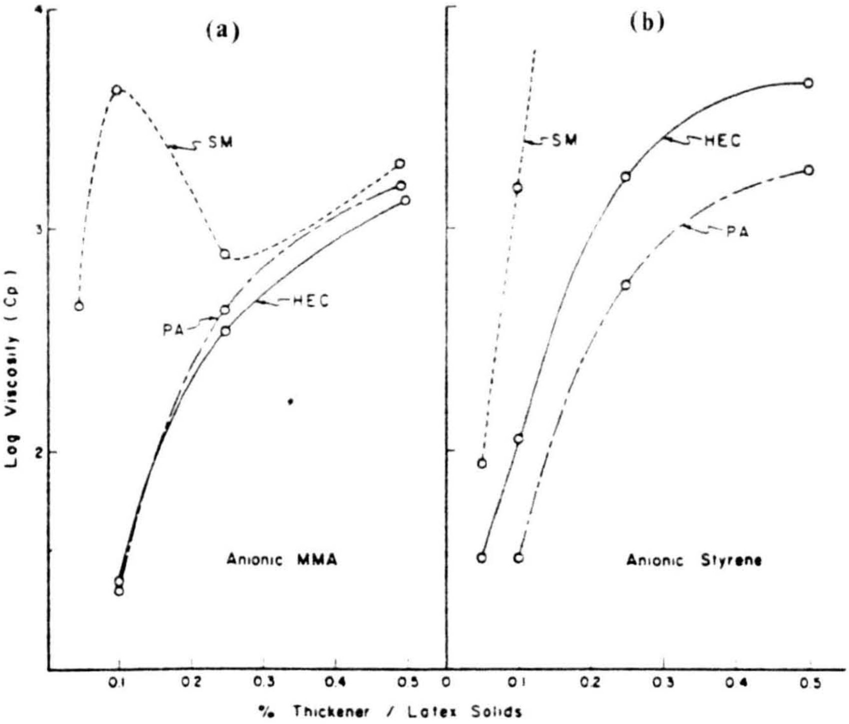


Fig. 2.8 : Effects of various water-soluble polymers upon viscosity of (a) an anionically-stabilised polymethyl methacrylate latex, and (b) an anionically-stabilised polystyrene latex(32)

enhancement of the viscosity of a latex by the addition of a water-soluble polymer was a consequence of two effects:

(1) increase of the viscosity of the aqueous phase by the dissolved polymer, and

(2) interaction between the polymer molecules and the latex particles to produce a specific type of "flocculation" or "structure".

A statistically-designed experiment has been conducted by White(33) in order to study the thickening of carboxylated styrene-butadiene copolymer latex systems by polyacrylate thickener. He found that the particle size of the latex had a great effect upon the thickening of latex. The smaller the latex particles, the higher the viscosity at any given level of thickener.

Tan(8) has investigated the effects of two different grades of water-soluble methylcellulose upon the viscosity of ammonia-preserved natural rubber latex. His results are illustrated in Fig. 2.9. These results suggests that the grade of higher viscosity is more effective in enhancing the viscosity than is the grade of lower viscosity. This increase in viscosity with the addition of methylcellulose was attributed to the adsorption of methylcellulose on to the particle surfaces, thereby promoting interparticle bridging and increasing the thickness of the hydration layer surrounding the particles

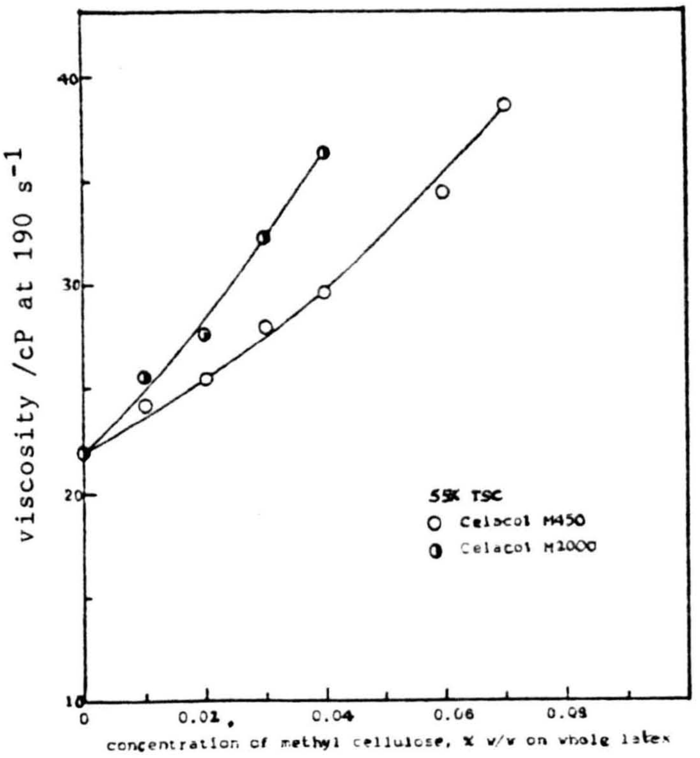


Fig. 2.9 : Effect of methylcellulose upon viscosity of ammonia-preserved natural rubber latex(8)

and hence the effective hydrodynamic size of the particles.

Swinyard and Gorton(34) have investigated the effects of various water-soluble polymers upon the viscosity of natural rubber latex. The water-soluble polymers used were commercially-available thickeners, based upon cellulose, polyacrylates, and polyacrylamides. Upto <u>ca</u> 4 parts per hundred parts of latex an approximately linear relationship was observed between the level of thickener and the viscosity of the latex compound. Of the polymers used, polyacrylates were found to be the most suitable thickeners for use in natural rubber latex, considering factors such as the ease of preparation of stock solution, its stability during storage, its compatibility with latex, the efficiency of the thickener in providing the required viscosity modification with the minimum addition, and stability of the thickened latex during long term storage.

2.2.4 Effects upon creaming

Twiss and Carpenter(35) have studied the effect of various water-soluble polymers, such as methylcellulose and sodium alginate, upon the creaming of ammonia-preserved natural rubber latex. They found that the minimum concentration of creaming agent (calculated on the aqueous phase) required to give a rubber-free serum was substantially constant for any one creaming agent as the rubber content of the latex was varied over the range 10% to 48%. Fig. 2.10 illustrates some of their results for the effect of concentration of creaming agent upon the creaming of NR latex. Twiss and Carpenter also found that the concentration of creaming agent in the aqueous phase of the resultant serum was about one-half of that in the aqueous phase of the original mixture. On the basis of this investigation, they suggested that, when a solution of a creaming agent is added to natural rubber latex, a part of it is adsorbed at the rubber-water interface and also

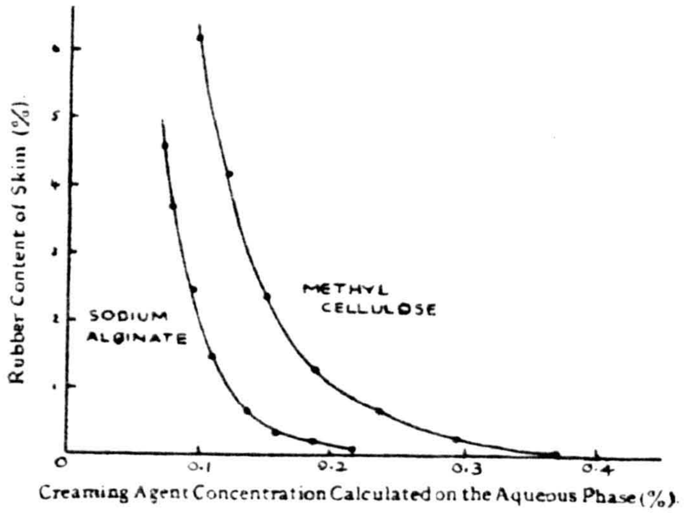


Fig. 2.10 : Effect of concentration of creaming agent upon creaming of ammonia-preserved NR latex(35)

becomes associated with the part which is dissolved in the bulk of the aqueous phase, thereby forming a loose network system of entrapped colloidal particles. The result of this effect is the restriction of the Brownian movement of the individual latex particles with consequent rapid creaming.

Noble(36) suggested that adsorption of heavily hydrated molecules of creaming agent at the particle surface results in a great increase in the effective size of the latex particles, with almost complete elimination of the Brownian movement, so that these particles would rise rapidly under the influence of buoyancy forces.

Stamberger(37) suggested that the creaming agent on adsorption at the rubber-water interface reduces the surface charge density sufficiently to enable the latex particles to approach one another and to cohere loosely. Complete coagulation of the rubber is prevented by a hydration layer surrounding the particles as a result of the extremely high affinity of the molecules of creaming agent for water molecules. Baker(38) also suggested that the molecules of creaming agents must be capable of adsorption on the latex particles and of becoming hydrated.

A microscopical investigation of the mechanism of the creaming of ammonia-preserved NR latex with creaming agents such as pectin, sodium polyacrylate, and tragacanth has been reported by Vester.(39) He observed that when a creaming agent is added to a latex of a very low rubber content an emulsion was formed consisting of very small drops which gradually coalesced and increased in size. In these drops, very small particles which were not easily visible were observed. On the basis of this investigation, Vester suggested that the agglomeration of the particles was caused by the viscous phase which enveloped the particles.

Bondy(40) has investigated the creaming of ammonia-preserved NR latex by sodium alginate, and showed that adsorption was unnecessary. He suggested that creaming was a consequence of partial dehydration of the adsorbed stabilising film brought about by the addition of water-soluble polymer.

Brown and Garrett(32) have studied the effects of two water-soluble polymers, namely, the ammonium salt of a styrene-maleic acid copolymer and sodium polyacrylate, upon the creaming of an anionically-stabilised styrene-butadiene copolymer latex. Their results are illustrated in Fig. 2.11. Brown and Garrett suggested that the decrease in creaming above a critical concentration of the thickener was a consequence of an increased viscosity of the aqueous phase and/or a change in the structure of the aggregates formed.

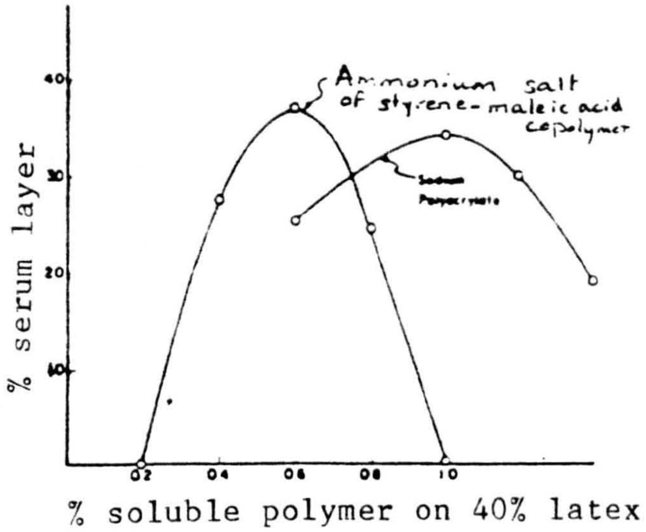


Fig. 2.11 : Effects of ammonium salt of styrene-maleic copolymer and sodium polyacrylate upon creaming of a styrene-butadiene copolymer latex(32)

2.3 Previous fundamental investigations related to the behaviour of water-soluble polymers in latices

It is apparent from the literature reviewed in the preceding section that the behaviour of an added hydrophilic polymer in modifying the properties of a latex such as stability, viscosity and creaming is dependent upon whether the hydrophilic polymer adsorb at the solid/solution interface or whether it merely dissolves in the dispersion medium. Over the last few decades, many papers have been published concerning the factors which control the adsorption of water-soluble polymers at solid/liquid interfaces, and the cognate matter of the stability of colloidal dispersions which contain adsorbed polymers. Colloid stability conferred by adsorbed lyophilic polymers is commonly referred to as the "steric stabilisation". These investigations have been carried out by using various latex systems. A brief summary of such investigations is given in this section.

2.3.1 Adsorption of polymers at solid/liquid interfaces

The adsorption of methylcellulose on monodisperse anionically-stabilised polystyrene latices, in the presence of an emulsifier (sodium lauryl sulphate, NaLS) has been investigated by Saunders.(41) The amount of methylcellulose adsorbed was found to decrease with increasing surface coverage by the emulsifier. Similar results have been published by Saunders and Sanders(4) for the adsorption of methylcellulose on an anionically-stabilised polystyrene latex.

Brodnyan and Kelly(42) have investigated the adsorption of two types of water-soluble polymers namely, polyacrylic acid (Acrysol A-5) and several hydroxyethylcelluloses of different molecular weights, on anionically-stabilised polyacrylate and polymethacrylate latices in the presence of two types of surfactants namely, a sodium alkylaryl polyether sulphonate (Triton X-202), sodium lauryl sulphate (NaLS). Polyacrylic acid was found to adsorb on all the polyacrylate and polymethacrylate latices, whilst the hydroxyethylcelluloses were not found to adsorb on polybutyl acrylate latices. The hydroxyethylcelluloses were found to adsorb on polybutyl methacrylate-methacrylic acid latices when NaLS was the surfactant. The extent of adsorption of hydroxyethylcelluloses on polybutyl methacrylate was found to decrease dramatically when Triton X-202 was the surfactant. These observations indicate the importance of the nature of the substrate for adsorption, and the extent to which the substrate can be altered by the presence of other components such as surfactants.

Sperry _et_ _al_.(7) have investigated the effects of a nonionic surfactant (an ethoxylated octylphenol, Triton X 405) upon the adsorption of hydroxyethylcellulose on anionically-stabilised acrylic copolymer and polystyrene latices. Their results are illustrated in Fig. 2.12. Triton X-405 prevented the adsorption of hydroxyethylcellulose on both latices.

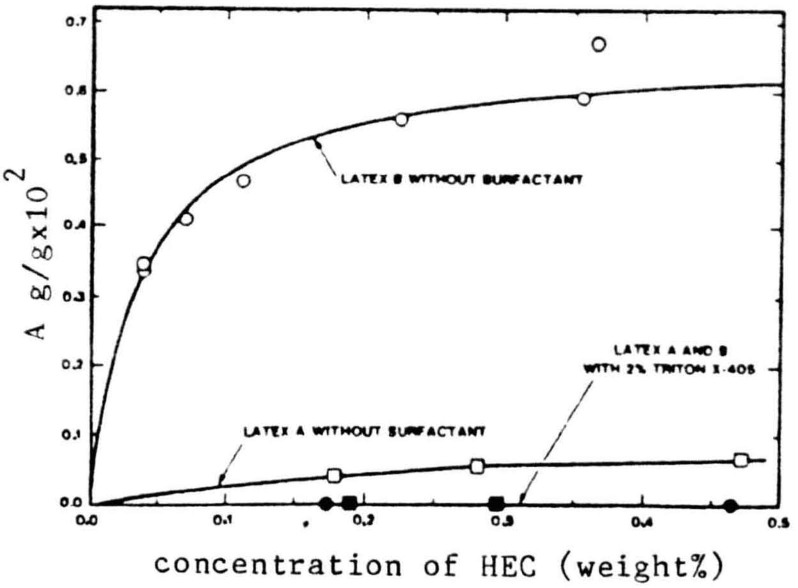


Fig. 2.12 : Adsorption of hydroxyethylcellulose on an acrylic copolymer latex (latex A) and a polystyrene latex (latex B)$^{(7)}$

The effects of the molecular weight of polyvinyl alcohol (PVA) upon its adsorption on to anionically-stabilised polystyrene latices has been investigated by Garvey et al.$^{(43)}$ The amount of PVA adsorbed at the surface of the latex particles was found to depend upon the molecular weight of the PVA. Some of their results are illustrated in Fig. 2.13. Garvey et al. also found that both the amount of PVA adsorbed at the plateau, Γ ,and the thickness of the adsorbed layer, δ , increased as the molecular weight of the PVA was increased. The increase was observed to be directly proportional to the square root of the molecular weight of the PVA. This is illustrated in Fig. 2.14.

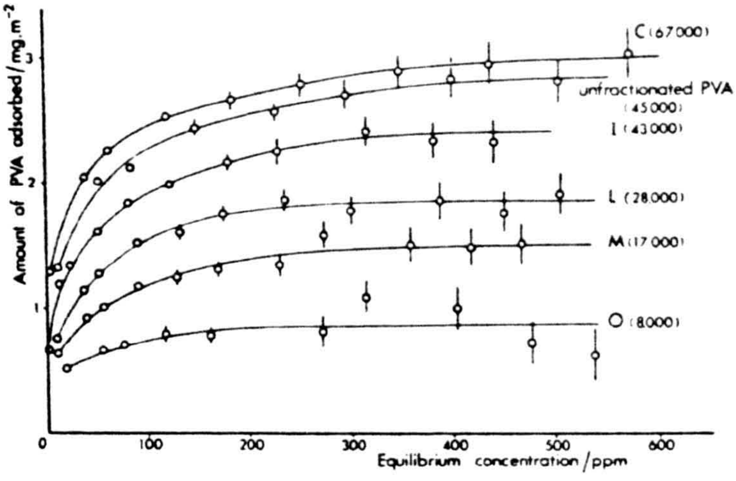


Fig. 2.13 : Adsorption of polyvinyl alcohol on a polystyrene latex at 25°C$^{(43)}$

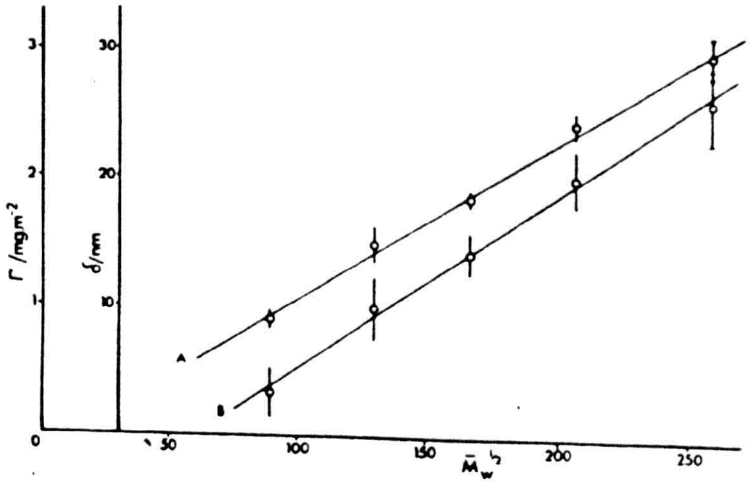


Fig. 2.14 : Effect of molecular weight of PVA upon plateau adsorption and thickness of adsorbed layer$^{(43)}$

Similar results have been reported by Cowell and Vincent$^{(44)}$ for the adsorption of polyethylene oxides of different molecular weights on an anionically-stabilised polystyrene latex, and by Tadros$^{(45)}$ for the adsorption of polyvinyl alcohol on an anionically-stabilised polystyrene latex.

The influence of temperature upon the extent of adsorption and thickness of the adsorbed layer of polyvinyl alcohols of various molecular weights on an anionically-stabilised polystyrene latices has been investigated by Boomgaard _et al._$^{(46)}$ They found that, for the PVAs of high molecular weight, the extent of adsorbed, Γ, increased slightly with temperature, whereas the thickness of the adsorbed layer, δ, decreased. Adsorption isotherms for PVA (M=65,000) at various temperatures are shown in Fig. 2.15.

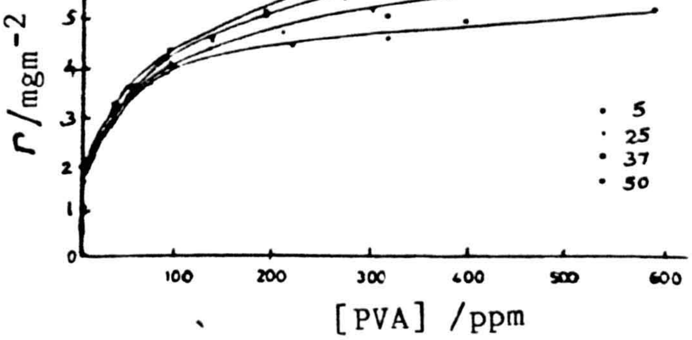


Fig.2.15 : Adsorption isotherms for PVA (M=65,000) on a polystyrene latex at various temperatures$^{(46)}$

The influence of temperature upon the adsorption of a polyethylene oxide-polypropylene oxide block copolymer on an anionically-stabilised polystyrene latex has been investigated by Tadros and Vincent.(47) Some of their results are shown in Fig. 2.16. There was a significant increase in extent of adsorption as the temperature was increased from 25 to 37°C, but increasing the temperature further from 37 to 50°C did not lead any further increase in adsorption.

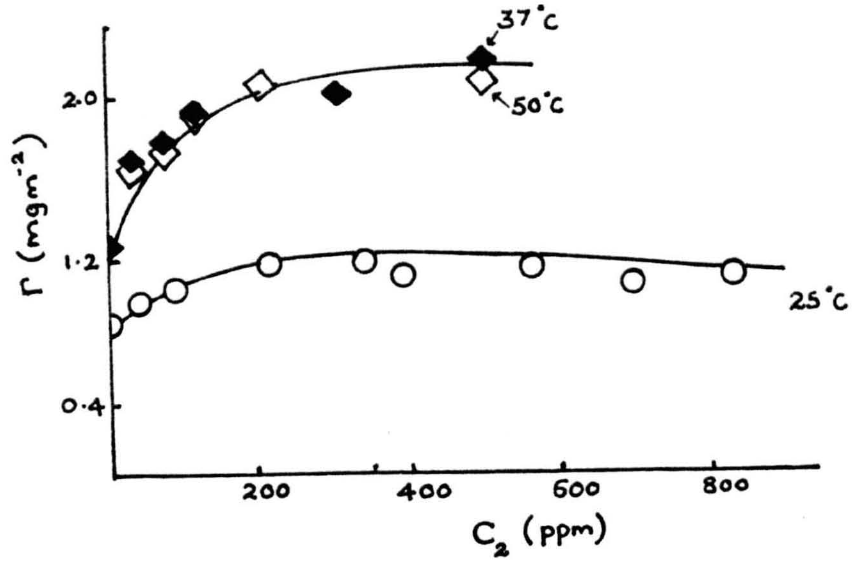


Fig. 2.16 : Adsorption of a polyethylene oxide-b-poly propylene oxide on a polystyrene latex(47)

Tadros and Vincent(47) also investigated the effect of various inorganic electrolytes upon the adsorption of the same copolymer on the same latex. The extent of adsorption in the presence of 0.5M potassium chloride was almost twice that obtained from pure water.

In the presence of 0.1M calcium chloride the extent of adsorption increased by a factor of approximately four. Amongst the inorganic electrolytes investigated, calcium chloride gave the greatest enhancement of extent of adsorption and potassium chloride gave the least.

The effects of some inorganic electrolytes upon the adsorption of polyvinyl alcohol on an anionically-stabilised polystyrene latex have also been investigated by Tadros and Vincent.(48) In contrast to what was observed for the polypropylene oxide-b-polyethylene oxide block copolymer/polystyrene system, the greatest increase in extent of adsorption was observed with sodium sulphate and the least with calcium chloride. However, for both systems all the electrolytes investigated caused an increase in the extent of adsorption. The increase in extent of adsorption caused either by increasing temperature or by adding an inorganic electrolyte was attributed to reduction of the solubility of the added polymer in the dispersion medium.

The adsorption of ethoxylated nonylphenols on monodisperse anionically-stabilised polystyrene and polyvinyl chloride latices has been investigated by Kronberg <u>et</u> <u>al</u>.(49) They found that the adsorption of these ethoxylated nonylphenols was dependent upon the number of ethylene oxide units in the added polymer. The extent of adsorption was found to decrease with increasing number of ethylene oxide units. Furthermore, they found that the extent of adsorption on polyvinyl chloride latex was slightly higher than that on polystyrene latex.

Ho and Howard(21) investigated the adsorption of vinyl pyridine/acrylamide copolymers on an anionically-stabilised polystyrene latex. The extent of adsorption was found to increase with acrylamide content of the copolymer. The addition of sodium chloride was found to increase the extent of adsorption.

2.3.2 Steric stabilisation

Steric stabilisation is imparted to colloidal particles by macromolecules that are attached to the surfaces of particles. The practical use of hydrophilic macromolecules for the stabilisation of aqueous hydrophobic colloidal dispersions is not new. The ancient Egyptians and Chinese used naturally-occurring polymers, such as gum arabic, casein, egg albumin, etc. to make stable dispersions of carbon black and other pigments.(50) Traditionally, colloid scientists have referred to stabilisation by natural macromolecules as "protection". Heller and Pugh(51) appear to have been the first to use the term "steric stabilisation", and this term is now generally used to describe the stabilising action of attached layers of non-ionic polymers.

It has long been known that best steric

stabilisers are amphipathic block or graft copolymers. One of the comonomers should form a polymer which is nominally immiscible with the dispersion medium and which is presumably miscible with the disperse phase, whereas the other monomer should form a polymer which is miscible with the dispersion medium. The former polymer, which serves to anchor the latter polymer to the colloidal particles, is referred to as the anchor polymer, and the "soluble" polymer, which imparts the steric stabilisation, is termed the stabilising moiety. Over the last few decades, a considerable amount of work has been done on the steric stabilisation of colloidal dispersions. Some of this work is reviewed in what follows.

2.3.2.1 Incipient instability of sterically-stabilised latices

Most of the studies on incipient instability has been performed on model polymer latices. Napper(52) has shown that the simplest way to induce instability in sterically-stabilised latices is to reduce the solvency of the dispersion medium for the stabilising moieties. The point at which flocculation is first observed on decreasing the solvency of the dispersion medium for the stabilising moieties is called the "critical flocculation point", CFPT. The reduction of the solvency of the dispersion medium for the stabilising moieties can in principle be achieved in at least three different ways: by altering the temperature, by changing the pressure, and by adding to the dispersion medium a non-solvent for the stabilising moieties. If it is a variation of temperature which causes instability, the CFPT is referred to as the critical flocculation temperature (CFT). If instability is brought about by an increase in temperature, the CFPT is called the upper critical flocculation temperature (UCFT) ; similarly if instability is brought about by a decrease in temperature, the CFPT is called the lower critical flocculation temperature (LCFT). If instability is brought by changing the pressure, the CFPT is referred to as the critical flocculation pressure (CFP). If instability is brought about by adding a non-solvent to the dispersion medium, the CFPT is called the critical flocculation volume (CFV).

The effects of various system parameters such as latex particle size, particle number concentration, and the nature of the anchor polymer, etc. upon the CFPT have been studied by several workers. Napper$^{(53)}$ has investigated the effects of such parameters as the anchor polymer, the disperse phase, the particle size, and the molecular weight of the stabilising polymer upon the CFT of some aqueous polyvinyl acetate latices in 0.39M magnesium sulphate. The latices were stabilised by block copolymers of polyethylene oxide and a polymer of either a vinyl or an acrylic monomer. Some of his results are given in Tables 2.1 to 2.4. From these results, it appears that the CFPT is independent of the latex particle size, the nature of the

disperse phase and anchor polymer	"CFT/K"	"θ/K"
polyvinyl acetate	318±2	319±3
polymethyl acrylate	320±2	319±3
polystrene	323±3	319±3

Table. 2.1 : Efects of nature of anchor group upon CFT of aqueous polyviunyl acetate latices in 0.39M magnesium sulphate(53)

anchor polymer	"CFT/K"	"θ/K"
polyvinyl acetate	318±2	319±3
polymethyl acrylate	314±2	319±3
polymethyl methacrylate	320±2	319±3
polystyrene	314±3	319±3
polyvinyl stearate	322±3	319±3

Table. 2.2 : Effects of nature of anchor polymer upon CFT of aqueous polyvinyl acetate latices in 0.39M magnesium sulphate(53)

mean particle diameter	"CFT/K"	"θ/K"
300	317±2	319±3
610	318	319±3
810	320	319±3
1100	319	319±3
1540	319	319±3
2300	315	319±3

Table. 2.3 : Effects of particle size upon CFT of aqueous polyvinyl acetate latices in 0.39M magnesium sulphate(53)

anchor polymer, the nature of the disperse phase, and molecular weight of the stabilising moieties. The results presented in Table 2.1 to 2.4 also confirm that the CFPT correlates strongly with the corresponding theta (θ)-point of the stabilising polymer in the dispersion medium.

polyethylene oxide	M_W	CFT/K	θ/K
Polyox WSR 301	1,000,000	317+2	315+3
Polyox WSR 205	800,000	316+2	316+3
Polyox WSRN 750	315,000	315+2	314+3
Polyox WSRN 80	96,000	316+2	315+3
Polyox WSRN 10	49,000	316+2	314+3
Polyglycol E 20,000	23,000	314+2	315+3
Polyglycol E 9,000	13,500	318+2	315+3
Carbowax 6,000	10,000	318+2	319+3
Carbowax 4,000	4,700	320+2	327+5
Carbowax 1,540	1,400	317+2	330+10
Carbowax 1,000	1,050	323+2	

Table 2.4 : Effect of molecular weight of stabilising moieties upon CFT of aqueous polyvinyl acetate in 0.39M magnesium sulphate(53)

Similar results have been reported for various non-aqueous latices.(54) These results suggest that the London attractions between the particles do not control flocculation of these systems. However, it has also been shown that if the core particles are large and the molecular weight of the stabilising moieties is low, the London attraction forces control the onset of instability. In these systems stability is dependent upon the particle size and the molecular weight of the stabilising moieties, and flocculation occurs under better-than-θ solvency conditions.

Cowell et al.$^{(55)}$ have investigated the dependence of the UCFT on the particle number concentration for a polystyrene latex of radius 87nm stabilised by polyethylene oxide of very low molecular weight (750). Their results are shown in Fig. 2.17. In all cases coagulation was observed under better than θ-solvency conditions, and the UCFT depended upon the volume fraction of the latex particles.

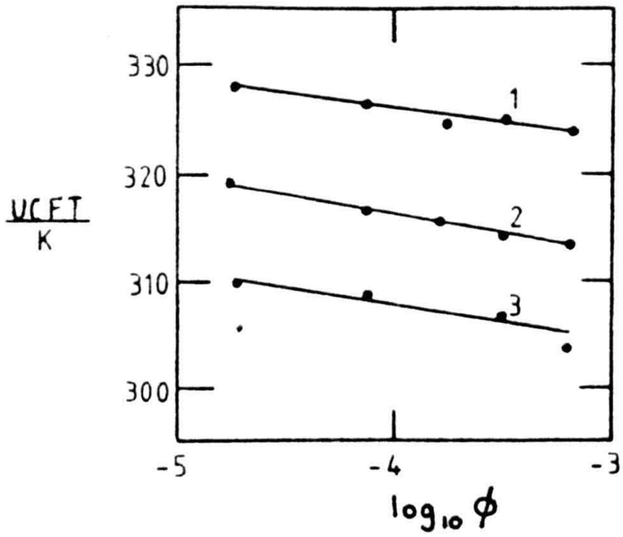


Fig. 2.17 : Effects of particle number concentration upon UCFT of aqueous polystyrene latices stabilised by polyethylene oxide of low molecular weight$^{(55)}$ 1 - 0.065M 2 - 0.163M 3 - 0.260M

Lambe et al.$^{(56)}$ have investigated the effects of particle volume fraction (ϕ) and polymer concentration upon the stability of aqueous polystyrene latices stabilised by polyvinyl alcohol (PVA). They have found that there is a strong dependence of the CFT upon particle volume fraction and even stronger dependence upon polymer concentration. Their results are illustrated in Fig. 2.18.

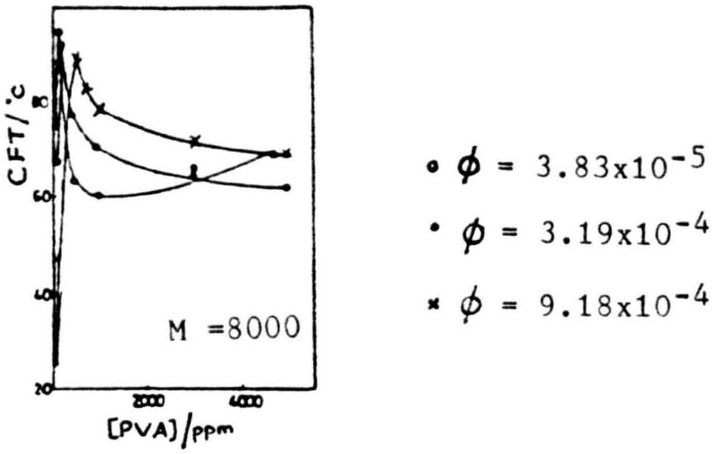


Fig. 2.18 : Effects of particle volume fraction and polymer concentration upon the CFT of aqueous polystyrene latices in 2M sodium nitrate stabilised by PVA(56)

Several other workers have also reported that there is a dependence of the CFPT upon the particle-number concentration for both aqueous and nonaqueous latices.(55, 57-60) However, there are published results which do not show the CFPT to depend upon particle number concentration. Thus Clarke and Vincent(61) have found that the LCFT of crosslinked microgel particles in n-butyl formate is constant over the volume fraction range 4x10^{-4} to 8x10^{-3}. Also, Everett and Stageman(62) have reported that polyacrylonitrile latices containing particles of radius 40nm in propane and stabilised by polymethyl siloxane moieties (molecular weight 30,000) exhibited no dependence of the UCFT upon particle concentration.

Napper(63) has given a reasonable explanation for the apparently conflicting results which have been reported for the dependence of CFPT upon particle number concentration. He suggested that, if the particles are relatively large and the stabilising moieties are of low molecular weight, the stability appears to be controlled by the relatively weak London attractions between the particles, whereas if the particles are small and fully coated by well-anchored stabilising moieties of high molecular weight, the stability is not controlled by the London attraction between the particles. This explanation is supported by Napper's studies on the effects of surface coverage upon the CFPT of both aqueous and nonaqueous latices. His results for the aqueous latices are shown in Fig.2.19. From these results, it is apparent that the CFPT

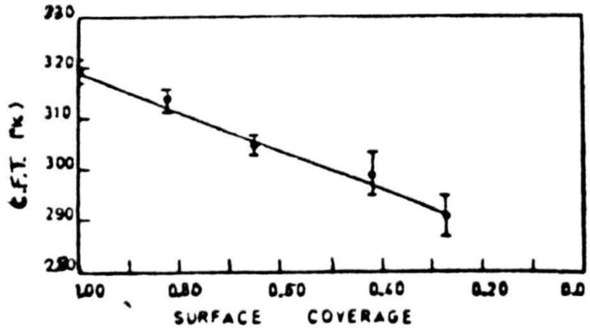


Fig. 2.19 : Effects of surface coverage upon CFT of aqueous polyvinyl acetate in 0.39M magnesium sulphate(63)

is dependent upon the extent to which the particle surface is covered by stabilising moieties. A similar pattern of behaviour has been observed for a nonaqueous latex.

2.3.2.2 Enhanced steric stabilisation

A different pattern of behaviour has been observed for some sterically-stabilised dispersions, in that stability is observed in dispersion media that are significantly worse solvents for the stabilising moieties than are θ-solvents. This phenomenon is termed enhanced steric stabilisation.

The phenomenon of enhanced steric stabilisation was discovered by Dobbie et al.(64) They showed that, by anchoring the stabilising chains to the particle surface at many points along the chain, the pattern of flocculation behaviour can be profoundly altered. The systems studied were two aqueous polystyrene latices, stabilised by an adsorbed polystyrene/polyethylene oxide block copolymer, and an aqueous polyvinyl acetate latex stabilised by an adsorbed polyvinylacetate/polyethylene oxide block copolymer. One of the polystyrene latices contained a high surface concentration of carboxyl groups, whereas the other possessed a low concentration of carboxyl groups. They found that, when sufficient stabiliser was present, the UCFT was close to the θ-temperature, and at low stabiliser concentration the UCFT fell below the θ-temperature, indicating that flocculation was occurring in better than θ-solvents. However, for latex particles containing significant surface concentrations of carboxyl groups, a region was observed where the UCFT greatly exceeded the θ-temperature at lower stabiliser concentration. This effect is illustrated in Fig. 2.20. It was suggested that this

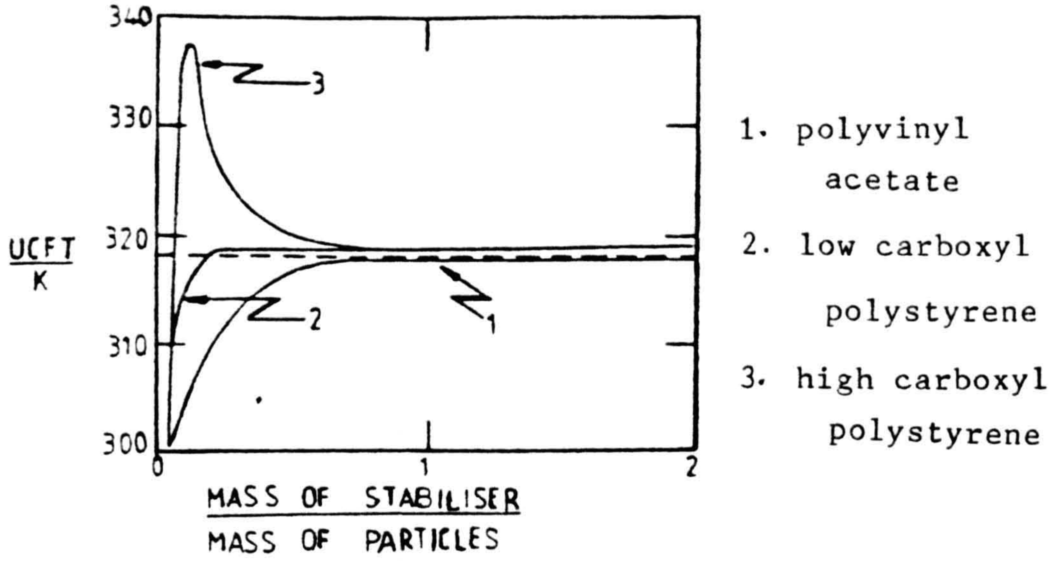


Fig. 2.20 : Effect of surface concentration of carboxyl groups upon variation of UCFT of various latices with concentrations of polyethylene oxide stabiliser(64)

enhancement of UCFT was brought about by association of surface carboxyl groups and ether oxygens of the polyethylene oxide chains. This hypothesis was tested by investigating the effects of pH upon the enhancement of the UCFT above the θ-point using polyethylene oxide of molecular weight 10,000 as the stabilising moiety. The results of this investigation are shown in Fig. 2.21. The magnitude of the enhancement of UCFT was found to increase with decreasing pH indicating the occurrence of hydrogen bonding between the surface carboxylic acid groups and ether oxygens in the polyethylene oxide chains.

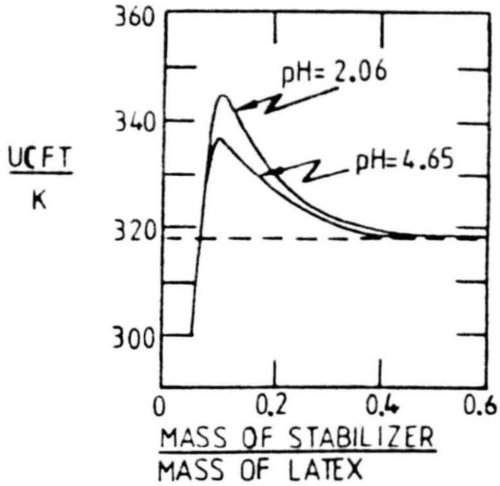


Fig. 2.21 : Effect of concentration of polyethylene oxide stabiliser upon UCFT of a high-carboxyl polystyrene latex at two different pH values(64)

Dobbie et al. also investigated the effects of the molecular weight of the stabilising moieties upon the extent of enhancement of the UCFT above the Θ-temperature. They found that the molecular weight of the stabilising moieties has a profound effect upon the extent of the enhancement of the UCFT. The results are shown in Fig. 2.22. As the molecular weight of the stabilising moieties was decreased, a small enhancement was observed for a molecular weight of 96,000, and this enhancement was increased as the molecular weight was further decreased.

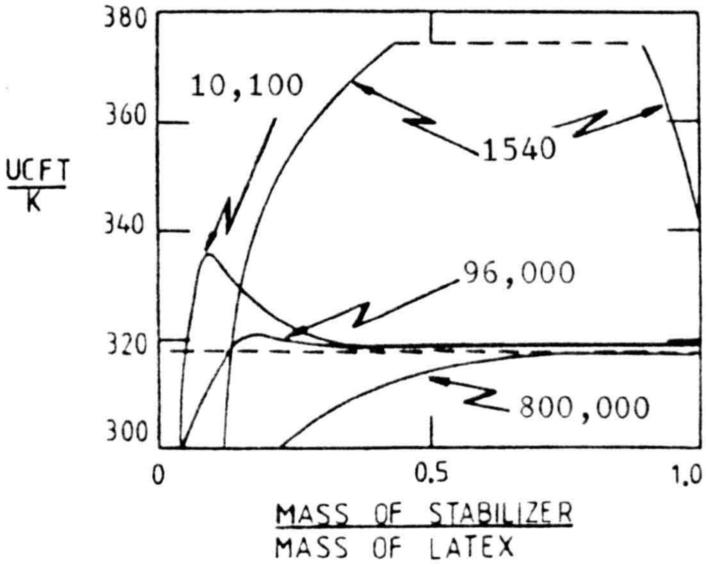


Fig. 2.22 : **Effect of molecular weight of polyethylene oxide stabiliser upon UCFT of a high-carboxyl polystyrene latices**(64)

The experiments of Lambe et al.(56) on the stability of polystyrene latices stabilised by polyvinyl alcohol also provide evidence for the concept of enhanced steric stabilisation. They have also published results for the dependence of the extent of the enhancement of stability upon the molecular weight of the stabilising moieties.

Tadros and Winn(65) have extended the results of Lambe et al. They confirmed that it is possible to prepare aqueous polystyrene latices in the presence of polyvinyl alcohol that are stable in dispersion media (1M potassium chloride) which are apparently significantly worse than θ solvents for polyvinyl alcohol. They found that, for polymers of low molecular weight, there is a strong dependence of the UCFT upon the polymer molecular weight. This is illustrated in Fig. 2.23 . The UCFT was found

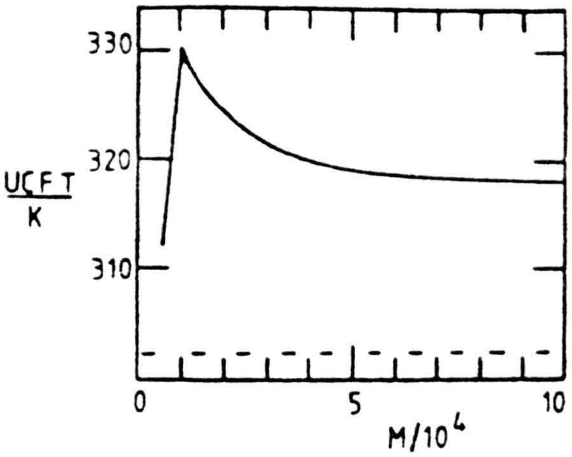


Fig. 2.23 : Effects of molecular weight (M) of polyvinyl alcohol stabiliser upon UCFT of polystyrene latex particles(65)

to increase to a maximum with increasing molecular weight of the stabilising moiety, and then to decrease to an approximately constant value. Stabilising moieties of very high molecular weight were not significantly influenced by interactions with the surface, presumably because most segments were rather distant from the surface. On the other hand, with stabilising moieties of very low molecular weight, almost all the segments were perturbed and a very large enhancement was evident.

CHAPTER THREE

THEORY OF STABILITY OF LYOPHOBIC COLLOIDS

3.1 Lyophobic colloids

The simplest type of colloid system is a dispersion of one phase in a second phase, in which the disperse phase is in a state of dispersion such that at least one dimension is in the range between 1 nm and 1000 nm.(66,67) Colloids are generally classified as lyophobic (*i.e*, there is no tendency for the disperse phase to mix with the dispersion medium) or lyophilic (*i.e.*, there is a strong tendency for the disperse phase to mix with the dispersion medium). Thus lyophobic colloids are essentially two-phase systems consisting of a disperse phase and a dispersion medium. The most important physical property of a lyophobic colloid is its colloid stability. Rubber latices are examples of lyophobic colloids. The factors which determine the colloid stability of a rubber latex are essentially those which determine the colloid stability of any lyophobic colloid. Because of the importance of colloid stability for the project which is reported in this thesis, it is desirable to review briefly the various theories which have been proposed to explain the stability of lyophobic colloids, and the factors which affect that stability.

3.2 Nature of the stability of lyophobic colloids

A lyophobic colloid is said to be stable if it persists as a colloidal dispersion over a period of time. However, all lyophobic colloids are thermodynamically unstable because of their high interfacial free energy which is a result of the high ratio of interfacial area to volume for the disperse phase. Aggregation or flocculation of the dispersed particles, which brings about a reduction of the interfacial area and free energy is therefore thermodynamically favourable. The stability/flocculation behaviour of a lyophobic colloid is governed by the various attractive and repulsive forces between the particles. The possible basic interparticle forces involved in colloidal systems of all types of can be listed as follows:(68,69)

1. Van der Waals attractive forces: These originate from the quantum-wave mechanical interaction between all the atoms in one particle and all the atoms in a neighbouring particle.

2. Electrostatic repulsive forces: These arise from the presence of a counterion cloud which surrounds the particles in the dispersion medium. The counterion cloud is brought into existence by the presence of electric charges of opposite polarity attached to the particle surfaces.

3. Steric repulsive forces: These arise from the presence of lyophilic macromolecules that are attached to the particle surfaces.

4. Solvation forces: These arise from the presence of solvent molecules which are tightly bound in the interfacial region.

5. Depletion or exclusion forces: These arise from the presence of lyophilic macromolecules dissolved in the dispersion medium

6. Born forces: These are very short-range repulsive forces.

Amongst these interparticle forces, at least four types of repulsive forces namely, electrostatic, steric, solvation, and depletion (exclusion) are believed to contribute to the stability of lyophobic colloids. The types of stabilisation conferred by these four types of repulsive forces are known, respectively, as electrostatic, steric, solvation and depletion (exclusion) stabilisation.

3.3 Van der Waals attraction

The particles of a colloidal system adhere when they collide because there are operative between them fairly strong, and quite long-range, van der Waals attractive forces. These forces increase with decreasing interparticle distance.(70) The van der Waals attractions between atoms or molecules may originate in three possible ways:(71) permanent dipole-permanent dipole (Keesom) forces;(72) permanent dipole-induced dipole (Debye) forces;(73) and transitory dipole-transitory dipole (London dispersion) forces.(71) With the exception of highly-polar substances, London dispersion forces are believed to account for nearly all of the van der Waals attraction operating between colloid particles.

According to the London theory,(71) for two identical atoms (or molecules) separated by distance r_a, the van der Waals interactive potential, V_a, is given by,

$$V_a = -\lambda / r_a^6 \qquad \text{....(3.1)}$$

where λ is a characteristic constant (the London constant) of the atoms (or molecules) under consideration. Approximate equations have been proposed for λ. The following equation has been derived by London:

$$\lambda = 3\alpha^2 h\nu_0/4 \qquad \text{....(3.2)}$$

where α is the polarisability of the atom, h is Plank's constant and ν_0 is a characteristic frequency of the atom considered.

An alternative approximate formula was derived by Slater and Kirkwood:(74)

$$\lambda = 11.25 \times 10^{-24} n_e^{1/2} \alpha^{3/2} \qquad \ldots.(3.3)$$

in which n_e is the number of electrons in the outermost shell of the atom.

The van der Waals attraction between two atoms or molecules is relatively short range. For colloidal particles, however, it is assumed that each atom or molecule of one particle attracts every atom in the other particle, thereby generating a long-range attraction between the particles that is of considerable strength.

Hamaker(75) and de Boer(76) extended London's theory to calculate the attraction energy between two particles. According to Hamaker(75), the van der Waals interaction potential energy, V_a, between two spherical particles, each of radius a, is given by

$$V_a = \frac{-A_H}{6}\left[\frac{2}{s^2-4} + \frac{2}{s^2} + \ln\left(\frac{s^2-4}{s^2}\right)\right] \qquad \ldots.(3.4)$$

where s is equal to R/a, R being the distance between the centres of the two particles, and A_H is the Hamaker constant. The Hamaker constant characterises the effective tendency of particles to attract each other when immersed in a particular dispersion medium. It is essentially a property of the material of the particles, and it includes the London constant λ. When the separation distance between the surfaces of the particles (H_o) is small compared with the particle radius, a, equation (3.4) reduces to,

$$V_a = -A_H a/12H_o \qquad \text{....(3.5)}$$

The equation (3.5) is not valid for values of H_o greater than about 10nm. At such distances, allowance must be made for the retardation effect, which is caused by the finite time necessary for the propagation of an electromagnetic wave from one atom to an other atom in which it is inducing a dipole. Approximate expressions for the retarded van der Waals interaction between two plates, between two spheres, and between a sphere and a plate have been given by Gregory.(77)

3.4 Electrostatic stabilisation

Electrostatic stabilisation of lyophobic colloids is a consequence of the presence of bound electric charges at the surface of the particles. The origin of the surface charge can be either ionisation of chemical groups at the surface of the particles or the adsorption of charged species from the dispersion medium at the particle surface. The theory of electrostatic stabilisation involves the concept of an electrical double layer at the particle surface.

3.4.1 Electrical double layer

The surface charge of the particles disturbs the distribution of nearby ions in the dispersion medium in such a way that ions of opposite charge (counterions) are attracted towards the surface and ions of like charge (co-ions) are repelled away from the surface. This leads to the formation of an "electrical double layer", which comprises the surface charge and the neutralising counterions. The concept of an electrical double layer was first introduced by Helmholtz(78) and later developed by Gouy(79) and Chapman(80) and by Stern.(81)

3.4.1.1 Helmholtz model for the electrical double layer(78)

Helmholtz proposed that the double layer consists of two layers of opposite charge, separated by a distance d, analogous to a parallel-plate condenser. This is the simplest model for an electrical double layer and is known as Helmholtz double layer. Fig.3.1 illustrates schematically (a) a Helmholtz double layer, and (b) the variation of surface potential, ψ, with distance from the surface. According to this model, the surface charge is neutralised completely by a layer of counterions adjacent to the surface, and the potential, ψ, drops linearly to zero across the double layer. The tendency of the layer of counterions to disperse under the influence of thermal motion is neglected in the Helmholtz model of the double layer.

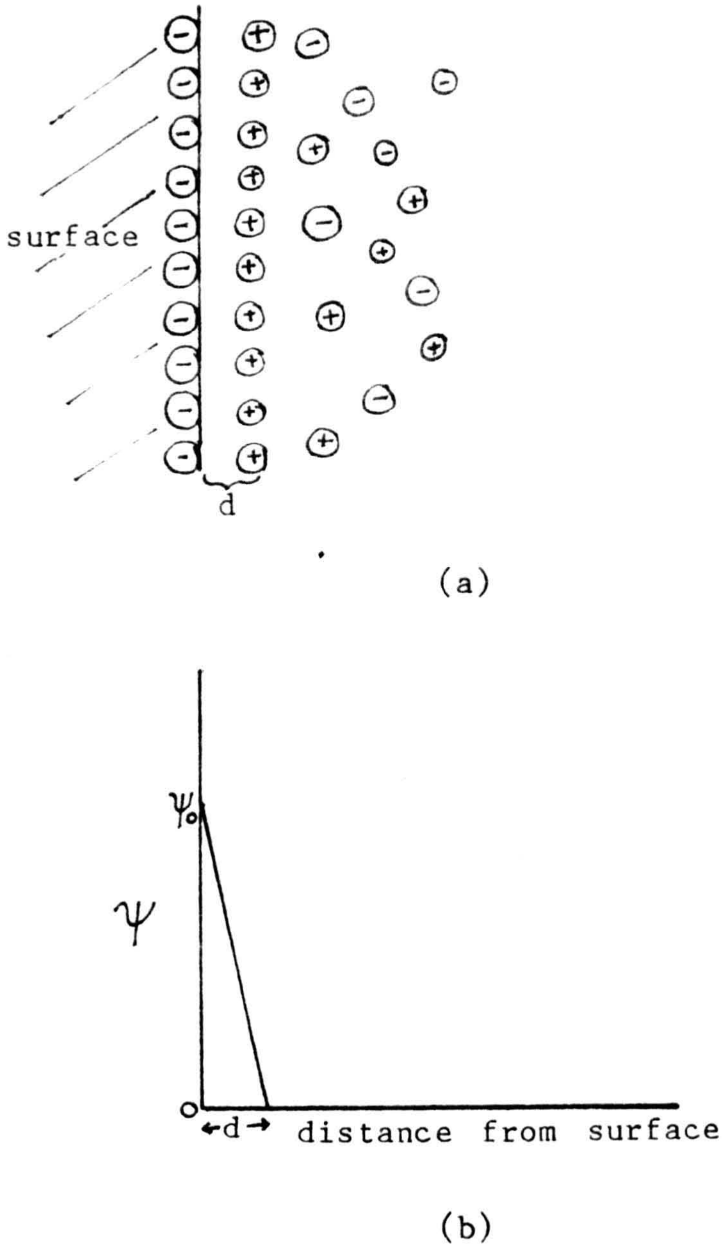


Fig. 3.1 : Schematic representation of (a) a Helmholtz double layer and (b) the variation of potential with distance from the surface

3.4.1.2 Gouy-Chapman model for the electrical double layer (79,80)

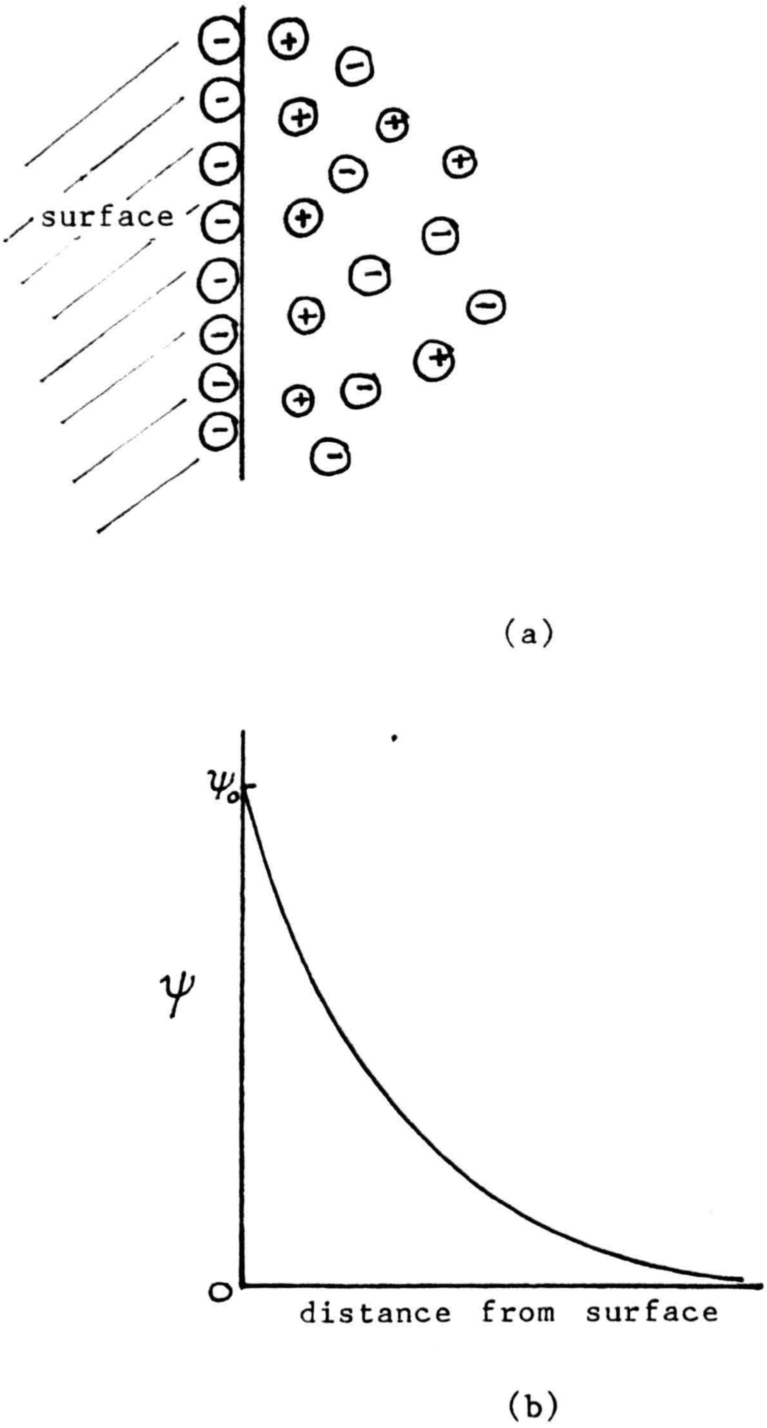
Gouy and Chapman modified the Helmholtz model for the electrical double layer. According to their model, the electrical attractions of the counterions in the dispersion medium towards the particle surface are opposed by thermal diffusion forces. This leads to the formation of a so-called "diffuse electrical double layer". Schematic representations of the diffuse electrical double layer, and the variation of potential, ψ, with distance from the surface are shown in Fig. 3.2. On the basis of this model, for a spherical particle of radius a, the potential in the dispersion medium at a distance r from the centre of the particle, ψ_r, is given for small potentials ($\psi_0 < 25$mV) by

$$\psi_r = \psi_0 a/r \exp\left[\kappa (a-r)\right] \qquad \ldots.(3.6)$$

the constant κ being given by

$$\kappa = (8\pi E^2 z^2 C_o / D k_B T)^{\frac{1}{2}} \qquad \ldots.(3.7)$$

where C_o is the number of ions per unit volume, z is the valency of the ions, E is the electronic charge, D is the dielectric constant of the dispersion medium, k_B is the Boltzmann constant, and T is the absolute temperature. κ has the dimensions of reciprocal length, and $1/\kappa$ is called the " thickness " of the double layer.



(a)

(b)

Fig. 3.2 : Schematic representation of (a) the diffuse electrical double layer and (b) variation of poltential with distance

3.4.1.3 Stern model for the electrical double layer(81)

A more sophisticated model of the electrical double layer has been given by Stern. It is a modified version of the Gouy-Chapman model with the following amendments:

1. Allowance is made for the finite dimensions of the ions in the layer immediately adjacent to the surface, as these ions will limit the inner boundary of the diffuse part of the double layer, since the centre of an ion can only approach the surface to within its hydrated radius without becoming specifically adsorbed.

2. Allowance is also made for the possibility of specific ion adsorption.

Introduction of these two amendments divides the counterion region of the double layer into two parts. One part consists of a layer of counterions adsorbed on to the surface, and the other part consists of a diffuse space charge as in the Gouy-Chapman model. The plane which separates these two parts of the double layer is called the Stern plane. The centres of any specifically adsorbed ions are located in the Stern layer, *i.e.*, between the surface and the Stern plane. Ions with centres located beyond the Stern plane form the diffuse part of the double layer. A Schematic representation of the Stern model of the electrical double layer, and of the variation of potential with distance from the surface are shown in Fig. 3.3. The potential changes from ψ_0 (the surface or wall potential) to ψ_S (the Stern potential) in the Stern layer, and decays

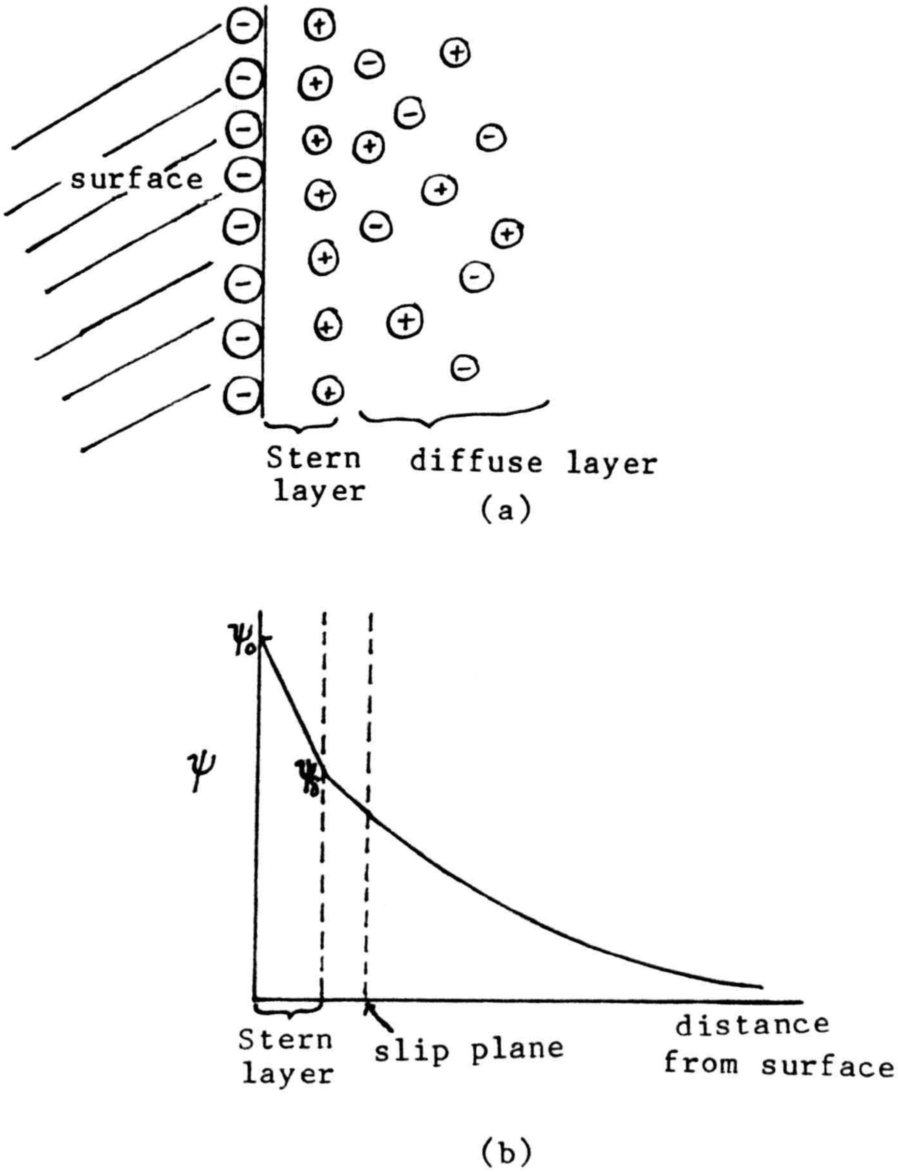


Fig. 3.3 : Schematic representation of (a) Stern model of the electrical double layer and (b) variation of potential with distance from the surface

from ψ_s to zero in the diffuse layer.

An electrical double layer as a whole is electrically neutral. The surface charge is equivalent to the total of the space charge in the Stern layer and the space charge in the diffuse layer. The total surface charge density, σ_o, is therefore given by

$$\sigma_o = \sigma_s + \sigma_d \qquad \text{....(3.8)}$$

where σ_s and σ_d are the charges equivalent to the surface charge density which are associated with the Stern layer and the diffuse layer.

Stern assumed that a Langmuir-type adsorption isotherm could be used to describe the equilibrium between ions adsorbed in the Stern layer and those in the diffuse part of the double layer. Making this assumption, it is found that surface charge density of the Stern layer is given by

$$\sigma_s = \frac{N_1 ze}{1+[(N_A/M_s n_o)\ \exp\ (-ze\psi_d)/k_B T]} \qquad \text{....(3.9)}$$

where N_1 is the number of adsorption sites per unit area, N_A is the Avegadro's number, M_s is the molecular weight of the solvent, n_o is the bulk concentraton of ionic species and ψ_d is the specific chemical adsorption potential of a counter ion adsorbed at the interface.

3.4.2 Electrostatic interaction between two spherical double layers

When two spherical particles, each carrying a diffuse layer, approach each other overlapping of the diffuse part of the double layers creates the repulsive force which discourages flocculation. No simple expression can be given for the energy of repulsion of spherical diffuse layers, but the following expressions are reasonable approximations.(66)

For small surface potentials (ψ_o) and small κa (extension of double layer much larger than particle radius),

$$V_r = 2\pi\epsilon\epsilon_0 a\psi_o^2 \frac{\exp(-\kappa H_o)}{1 + H_o/2a} \qquad \ldots.(3.10)$$

For large κa, symmetrical electrolytes (for an electrolyte which generates only ions of charge numbers +z and -z), and relatively large distances (κH_o large),

$$V_r = 32\pi\epsilon\epsilon_0 a(RT\gamma/zF)^2 \ln[1+\exp(-\kappa H_o)] \qquad \ldots.(3.11)$$

where $\gamma = \tanh(zF\psi_o/4RT)$
and R is the gas constant and F is the Faraday constant.

For small values of ψ_o and small values of

$\exp(-\kappa H_0)$, the equation (3.11) simplifies to

$$V_r = 2\pi\varepsilon\epsilon_0 a \psi_0^2 \exp(-\kappa H_0) \qquad \ldots.(3.12)$$

In the above expressions, it is assumed that, during the approach of two particles, the surface potential ψ_0 remains constant.

3.5 Total potential energy of interaction between two electrostatically-stabilised spherical particles

The total potential energy of interaction, V_T, between two electrostatically-stabilised spherical particles is given by the algebraic sum of the van der Waals attraction energy, V_a, and the electrostatic repulsion energy, V_r, i.e.,

$$V_T = V_a + V_r \qquad \ldots.(3.13)$$

The first quantitative theory of the stability of lyophobic colloids based upon equation (3.13) was developed independently by Deryaguin and Landau(82) in Russia, and by Verwey and Overbeek(66) in the Netherlands. Today, it is well known as the DLVO theory. The result for the total potential energy of interaction as a function of the distance of separation of two electrostatically-stabilised spherical particles is shown schematically in Fig. 3.4. This curve exhibits a number of characteristic

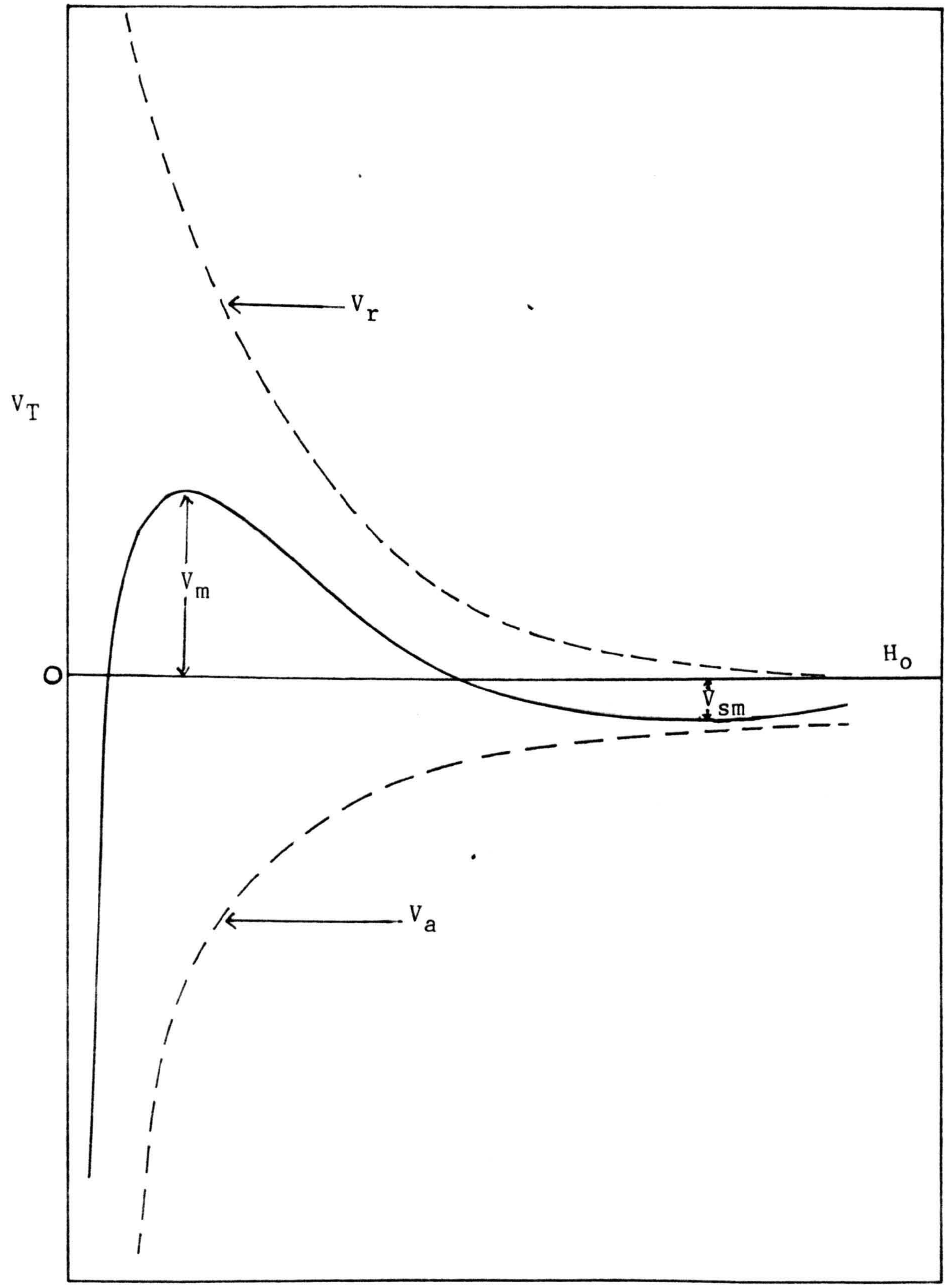


Fig. 3.4 : Schematic representation of variation of potential energy of interaction, V_T, with interparticle distance, H_o, for two electrostatically-stabilised spherical particles

features. At short distances, a deep minimum in the potential energy curve occurs. This is called the primary minimum. Its position determines the distance of closest approach between the particle surfaces. At intermediate distances, a maximum potential energy of interaction of magnitude, V_m, occurs, this is termed as the primary maximum. Arbitrary values for V_m ranging from 25 to 0 kT have been selected as the demarcation between stable and unstable lyophobic colloid systems.(66,83-85) At larger distances, a shallow secondary minimum, V_{sm}, may occur in the curve. The difference between V_m and V_{sm} is often referred to as the potential energy barrier. If the particles are able to overcome this potential energy barrier, they will make a permanent contact in the primary minimum. This aggregation is an essentially irreversible process. The depth of the secondary minimum is small for small particles, but becomes.enhanced as the particle size increases. Aggregation in the secondary minimum is reversible.

3.6 Kinetics of coagulation

3.6.1 Smoluchowski theory of rapid coagulation(70)

In 1917, Smoluchowski presented a theory for the kinetics of the coagulation process in which coagulation is regarded as a diffusion-controlled process. He showed that the rate of disappearance of primary particles in the initial stages of coagulation could be written as

$$-dN/dt = K_rN_o^2 \qquad \ldots.(3.14)$$

where N_o is the number of primary particles per unit volume present initially and K_r is the rate constant. For rapid coagulation, <u>i.e.</u>, coagulation in the absence of an energy barrier, the process is diffusion-controlled and $K_r=K_0=8\pi Da$ where D is the diffusion coefficient of a single particle and a is the collision radius of the particles. According to Einstein's theory, the diffusion coefficient, D, can be expressed as follows:

$$D = K_BT/6\pi\eta_oa \qquad \ldots.(3.15)$$

where K_B is the Boltzmann constant, T is the absolute temperature, and η_o is the viscosity of the dispersion medium. Thus the equation (3.14) can be rearranged to give,

$$-dN/dt = 4K_BTN_o^2/3\eta_o \qquad \ldots.(3.16)$$

where $4K_BT/3\eta_o$ is the rate coefficient for rapid coagulation, K_o. Integration of equation (3.16) gives

$$1/N = (1/N_o)+(4K_BTt/3\eta_o) \qquad \ldots.(3.17)$$

where N is the total number of particles that are present at time t. Thus according to the Smoluchowski theory, the reciprocal of the particle concentration increases linearly with time during rapid coagulation. Such linear plots have been reported by several workers.(86-91)

Smoluchowski expressed his results in terms of the "half-life" of the system, i.e., the time taken to reduce the number of particles to half of the original value, N_o. He showed that the half-life of the system, $t_{\frac{1}{2}(\text{rapid})}$, is given by the equation

$$t_{\frac{1}{2}}(\text{rapid}) = 1/K_rN_o \qquad \text{....(3.18)}$$

Combining equations (3.17) and (3.18),

$$t_{\frac{1}{2}}(\text{rapid}) = 3\eta_o/4K_BTN_o \qquad \text{....(3.19)}$$

Two important factors, namely, the van der Waals attraction between the particles, which tends to accelerate the particle motion, and the hydrodynamic resistance between the particles, which tends to retard the particle motion, have not been taken into account in this theory. Attempts have been made to modify the Smoluchowski theory taking the effects of these factors into account.(92,93) Lichtenbelt et al.(94) have shown experimentally that the rate of rapid coagulation, and hence the frequency of collision between the particles, is about half the rate predicted by the

Smoluchowski theory.

3.6.2 Slow coagulation

Smoluchowski(70) suggested that the coagulation would be slowed down by the presence of a potential energy barrier between the particles, although it is still regarded as being a diffusion-controlled process. Coagulation under such conditions is referred to as retarded or slow coagulation. He suggested that

$$t_{\frac{1}{2}}(\text{slow}) = t_{\frac{1}{2}}(\text{rapid})/\alpha \qquad \ldots.(3.20)$$

where α is the fraction of the number of the collisions which lead to permanent contact. In 1934 Fuchs(95) obtained a relationship between α and the potential energy of interaction, V_T, as a function of interparticle separation. He showed that

$$t_{\frac{1}{2}}(\text{slow}) = t_{\frac{1}{2}}(\text{rapid})\,2a\int_{2a}^{\infty}\exp(V_T/K_BT)\,dR/R^2 \qquad \ldots.(3.21)$$

where R is the distance between the centres of the particles. The factor by which the coagulation process is retarded is called stability ratio, W. It is equal to $1/\alpha$. According to the Fuchs theory, it is given by

$$W = 2a\int_{2a}^{\infty}\exp(V_T/K_BT)\,dR/R^2 \qquad \ldots.(3.22)$$

Since V_T is approximately proportional to the particle radius, a, it is expected that, other things being equal, the coagulation of large particles is slowed down more strongly than that of small particles. This, however, has not been confirmed by experiments.(96) The experiments show that W is approximately independent of particle radius.

3.7 Steric stabilisation

As has been stated in the literature review (Chapter 2), the ability of polymeric substances to stabilise lyophobic colloids has long been known. In spite of their wide application for many years, it is only during the last few decades that the theories of the mechanism of steric stabilisation have been developed. During this period, several theories have been developed to describe the adsorption and conformation of polymers at the solid/liquid interface. At the same time, theories have also been developed for the interaction of colloid particles having adsorbed lyophilic macromolecules at their surfaces.(97-100)

3.7.1 Conformation of polymer molecules adsorbed at solid/liquid interfaces

Theories of polymer adsorption assume that the configuration of an adsorbed polymer on a solid surface can be represented as a flexible chain of segments, some of which are in direct contact with the surface, whilst others extend into the dispersion medium. A schematic representation of the conformation of an adsorbed polymer molecule at a plane interface is shown in Fig. 3.5. Those segments which are in direct contact with the surface are referred to as "trains", and those in between and extending into the dispersion medium are referred to as "loops". The free ends of the adsorbed polymer also extending into the dispersion medium are referred to as "tails".

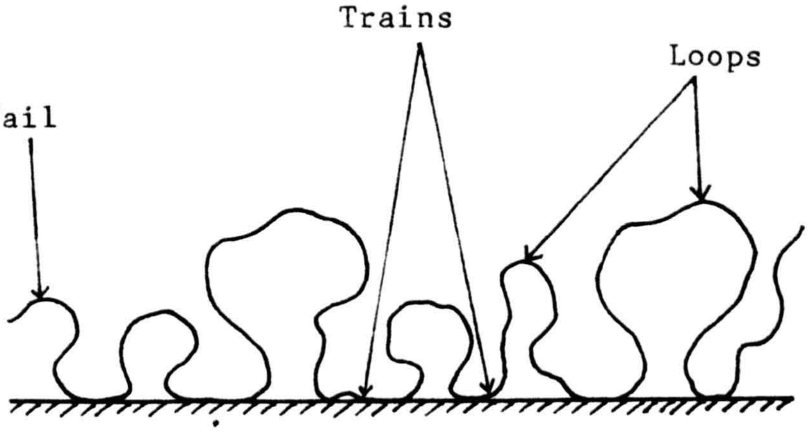


Fig. 3.5 : Schematic representation of conformation of an adsorbed polymer molecule at a plane interface

A detailed description of adsorption of a polymer molecule at a solid/liquid interface would require a knowledge of the following matters:

1. the amount of adsorption per unit area of the

surface, Γ;

2. the fraction of segments in contact with the surface, p;
3. the distribution of the segments in the vicinity of the surface, p(z).

These characteristics depend upon a number of variables such as the nature and molecular weight of the adsorbed polymer, the nature of the adsorbent, the solvent and the temperature.(101) Of these characteristics, a knowledge of the distribution of the segments in the vicinity of the surface, p(z), is of particular importance, especially in connection with the evaluation of the interaction between two colloidal particles containing adsorbed polymers.

Hoeve(102) was the first to calculate p(z) for an adsorbed homopolymer at a solid/liquid interface. He showed that at a distance from the interface corresponding to the thickness of the trains, there is a discontinuity in the distribution of the polymer segments. Beyond this distance, the density of the segments falls exponentially with distance. This is shown schematically in Fig. 3.6. Meier(103) developed a similar theory for the segment-density distribution of a single terminally adsorbed tail. Hesselink(104) has developed Meier's theory to give segment density distributions for single tails, single loops, homopolymers and random copolymers. These are shown in

Fig. 3.7.

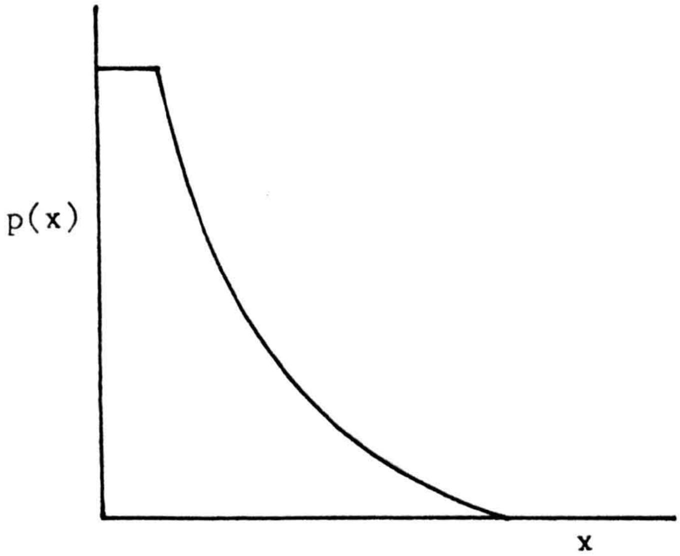


Fig. 3.6 : Variation of segment density distribution with the distance

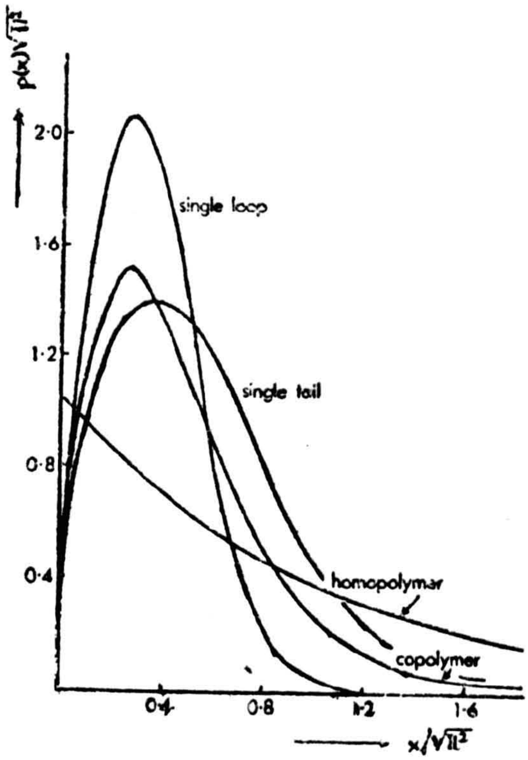


Fig. 3.7 : Variation of segment density distribution with distance for single tails, single loops, homopolymers and random coplymers$^{(104)}$

In 1979, Scheutjens and Fleer(105) gave a more refined picture of the segment-density distribution. According to their theory, close to the surface the density of the segments decays roughly exponentially with the distance, but at larger distances the decay is much slower. It was suggested this is a consequence of the presence of the considerable fraction of adsorbed segments in the form of long dangling chains.

3.7.2 Interaction between colloidal particles having lyophilic macromolecules adsorbed at their surfaces

The interaction forces between sterically-stabilised colloidal particles which tend to keep the particles dispersed in solution by counteracting the ever-existing attraction arising from van der Waals forces, are of two major kinds:

1. Entropic interactions : These result from the loss in configurational entropy of a polymer molecule on the approach of a second particle. The reduction in configurational entropy of the adsorbed polymer molecule is a result of the compression of the adsorbed polymer chains which reduces the total volume available for each polymer chain. This effect is also called the "volume-restriction" or "elastic" effect.

2.Mixing interactions : These result from the interpenetration of the polymer molecules adsorbed on colloidal particles. When the layers of adsorbed polymer chains on two particles interpenetrate, the higher polymer segment concentration between the particles leads to an increase in the local osmotic pressure and free energy.

Whether interpenetration or compression, or both, occurs depends to a large extent on the segment density distribution. If the surface concentration is relatively high and uniform, compression rather than interpenetration may occur. This is usually the case with polymers of low molecular weight and with branched polymers. On the other hand, with polymers of high molecular weight, where the segment density at the periphery of the adsorbed layer is small, and also at low surface coverage, the dominant mode of interaction is interpenetration.

3.7.2.1 Entropic interactions

Mackor(106) and van der Waarden(107) have considered the entropic interactions in order to explain the stability of carbon black dispersions in hydrocarbon media in the presence of long chain alkyl benzenes. They considered a simple model based upon inflexible rods terminally adsorbed on a flat surface. The number of configurations, Ω, available to the rods was assumed to be proportional to the surface area of the plane surface swept out by the rods. Hence, by calculating the loss in the number configurations on the approach of a second surface, the decrease in configurational entropy, ΔS, was calculated using the Boltzmann expression

$$\Delta S = K_B \ln \Omega \qquad \text{....(3.24)}$$

where K_B is the Boltzmann constant.

The free energy of repulsion, ΔG_{VR}, is then given by

$$\Delta G_{VR} = N_s K_B T\, \theta_\alpha \ln \Omega \qquad \text{....(3.25)}$$

where θ_α is the fraction of surface covered by the adsorbed layer when the surfaces are at infinite separation, and N_s is the number of adsorbed rods per unit area.

As the lateral interactions between the adsorbed neighbouring rods were not taken into account, this treatment only applies at very low surface coverages. Later, an extension of this theory for high surface coverages was given by Mackor and van der Walls.(108) In this treatment, interactions between adsorbed and non-adsorbed polymer molecules were neglected. Hence the applicability of this treatment is restricted to dilute solutions.

Clayfield and Lumb$^{(109)}$ calculated the steric repulsion for flexible terminally adsorbed polymers containing up to 100 links. In this treatment, excluded-volume effects were taken into account. It was assumed that the adsorbed layers do not interpenetrate each other. The decrease in the configurational entropy, ΔS, which was calculated using the Boltzmann expression, was given by

$$\Delta S = K_B \ln [1/W(l_1)] \qquad \ldots.(3.26)$$

where $W(l_1)$ is the proportion of the total number of configurations for which the distance of furthest extremity of the chains from the surface is less than l_1. Thus the free energy of interaction per polymer molecule, ΔG_{VR}, is given by

$$\Delta G_{VR} = -K_BT \ln W(l_1) \qquad \ldots.(3.27)$$

The following approximate expression has been derived by Hesselink et al.$^{(110)}$ for the total increase in free energy when two interfaces both covered by v polymer loops of i segments each of length l approach each other to a distance d:

$$\Delta G_{VR} = 2vK_BTV(i,d) \qquad \ldots.(3.28)$$

where $V(i,d) = -2(1-12d^2/il^2)\exp(-6d^2/il^2)$

3.7.2.2 Mixing interactions

ΔG_M denotes the increase in free energy caused by the increase in the local osmotic pressure which is a result of the interpenetration of the adsorbed polymer segments when the particles approach to distances shorter than twice the thickness of the adsorbed layer. Fisher$^{(111)}$ calculated ΔG_M assuming that the segment concentration in the adsorbed layer is uniform and that the segment concentration in the overlap region is the sum of the individual concentrations from both adsorbed layers. The total change in the free energy of mixing for the whole interaction zone, V, is given as

$$\Delta G_M = 4\pi K_B T\phi_2^2\ (1/2-\chi)V/3V_1 \qquad \ldots.(3.29)$$

where V_1 is the molar volume of the solvent, ϕ_2 is the volume fraction of the polymer, and χ is the Flory-Huggins interaction parameter. Introducing a reasonable estimate for the volume, V, of the interaction zone gives

$$\Delta G_M = 4\pi K_B T\phi_2^2\ (1/2-\chi)(\delta-H_o/2)^2\ (3a+2\delta+H_o/2)/3V_1 \qquad ..(3.30)$$

where δ is the thickness of the adsorbed layer and H_o is the minimum distance between the particle surfaces.

For polymers of high molecular weight, the assumption that the segment concentration in the overlap region is the sum of the individual concentrations may be valid, at least for small degrees of interaction. However, the assumption of uniform segment density in the adsorbed layer is invalid. In order to obtain an expression for the mixing term for particles with adsorbed or anchored polymers, the segment-density distribution must be taken into account.(103,104) the following is then obtained for the free energy of mixing per unit area over the whole volume of the interaction zone:

$$\Delta G_M = K_B T V_2^2 \; (1/2-\chi)\left[\int_0^d (\rho_A+\rho_B)_d^2 \, dx - \int_0^d (\rho_A+\rho_B)_\infty^2 \, dx\right] / \; V_1 \qquad (3.31)$$

where V_2 is the volume of a segment, ρ_A and ρ_B are segment-density distributions for the polymers adsorbed on each surface, and d is the distance between the surfaces. The following approximate analytical expression for ΔG_M has been given by Hesselink <u>et al</u>.(110) for loops of equal size:

$$\Delta G_M = 2(2\pi/9)^{3/2} \; v^2 \; K_B T(\alpha^2-1)\langle r^2\rangle M_{(i,d)} \qquad \ldots.(3.32)$$

where $M_{(i,d)} = 3\pi^{\frac{1}{2}}(6d^2/il^2-1)\exp(-3d^2/il^2)$

$\langle r^2\rangle^{\frac{1}{2}}$ is the root-mean-square end-to-end length of a polymer molecule in solution, and α is the expansion factor which is given by

$$\alpha = \langle r^2\rangle^{\frac{1}{2}}/\langle r^2\rangle_0^{\frac{1}{2}} \qquad \ldots.(3.33)$$

where $\langle r^2 \rangle_0^{\frac{1}{2}}$ is the unperturbed root-mean-square end-to-end length.

3.7.2.3 Total steric interaction

The total interaction between two sterically-stabilised collidal particles is given by

$$\Delta G_T = \Delta G_A + \Delta G_S \qquad \ldots.(3.34)$$

where ΔG_A is the van der Waals attraction and ΔG_S is the steric repulsion. ΔG_S is itself the sum of two components:

$$\Delta G_S = \Delta G_{VR} + \Delta G_M \qquad \ldots.(3.35)$$

considering the case where adsorbed layers have no effect upon ΔG_A, ΔG_T for two flat plates is given by the expression,

$$\Delta G_T = \Delta G_{VR} + \Delta G_M - (A_H/12\pi d^2) \qquad \ldots.(3.36)$$

where A_H is the Hamaker constant.

Combining equations (3.28) and (3.32) gives

$$\Delta G_T = 2vK_BTV(\bar{i},d)+2(2\pi/9)^{3/2}\ v^2K_BT(\alpha^2-1)\langle r^2\rangle\ldots$$
$$\ldots.\ M_{(i,d)}-(A_H/12\pi d^2) \qquad (3.37)$$

Thus, the main parameters which determine the change in free energy on the approach of the two particles are:

- a. the average number of segments per loop (or tail), or rather, the mean-square loop size $\tilde{\imath}l = \langle r^2 \rangle \alpha^2$ in which $\langle r^2 \rangle$ is proportional to the molecular weight, M, of the loops
- b. v, the number or weight of adsorbed loops (or tails) per unit area
- c. χ, the quality of the solvent
- d. the mode of attachment of the polymer
- e. A_H, the net Hamaker constant

Hesselink et al.(110) have calculated the ΔG_T for colloidal particles covered by polystyrene by means of equation (3.37). Their results are shown in Fig.3.8. At large values of d, ΔG_A predominates, but at shorter distances a very steep repulsion prevent further approach. Unlike in the potential energy-separation curve for a pair of electrostatically-stabilised particles, only one minimum, ΔG_{min}, is found even at very low coverages over the whole range of d. This is understandable because osmotic repulsion starts as soon as the polymer layers overlap, whereas the volume restriction effects start after some degree of interaction between the adsorbed layers has taken place.

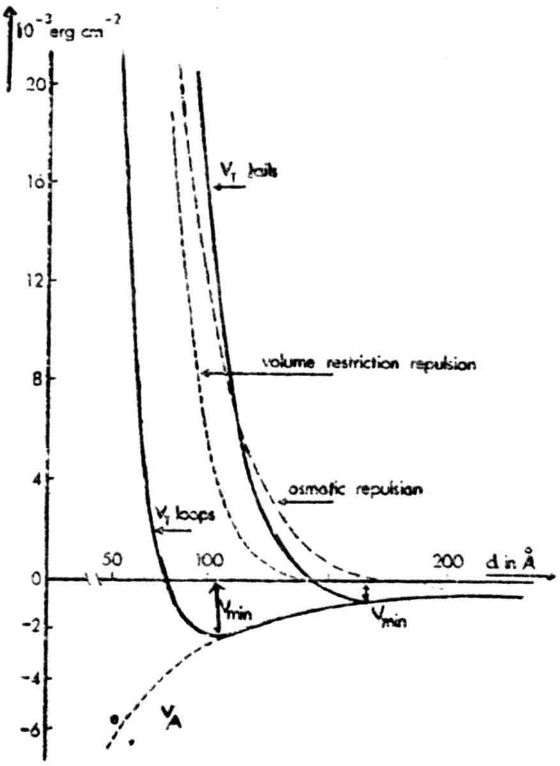


Fig.3.8 : Total interaction energy between two flat plates having adsorbed tails or loops: A = 10^{-20} J, α = 1.2, M = 6000, $\langle r^2 \rangle^{\frac{1}{2}}$ = 5.2 nm, area per chain = 50 nm^2(110)

3.7.3 Classification of sterically-stabilised dispersions

As has been stated in the literature review, one of the characteristic features of sterically-stabilised colloidal dispersions, which distinguishes them from electrostatically-stabilised dispersions, is the extent to which the colloid stability can depend upon temperature. Some dispersions flocculate on heating;(112,113) others flocculate on cooling.(113,114) In some cases, dispersions can be produced which do not flocculate at any accessible temperature,(114) whilst some sterically-stabilsed dispersions have been found to flocculate on both heating and cooling.(115,116) These observations provide a clue to the thermodynamic processes that govern stabilisation. The temperature-dependence of the total free energy of interaction is give by(115)

$$\Delta G_T = \Delta H_T - T\Delta S_T \qquad \text{....(3.38)}$$

where ΔG_T is the free energy change accompanying close approach of two sterically-stabilised colloid particles, and ΔH_T and ΔS_T are the corresponding enthalpy and entropy changes. Thus the sign of ΔG_T will depend upon the signs and relative magnitude of ΔH_T and ΔS_T, as summarised in Table 3.1. On this basis, three types of steric stabilisation can be distinguished. Enthalpically-stabilised dispersions are characterised by flocculation on heating, whereas entropically-stabilised dispersions are

ΔH_T	ΔS_T	$\lvert\Delta H_T\rvert/\lvert\Delta S_T\rvert$	type	flocculation
+	+	>1	enthalpic	on heating
-	-	<1	entropic	on cooling
+	-	<1	combined	not accessible

Table 3.1 : Types of steric stabilisation(115)

characterised by flocculation on cooling. For the combined type of stabilisation, dispersions do not, in principle, flocculate at any accessible temperature.

3.8 Limitations of theories of electrostatic and steric stabilisation

A discussion of the strong and weak points of the theory of steric stabilisation has been given by Overbeek.(117) Some of the theory of electrostatic stabilisation can be outlined as follows:

1. The repulsion equation is based upon a theory of the electrical double layer in which the ions are treated as point of charges. This treatment is incorrect, because it allows the concentrations of ions to reach impossibly high values near the surface.
2. A further serious consequence of the Stern-Gouy Chapman model is the fact that, under coagulation conditions, the Stern potential is neither high nor independent of the concentration and charge number of the ions.
3. The simple model with deep primary minimum would make coagulation quite irreversible and would not allow repeptisation. However, it has been shown(118,119) that repeptisation is the rule rather than exception, and that irreversibility is

found only after the particles have been coagulated for some time.

Some of the weak points of the theory of steric stabilisation can be outlined as follows:

1. Quantitative application of the present theory is limited.
2. Adsorption of the polymer molecules is obviously a key factor in the protection mechanism, but adsorbability is hard to predict.

3.9 Solvation stabilisation

The stability of electrostatically-stabilised dispersions has been found to deviate markedly from the predictions of DLVO theory. It has been suggested the presence of a solvation layer around the particles is responsible for this deviation.(120,121) There is evidence in the literature to show the presence of solvation layer near the solid surface.(122-125) The extent of solvation depends to a considerable extent upon the chemical nature of the stabiliser.

There are at least four possible effects that the presence of a solvation layer might have upon the stability of a lyophobic colloid:

1. The solvation layer may decrease the Hamaker constant, and hence also the van der Waals attraction between the particles.
2. Desolvation from the interaction zone, which has to occur before destabilisation, will result in an increase of the free energy, and hence will bring into existence a repulsive force between the particles.
3. Because of volume restriction effect, the solvation layer will act as a mechanical barrier to prevent the particles approaching one another closely.
4. The interfacial free energy between the outer surface of the solvated particle and the dispersion medium is virtually zero.

All these effects promote the stabilisation of the colloidal dispersion.

3.10 Depletion (exclusion) stabilisation

It has been shown that colloid stability can be imparted by the presence of free polymer dissolved in the dispersion medium.(126) This type of stabilisation is referred to as "depletion" or "exclusion" stabilisation. It has been suggested that the stability arises from the depletion of the concentration of free polymer between the surfaces of the particles when are in close proximity. Closer approach of the particles can only be achieved by a further depletion of the segment concentration between the particles. At much closer approach between the particles, almost complete exclusion of polymer molecules from between the surfaces of the particles occurs. In a good solvent this is energetically unfavourable.

CHAPTER FOUR

EXPERIMENTAL

4.1 Materials

4.1.1 Latices

Two types of natural rubber latices were used in this investigation, namely, a high-ammonia centrifuged latex concentrate and a low-ammonia centrifuged latex concentrate called "Dynatex", both supplied by LRC International Ltd. Several batches of latices were used. The characteristics of each batch of latex as determined by the procedures specified in BS 1672:1972 are summarised in Table 4.1.

property	type of latex			
	low-ammonia			high-ammonia
	Batch 1	Batch 2	Batch 3	Batch 4
total solids content/%	61.45	62.05	61.23	62.26
dry rubber content/%	60.16	60.45	60.06	60.60
alkalinity/g NH_3 per 100g of aqueous phase	0.61	0.51	0.60	1.07
mechanical stability time/seconds	975	812	960	1120
KOH number	0.62	0.61	0.61	0.61
VFA number	0.03	0.09	0.03	0.02
pH	9.91	9.63	9.89	10.32

Table 4.1 : Properties of various batches of natural rubber latices used

4.1.2 Reagents

Acrylic acid : supplied by Aldrich Chemical Co. Ltd.; purity 98%; stored at room temperature; used without further purification.

Methacrylic acid : supplied by Aldrich Chemical Co. Ltd.; purity 98.5%; stored at room temperature; used without further purification.

Methyl acrylate : supplied by BDH Chemicals Ltd.; purity 95%; stored at room temperature; used without further purification.

2-Ethylhexyl acrylate : supplied by Fluka AG.; purity 98%; stored in a refrigerator at a temperature of about 5°C; used without further purification.

2-Hydroxyethyl methacrylate : supplied by BP chemicals; technical grade; stored at room temperature; used without further purification.

Ethyleneglycol dimethacrylate : supplied by Koch-Light Laboratories Ltd.; stored in a refrigerator at a temperature of about 5°C; used without further purification.

2,2'-Azo bis-(2-metyhyl propionitrile) : supplied by Aldrich Chemical Co. Ltd.; stored in a refrigerator at a temperature of about 5°C; used without further purification.

Ammonia : supplied by BDH Chemicals Ltd.; as a 35% solution. Two dilute solutions of ammonia, namely, 1.6% (W/V) and 0.6% (W/V) were prepared by diluting the stock solution with distilled water.

Hydroquinone : supplied by Aldrich Chemical Co. Ltd.; purity 98.5%

Sodium hydroxide : supplied by Fisons; purity 96%.

Potassium hydroxide : supplied by Fisons; purity 95%.

Zinc oxide : supplied by BDH Chemicals Ltd.; Analar grade.

Ammonium acetate : supplied by BDH Chemicals Ltd.; Analar grade.

Vulcastab LW : supplied by ICI Ltd.; used as a 20% aqueous solution.

Dispersol LN : supplied by ICI Ltd.; used as a 10% aqueous solution.

Polyvinyl methyl ether : supplied by BASF Ltd.; used as a 50% aqueous solution.

Zinc sulphate : supplied by BDH Chemicals Ltd.; Analar grade.

Potassium hydroxide : supplied by Fisons; purity 98%.

Potassium hydrogen phthalate : supplied by Fisons; Analar grade

Phenolphthalein : supplied by BDH chemicals Ltd. as a 1% solution in propan-2-ol.

Sodium alginate : supplied by Hopkins and Williams Ltd.

t-Dodecyl mercaptan : supplied by Koch-light Laboratories Ltd.

Distilled water : all the distilled water used in this work was obtained from a Manesty Type S45 distillation unit.

4.2 Experimental Procedures

4.2.1 Preparation of polymers

Two methods were used for the preparation of polymers. Both methods were similar in the sense that both of them were free-radical-initiated solution polymerisations. The method of addition of polymerisation reactants, and, hence the rates of polymerisation for the two methods were different.

Method 1

This method was similar to that used by P.A.Bradbury, a previous research worker in this School, to prepare terpolymers and copolymers of three types of monomers, namely, hydrophilic non-ionogenic monomers, hydrophilic ionogenic monomers and hydrophobic monomers. The composition of some of the polymers prepared by Bradbury are indicated in Fig. 4.1 as points on a triangular composition diagram. A preliminary investigation was carried out of the effects of these polymers upon the mechanical stability time (MST) of NR latex (Batch 1) at the 0.50 pphls level of addition. The results showed that that copolymers of MAA and EHA were more effective in enhancing the MST of NR latex than were the copolymers of MAA and HEMA, and the terpolymers of MAA, EHA, and HEMA. Therefore in this investigation hydrophilic ionogenic monomers such as MAA and hydrophobic monomers

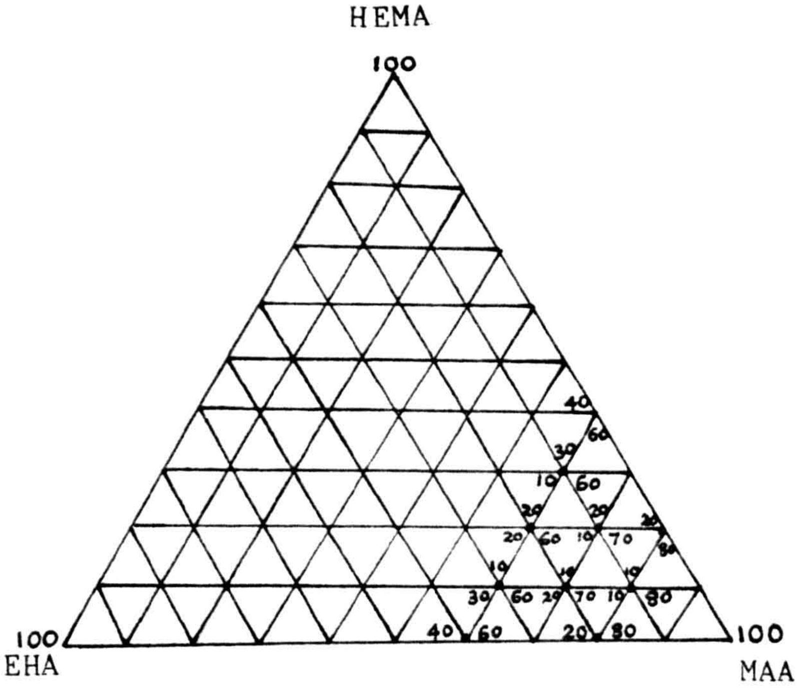


Fig. 4.1 : Compositions (in mole percentages) of some of the polymers prepared by Bradbury

HEMA - 2-hydroxyethyl methacrylate

MAA - methacrylic acid

EHA - 2-ethylhexyl acrylate

such as EHA were chosen as the comonomers for the preparation of the polymers.

All the polymers were prepared by free-radical-initiated solution polymerisation, using industrial methylated spirits (IMS) as the solvent. IMS (350cm^3) was purged with nitrogen and refluxed in a 2-litre reaction vessel fitted with a stirrer and a dropping funnel. The initiator was 2,2'-azobis-(2-methyl propionitrile). It was dissolved in warm IMS (100cm^3) and added to the reaction vessel. The requisite amounts of the monomers were mixed together and added to the reaction mixture by means of the dropping funnel. The glassware was washed with 50cm^3 of IMS and added to the reaction mixture. All the additions were completed in less than 20 minutes. The mixture was refluxed for 6 hours, and left to cool overnight. It was thought that this 6-hour reaction period would be sufficient for the completion of the polymerisation, as Bradbury had found that this reaction period was sufficient to achieve conversions above 95% for the polymerisation of similar monomers under the same reaction conditions at the 1% level of initiator (based on the weight of the monomers). The polymers were isolated by evaporating the solvent and unreacted monomers under low pressure at 30-40°C. Details of the composition of the various reaction systems used to prepare polymers by this method are given in Table 4.2. As shown in Table 4.2, a code was assigned to each polymer, so that its nature was immediately apparent. For instance, the code MAA/EHA(80:20)Ca indicates a polymer synthesised using an 80:20 mole:mole mixture of MAA and EHA. The letters A, B, C and D were assigned to indicate the initiator level used, and the letters a and b were assigned to indicate the level of branching agent (ethyleneglycol dimethacrylate) which had been added to the monomer mixture in some cases. The quantitative significance of the letters A, B, C and D is

group	polymer	weight % of total weight of monomers		feed composition /mole%		
		AZDN^x	EGDMA^y	MAA	MA	EHA
MAA	MAA-B	4.0	-	100	-	-
	MAA-C	1.0	-	100	-	-
	MAA-Ca	1.0	0.5	100	-	-
	MAA-Cb	1.0	1.0	100	-	-
	MAA-D	0.1	-	100	-	-
MAA/MA(80:20)	MAA/MA(80:20)B	4.0	-	80	20	-
	MAA/MA(80:20)C	1.0	-	80	20	-
	MAA/MA(80:20)Ca	1.0	0.5	80	20	-
	MAA/MA(80:20)Cb	1.0	1.0	80	20	-
	MAA/MA(80:20)D	0.1	-	80	20	-
MAA/MA(60:40)	MAA/MA(60:40)B	4.0	-	60	40	-
	MAA/MA(60:40)C	1.0	-	60	40	-
	MAA/MA(60:40)Ca	1.0	0.5	60	40	-
	MAA/MA(60:40)Cb	1.0	1.0	60	40	-
	MAA/MA(60:40)D	0.1	-	60	40	-
MAA/EHA(80:20)	MAA/EHA(80:20)A	6.0	-	80	-	20
	MAA/EHA(80:20)B	4.0	-	80	-	20
	MAA/EHA(80:20)C	1.0	-	80	-	20
	MAA/EHA(80:20)Ca	1.0	0.5	80	-	20
	MAA/EHA(80:20)Cb	1.0	1.0	80	-	20
	MAA/EHA(80:20)D	0.1	-	80	-	20
	MAA/EHA(80:20)E	0.05	-	80	-	20
MAA/EHA(70:30)	MAA/EHA(70:30)B	4.0	-	70	-	30
	MAA/EHA(70:30)D	0.1	-	70	-	30
MAA/EHA(60:40)	MAA/EHA(60:40)B	4.0	-	60	-	40
	MAA/EHA(60:40)C	1.0	-	60	-	40
	MAA/EHA(60:40)Ca	1.0	0.5	60	-	40
	MAA/EHA(60:40)Cb	1.0	1.0	60	-	40
	MAA/EHA(60:40)D	0.1	-	60	-	40
MAA/EHA(50:50)	MAA/EHA(50:50)A	6.0	-	50	-	50
	MAA/EHA(50:50)B	4.0	-	50	-	50

Table 4.2 : Compositions of reaction systems used to prepare polymers by Method 1

x - 2,2'-azo bis-(2-methyl proprionitrile)

y - ethylene glycol dimethacrylate

6.0%, 4.0%, 1.0% and 0.1% and that of the letters a and b is 0.5% and 1.0% respectively, based on the total weight of the monomers. Apart from MAA and EHA, methyl acrylate was also used for the synthesis of these polymers:

The weight conversions of polymerisation reactions of two polymers, namely, MAA/EHA(80:20)B and MAA/EHA(80:20)D, were determined gravimetrically using the folowing expression:

$$\text{weight conversion} = \frac{W_p}{W_m} \times 100 \qquad \ldots.(4.1)$$

where W_p = weight concentration of the polymer formed
W_m = weight concentration of the monomers used

The polymers prepared by this method will be referred to as polymers of Type 1.

Apart from the polymers given in Table 4.2, a few other polymers belonging to group MAA/EHA(80:20) were also prepared. All of these were prepared using the same polymerisation recipe, used for the preparation of polymer MAA/EHA(80:20)B but the period of polymerisation was varied. The details of the syntheses of these polymers are given in Table 4.3. The intention of carrying out this set of polymerisations was to find out if there is a composition drift with conversion in the case of MAA/EHA copolymers. The significance of this matter will be discussed in Section 5.10.

polymer	feed composition /mole %		concentration of AZDN/ (% by weight of the monomers)	period of polymerisation/ hours
	MAA	EHA		
MAA/EHA(80:20)B	80	20	4	0.5
MAA/EHA(80:20)B	80	20	4	1.0
MAA/EHA(80:20)B	80	20	4	3.0
MAA/EHA(80:20)B	80	20	4	6.0

Table 4.3 : Details of synthesis of polymers of sub-group MAA/EHA(80:20)B with various conversions

As will become apparent from the results to be presented subsequently (see Section 5.11), considerable drift of copolymer composition with conversion could occur when polymers were prepared by Method 1. A modified procedure referred to as Method 2, was therefore used in an attempt to overcome the problem of copolymer composition drift during conversion. In this modified procedure, the opportunity was also taken of minimising changes in initiator concentration with conversion caused by initiator decomposition.

Method 2

This method was a slight modification of Method 1. In this method, the monomer mixture was continuously added to the reaction system under "monomer starved" conditions, i.e., at such a rate that the amount of unreacted monomer in the reaction system was at all times low. The appropriate amount of IMS was purged with nitrogen in a 2-litre reaction vessel fitted with a stirrer and a teat pipette. The teat pipette was fixed to the reaction vessel in an inverted position by means of a screw-headed adaptor as shown in Fig 4.2. The requisite amounts of monomers and initiator, which was dissolved in IMS (100 cm^3), were mixed together and placed in a separating funnel. This separating funnel was connected to a peristaltic pump, which was equipped with a speed controller (see Fig. 4.2). The IMS in the reaction vessel was heated to reflux. The mixture in the separating funnel was transferred to the reaction vessel containing the refluxing IMS via the inverted teat pipette over a period of 6 hours. After the addition of the polymerisation reactants was complete, the mixture was allowed to reflux overnight. The procedure used for the isolation of the polymers was similar to that used in Method 1. Details of the compositions of the various reaction systems used to prepare polymers by this method are given in Table 4.4. The polymers prepared by this method will be referred to as polymers of Type 2. The coding system used for the identification of these polymers was similar but not identical to that used for the identification of polymers of Type 1. For example, the code MAA/EHA(80:20)A indicates the composition of the polymer in exactly the same way a for polymers of Type 1, but the letter A indicates the order of the molecular weight within the group of the

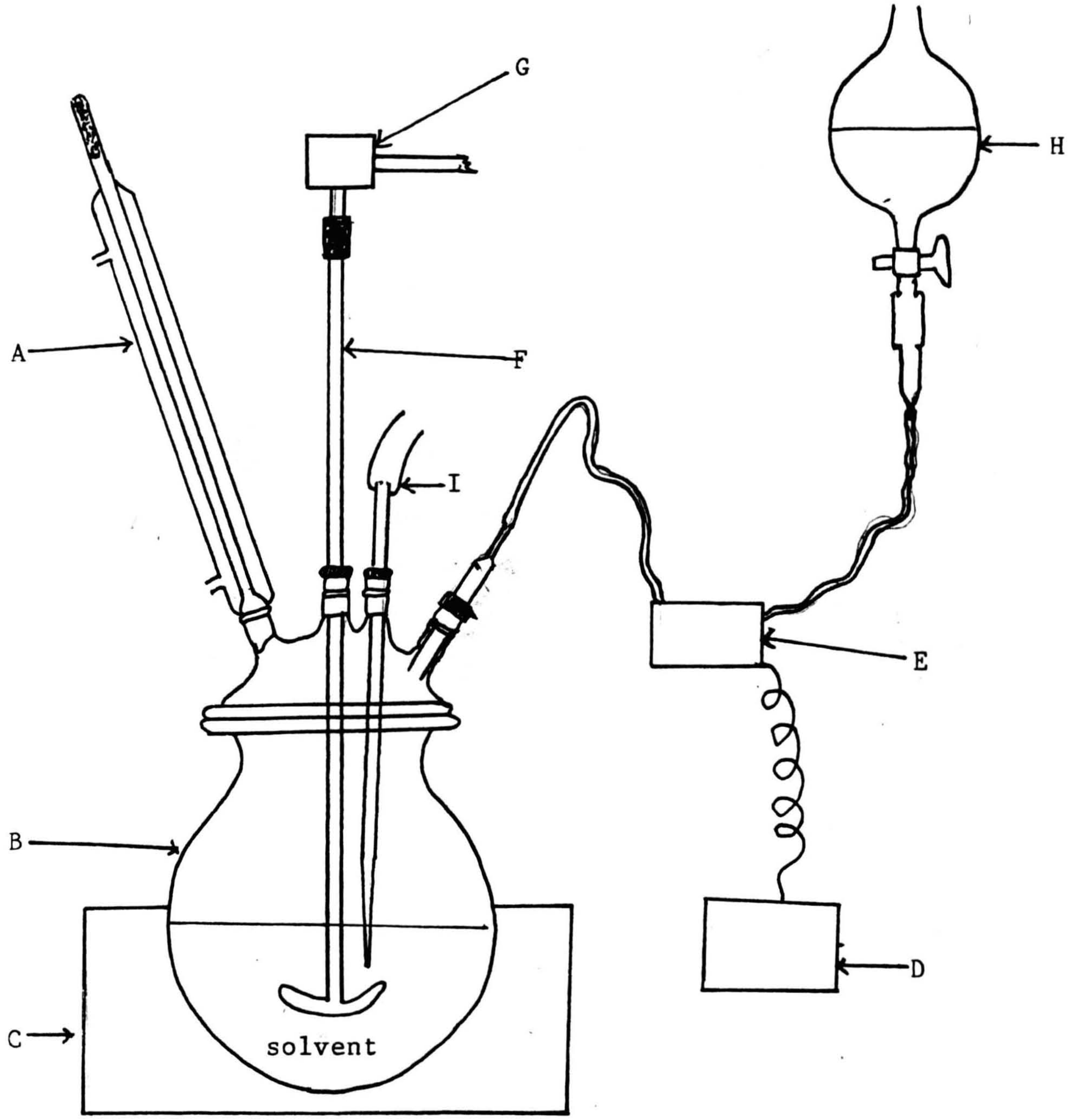


Fig. 4.2 : Apparatus for the preparation of polymers by Method 2
A - condenser B - reaction vessel C - heating mantle
D - speed controller E - peristaltic pump F - stirrer
G - motor H - separating funnel I - N_2 inlet

group	polymer	feed composition							
		mole %			weight % of total weight of reaction mixture				weight % of total weight of monomers
		MAA	AA	EHA	MAA	AA	EHA	AZDN	TDM
MAA/EHA(90:10)	MAA/EHA(90:10)A	90	-	10	8.7	-	2.1	0.43	-
	MAA/EHA(90:10)B	90	-	10	15.7	-	3.7	0.77	-
	MAA/EHA(90:10)C	90	-	10	8.7	-	2.1	0.11	-
	MAA/EHA(90:10)D	90	-	10	15.7	-	3.7	0.19	-
MAA/EHA(80:20)	MAA/EHA(80:20)A	80	-	20	13.6	-	7.3	0.84	-
	MAA/EHA(80:20)B	80	-	20	19.8	-	10.6	1.22	-
	MAA/EHA(80:20)C	80	-	20	13.6	-	7.3	0.42	-
	MAA/EHA(80:20)D	80	-	20	9.9	-	5.3	0.15	-
	MAA/EHA(80:20)E	80	-	20	10.4	-	5.6	0.16	-
	MAA/EHA(80:20)F	80	-	20	13.6	-	7.3	0.21	-
MAA/EHA(70:30)	MAA/EHA(70:30)A	70	-	30	4.6	-	4.2	0.35	-
	MAA/EHA(70:30)B	70	-	30	6.6	-	6.1	0.51	-
	MAA/EHA(70:30)C	70	-	30	11.7	-	10.7	0.89	-
	MAA/EHA(70:30)D	70	-	30	6.6	-	6.1	0.13	-
MAA/EHA(60:40)	MAA/EHA(60:40)A	60	-	40	3.0	-	4.3	0.29	1.0
	MAA/EHA(60:40)B	60	-	40	5.6	-	7.9	0.54	-
	MAA/EHA(60:40)C	60	-	40	7.6	-	10.8	0.73	-
	MAA/EHA(60:40)D	60	-	40	9.8	-	13.9	0.95	-
	MAA/EHA(60:40)E	60	-	40	5.6	-	8.1	0.14	-
	MAA/EHA(60:40)F	60	-	40	7.2	-	10.2	0.17	-
	MAA/EHA(60:40)G	60	-	40	9.9	-	14.1	0.24	-
	MAA/EHA(60:40)H	60	-	40	9.9	-	14.1	0.12	-
MAA/EHA(50:50)	MAA/EHA(50:50)A	50	-	50	4.6	-	9.9	0.58	-
	MAA/EHA(50:50)B	50	-	50	8.0	-	17.2	1.01	-
	MAA/EHA(50:50)C	50	-	50	4.6	-	9.9	0.14	-
	MAA/EHA(50:50)D	50	-	50	8.0	-	17.2	0.25	-
AA/EHA(80:20)	AA/EHA(80:20)A	-	80	20	-	6.5	4.1	0.43	1.0
	AA/EHA(80:20)B	-	80	20	-	6.5	4.1	0.43	-
	AA/EHA(80:20)C	-	80	20	-	11.7	7.5	0.77	-
	AA/EHA(80:20)D	-	80	20	-	11.7	7.5	0.19	-
AA/EHA(60:40)	AA/EHA(60:40)A	-	60	40	-	4.7	8.1	0.51	1.0
	AA/EHA(60:40)B	-	60	40	-	4.7	8.1	0.51	-
	AA/EHA(60:40)C	-	60	40	-	4.7	8.1	0.13	-
	AA/EHA(60:40)D	-	60	40	-	8.4	14.4	0.23	-

Table 4.4 : Compositions of reaction systems used to prepare polymers by Method 2

TDM - t-dodecyl mercaptan

polymers. In due course, this letter will be replaced by the intrinsic viscosity of the polymer, after reporting the results of the intrinsic viscosity measurement determination. This modified method of coding was adopted for the following reasons:

1. To simplify the code - It should also be noted that, in the preparation of these polymers, the concentration of the monomers was also varied both by varying the volume of the solvent and by varying the weight of the monomers in order to control the molecular weight of the polymer. If all these variable factors had been taken into consideration in coding the polymers, the codes would have been unduly long.

2. To avoid the possible complications which might have occurred in comparing the effects of the polymers of Type 1 and Type 2 upon the properties of NR latex.

The monomers used in the preparation of polymers of Type 2 were acrylic acid (AA), MAA and EHA.

4.2.2 Characterisation of polymers

4.2.2.1 Determination of intrinsic viscosity of polymer solutions

The intrinsic viscosities of some of the polymers of Type 1 and all of the polymers of Type 2 were determined using an Ubbelohde suspended-level viscometer. Methanol was used as the solvent for the polymethacrylic acids, and tetrahydrofuran (THF) was used as the solvent for all the other polymers. The intrinsic viscosity determinations were carried out at 25±1°C.

4.2.2.2 Gel permeation chromatographic analyses of polymers

Gel permeation chromatographic analysis (GPC) of some of the polymers of Type 1 were carried out by Dr. Holding at RAPRA. According to Dr. Holding, the following were the GPC operating conditions.

column material	: crosslinked polystyrene
flow rate	: $1.0 cm^3/min$
solvent	: tetrahydrofuran
temperature	: ambient
calibration	: derived from polystyrene
concentration of polymer in THF solution	: 0.2%/(w/v)

4.2.2.3 Determination of hydrophilicities of polymers

An indication of the hydrophilicities of some of the polymers of Type 1 and all the polymers of Type 2 was obtained by titrating $10.00cm^3$ of 1%(w/v) polymer solutions in IMS with distilled water at room temperature. The volume of distilled water required to produce the first permanent cloudy appearance of the polymer solution was taken as a measure of the hydrophilicity of the polymer.

4.2.2.4 Determination of acid contents of polymers by acidimetric titrations

An attempt was made to determine the acid contents of some of the polymers of Type 1 by acidimetric titrations. This was done by titrating $10.00cm^3$ of 1% (w/v) polymer solution in IMS with approximately 0.1M aqueous potassium hydroxide solution, using phenolphthalein as the indicator. During the titration, enough distilled water was added to the titrand to prevent precipitation of the potassium salt of the polymer. The potassium hydroxide solution was standardised by titrating with a standard potassium hydrogen phthalate solution (0.10M)

4.2.2.5 Determination of acid contents of polymers by infra-red spectrophotometry

Infra-red spectra of the polymers were obtained in order to determine the acid contents of the polymers, as the acidimetric titrations were not found to give satisfactory results (see Section 5.6). A Pye-Unicam spectrophotometer was used for this purpose. IR spectra of the polymers were obtained using thin films cast on to sodium chloride discs from tetrahydrofuran solution. The absorbances of the carboxylic acid peak (1710 cm^{-1}) and the ester peak (1740 cm^{-1}) were measured from the IR spectrum. Then the absorbance ratios were calculated as follows:

$$\text{absorbance ratio} = L = \frac{\log_{10}(h_o/h \quad \text{at } 1710\mathrm{cm}^{-1})}{\log_{10}(h_o/h \quad \text{at } 1740\mathrm{cm}^{-1})}$$

h and h_o were measured from a spectrum as indicated in Fig.4.3.

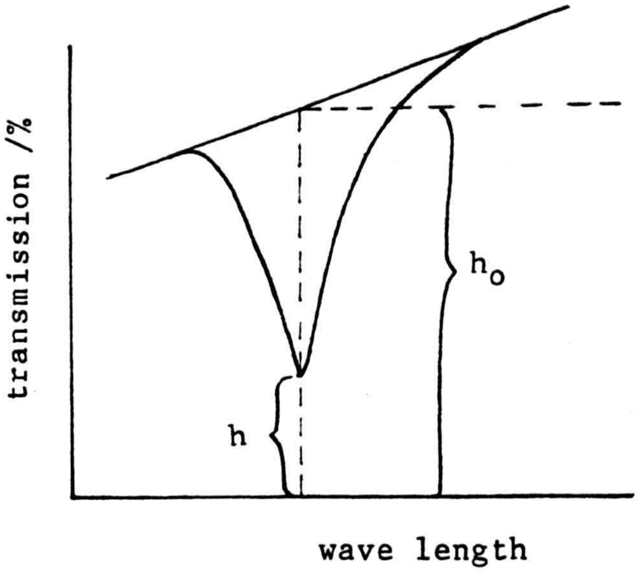


Fig. 4.3 : Measurement of h and h_o from an IR spectrum

The acid content of the polymer was determined using the value of L. A calibration curve was used for this purpose. The calibration curve was a plot of L against mole percentage of MAA for a mixture of MAA and EHA, and was obtained by measuring the L values of spectra of mixtures of MAA and EHA monomers of known composition. This calibration curve is shown in Fig. 4.4.

4.2.2.6 Assessment of tendency of polymers to form insoluble products by interaction with zinc ions and zinc-ammine ions

In order to assess the possible interactions between zinc ions and polymers to give insoluble products, 10.00cm^3 of a 2% (w/w) aqueous solution of the polymer (pH=7) was mixed with the equivalent amount of a 2% (w/w) aqueous anhydrous zinc sulphate solution at room temperature. The mixture was then allowed to stand and observed for signs of precipitation.

The procedure used to assess the possible interactions between zinc-ammine ions and the polymers to give precipitates was identical to the above procedure, except that the zinc sulphate solution was replaced by an aqueous zinc ammine sulphate solution which was prepared by adding sufficient ammonium hydroxide solution to a 2% (w/w) aqueous anhydrous zinc sulphate solution just to redissolve the precipitate which first formed.

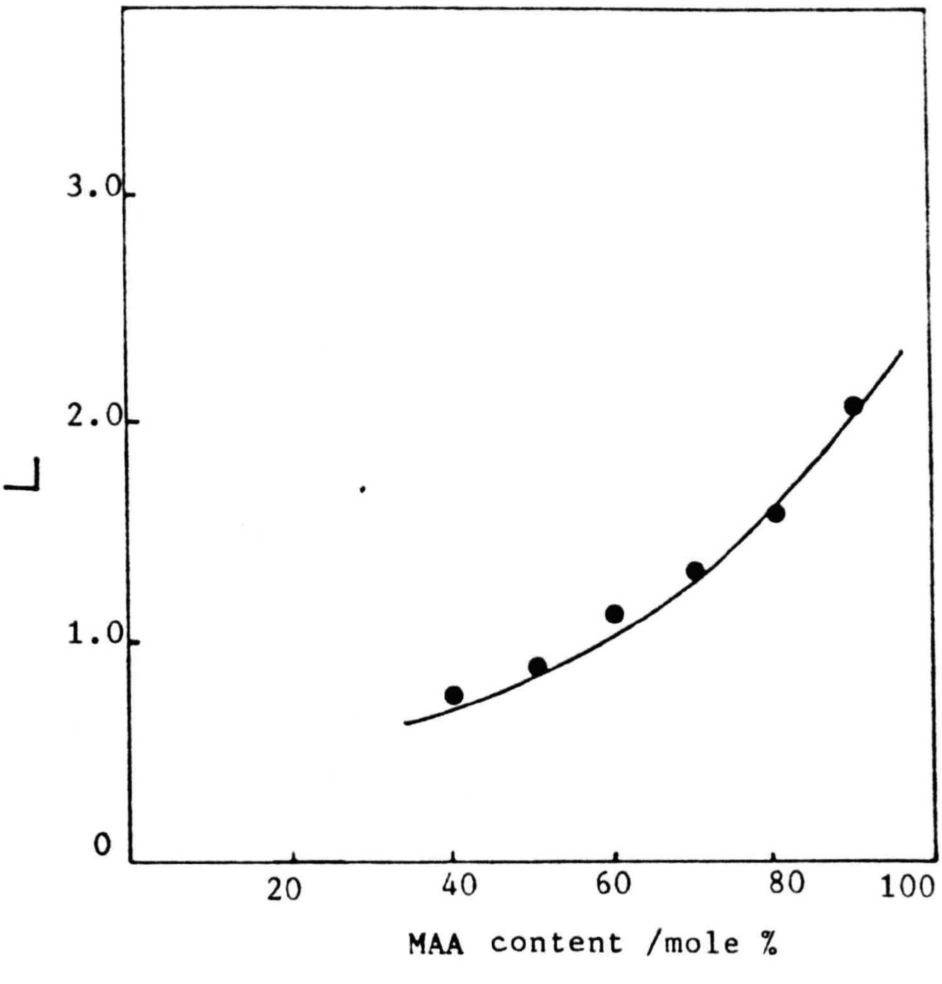


Fig. 4.4 : Calibration curve used for determination of acid content of polymers by infra-red analysis

4.2.3 Investigation of effects of added polymers upon some properties of NR latex

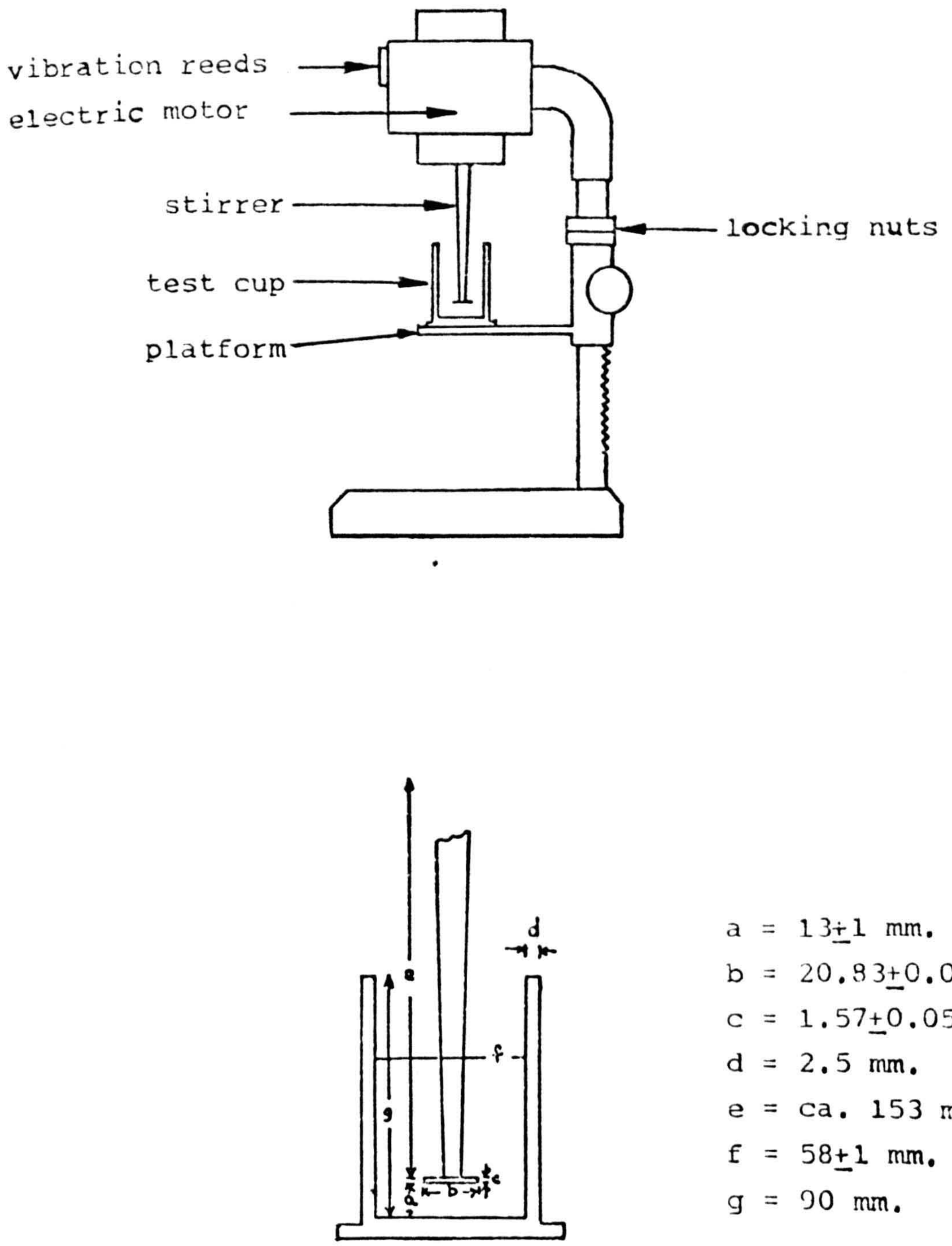
4.2.3.1 Investigation of effects of added polymers upon mechanical stability of NR latex

The effect of each polymer upon the mechanical stability of NR latex was investigated at each of four levels of addition, namely, 0.25, 0.50, 0.75 and 1.00g of polymer per 100g of latex solids. The polymer was added to the latex as a 5% (w/v) aqueous solution. The polymer solution was prepared as follows: 5g of polymer were accurately weighed and added to a mixture of 10% (w/w) aqueous sodium hydroxide ($5cm^3$) and distilled water ($50cm^3$). The resultant mixture was stirred with a magnetic stirrer until the polymer was completely dissolved. Further additions of sodium hydroxide were made from a burette until the pH of the solution was approximately equal to the pH of the latex. The solution was then diluted to $100cm^3$.

The latex samples for this investigation were prepared by adding appropriate amount of polymer solution and then diluting the latex to 55% total solids content with aqueous ammonia solution of concentration 0.6% (w/w) in the case of low-ammonia latex and 1.6% (w/w) in the case of high-ammonia latex. The latex samples were then allowed to mature for 2 days at 25 ± 1^oC before the mechanical stabilities were determined, in order to allow opportunity for adsorption equilibrium. At the end of the maturation period, the mechanical stabilities of the latex samples were determined using a conventional Klaxon mechanical stability test apparatus (Fig. 4.5). The test was carried out according to the procedure specified in BS 1672:1972. Two methods were used to determine the end-point; both gave similar results. One method was to drop small quantities of latex on to the surface of distilled water in a petri-dish and take the end-point as the time at which small particles of coagulum first become permanently visible on the surface of the water. In the other method, the end-point was taken as the first appearance of flocculum when a film of latex was drawn over the palm of the hand by means of a clean glass rod. Each mechanical stability was determined in duplicate, and the average of the two values was taken.

4.2.3.2 Investigation of effects of added polymers upon viscosity of NR latex

The effect of each polymer upon viscosity of NR latex was investigated at each of four levels of addition, namely, 0.25, 0.50, 0.75 and 1.00g of polymer per 100g of latex solids. The method for preparing the latex samples was exactly the same as that described for mechanical stability. After maturing the latex samples for 2 days at 25±1°C, the viscosities of the latex samples were measured using a Haake-Rotovisko viscometer. This instrument



a = 13±1 mm.
b = 20.83±0.03 mm.
c = 1.57±0.05 mm.
d = 2.5 mm.
e = ca. 153 mm.
f = 58±1 mm.
g = 90 mm.

Fig. 4.5 : Apparatus for mechanical stability testing of latex

measures the torque which is applied to the bob (inner cylinder) as it rotates with a constant angular velocity in a fixed cylindrical cup containing the latex sample under investigation. The bob and cup are illustrated in Fig. 4.6. The following procedure was used to measure the viscosity: The bob inserted into the latex which was maintained at 25±1°C. The bob was then rotated at a constant shear rate, usually 190 s^{-1} (speed factor U=6). The dial reading, S, was noted after 15 seconds. The latex viscosity, η , was then calculated from the following equation:

$$\eta = 0.271 \times U \times S \text{ cP}$$

4.2.3.3 Investigation of effects of added polymers upon chemical stability of NR latex

The effects of some of the polymers of Type 1 upon the chemical stability of NR latex were determined by measuring the mechanical stability of NR latex which had been destabilised by the addition of 1.00 pphls of potassium chloride as a 10% (w/w) aqueous solution. The destabilised latex samples were then compounded with the requisite amounts of the polymers and allowed to mature for 2 days at 25±1°C. Mechanical stabilities were then determined as described in Section 4.2.3.1.

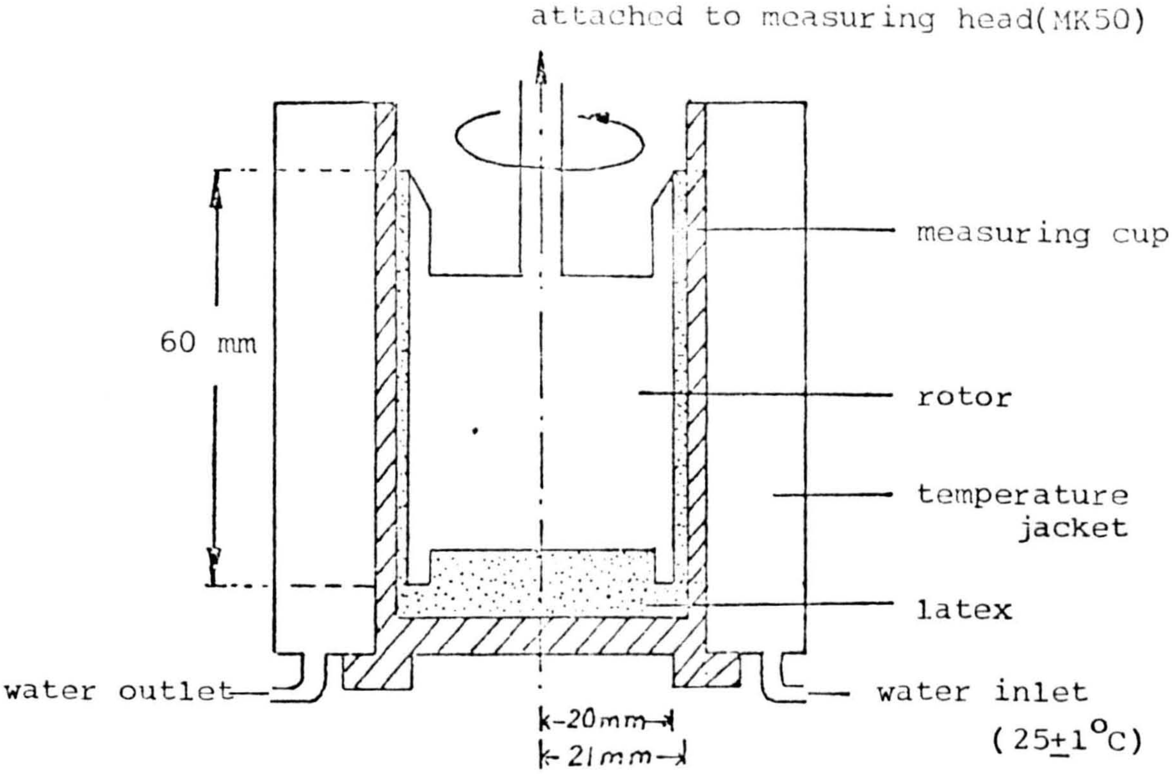


Fig. 4.6 : Measuring cup and bob for determination of latex viscosity

4.2.3.4 Investigation of effects of added polymers upon zinc-oxide thickening of NR latex

The formulation used for investigating the effects of added polymers upon the zinc-oxide thickening of NR latex is given in Table 4.5. The procedure for preparing the latex compounds was as follows: The requisite amount of polymer was added to the latex as a 5% (w/w) aqueous solution. The latex was then diluted to 55% total solids content with aqueous ammonia solution of concentration 0.6% (w/w) in the case of low-ammonia latex and 1.6% (w/w) in the case of high-ammonia latex. The latex samples were then allowed to mature for 3 days at room temperature (25±1°C) in order to allow opportunity for the attainment of adsorption equilibrium. The remaining ingredients were then added in the following order: 20% ammonium acetate solution, 20% zinc oxide dispersion. The latex compound was then allowed to mature at 25±1°C for

ingredient	parts by weight/dry
natural rubber (as 62% latex)	100.0
ammonium acetate (as 20% aqueous solution)	0.5
zinc oxide (as 20% aqueous dispersion)	3.5
polymer (as 5% aqueous solution)	variable

Table 4.5 : Formulation for investigating effects of added polymers upon zinc-oxide thickening of NR latex

various periods from 2 days to 16 days. At the end of the maturation period, the viscosity of the latex compound was measured at 25±1°C using a Haake-Rotovisko viscometer according to the procedure described in Section 4.2.3.2.

4.2.3.5 Investigation of the effects of added polymers upon heat-sensitisation of NR latex in the presence of zinc-ammine ions

The formulation used for investigating the effects of added polymers upon the heat-sensitisation of NR latex in the presence of zinc-ammine ions is given in Table 4.6. The procedure for preparing the latex compound was as follows: The requisite amount of polymer was added to the latex, and the mixture allowed to stand for 3 days at 25±1°C in order to allow opportunity for the attainment of adsorption equilibrium. The latex was then compounded

ingredient	parts by weight/dry
natural rubber (as 62% latex)	100.0
ammonium acetate (as 20% aqueous solution)	1.0
zinc oxide (as 50% aqueous dispersion)	3.5
polymer (as 5% aqueous solution)	0.5

Table 4.6 : Formulation for investigating effects of added polymers upon heat-sensitisation of NR latex in in the presence of zinc-ammine ions

with 20% ammonium acetate solution and 50% zinc oxide dispersion in that order. The compounded latex was allowed to mature for 2 days at 25±1°C before any attempt was made to assess its heat sensitivity.

The procedure used to assess the heat-sensitivity of the latex compounds consisted of immersing a heated former in to a beaker containing the latex under investigation. The former was a hollow cylindrical aluminium tube closed at one end. The length of the former was 20.5cm and its external diameter was 3cm. The open end of the former was closed with a bung through which a thermometer and tubes for circulation of hot water were inserted. The formers were maintained at the desired temperature by circulating water from a thermostatically-controlled water bath by means of a "circotherm" unit.

The immersion was carried out using a Costwold dipping machine. The former was mounted so that it was held stationary in the upper part of the machine, whereas the beaker containing the latex was supported on the movable platform.

On reaching a steady temperature, which was 75°C in all cases, the former was dipped into the latex compound, which was initially at 25±1°C, at a speed of approximately 1.2cm/s. The depth of immersion was approximately 8cm from the base. At the end of the dwell time, which varied from 30s to 60s, the beaker of latex was withdrawn from the former at a rate of 0.82cm/s. After circulating water through the former for a period of 1 minute, the circulation was stopped, the bung removed, and the water poured out of the former. The former with the deposit was then dried in an air oven maintained at 75±1°C.

The dried film was stripped from the former and lightly dusted with zinc stearate powder on both sides. Its thickness was measured using a Mercer gauge. The mean of five values was taken as the average thickness of the film. The mean of the average thicknesses of the three films obtained from each latex compound was taken as a measure of the heat-sensitivity of the latex compound.

4.2.3.6 Investigation of effects of polymers as replacements for polyvinylmethyl ether (PVME) as heat-sensitisers for NR latex

A low-ammonia latex concentrate (Batch 1) was used in this investigation. As the degree of heat-sensitisation imparted to NR latex by PVME depends to a large extent upon the pH of the latex, it was necessary to deammoniate latex partially in order to reduce the pH to approximately 9.0. This was done by aeration. Aeration was carried out by blowing air across the surface of the latex whilst stirring the latex slowly with a Peerless mixer. The deammoniated latex was strained through a cheese cloth and allowed to stand overnight. Air bubbles were removed from the latex by scavenging the surface with a filter paper.

The formulation used for the heat sensitisation of NR latex by the PVME system is given in Table 4.7. The procedure for preparing the latex compounds was as follows: The requisite amounts of polymer, Vulcastab LW and zinc oxide was added to deammoniated latex in that order and allowed to mature for 4 days at 25±1°C. The zinc oxide and Vulcastab LW were added as a 50% aqueous dispersion and 20% aqueous solution respectively. The role of zinc oxide is to react with fatty-acid anions forming insoluble zinc soaps and, hence to increase heat-sensitivity. The non-ionic stabiliser, Vulcastab LW, provides good mechanical

ingredient	parts by weight/dry
natural rubber (as 55% latex)	100.0
PVME (as 15% aqueous solution) or polymer (as 5% aqueous solution)	1.0
zinc oxide (as 50% aqueous dispersion)	1.0
Vulcastab LW (as 20% aqueous solution)	0.1

Table 4.7: Formulation for investigating effects of polymers as replacements for polyvinylmethyl ether as heat sensitisers for NR latex

stability and adequate storage life to the compound. At the end of the maturation period, the heat sensitivities of the latex compounds were assessed by the procedure described in Section 4.2.3.5. Dipping experiments were carried out at two different pH values, namely, pH=8.0 and pH=8.5. The reduction of pH of latex to pH=8.0 and pH=8.5 was done by the addition of 10% aqueous formaldehyde solution.

4.2.3.7 Investigation of effects of added polymers upon creaming of NR latex

The requisite amount of polymer was added to the latex (Batch 1) in a measuring cylinder and the mixture was then diluted to 55% total solids content with 0.6% aqueous ammonia solution and allowed to mature for three weeks at 25±1°C. The amounts of serum and cream layers which formed were observed. The height of the serum layer expressed as a percentage of the initial height of the latex, was taken as a measure of the ability of each polymer to promote creaming of the latex. Fig. 4.7 illustrates the method for determining the effects of added polymer upon creaming of NR latex. The measure of ability of added polymer to promote creaming was calculated as $(H_s/H_0)\times 100$ where H_0 is the height of the initial latex sample and H_s is the height of the serum layer after the maturation.

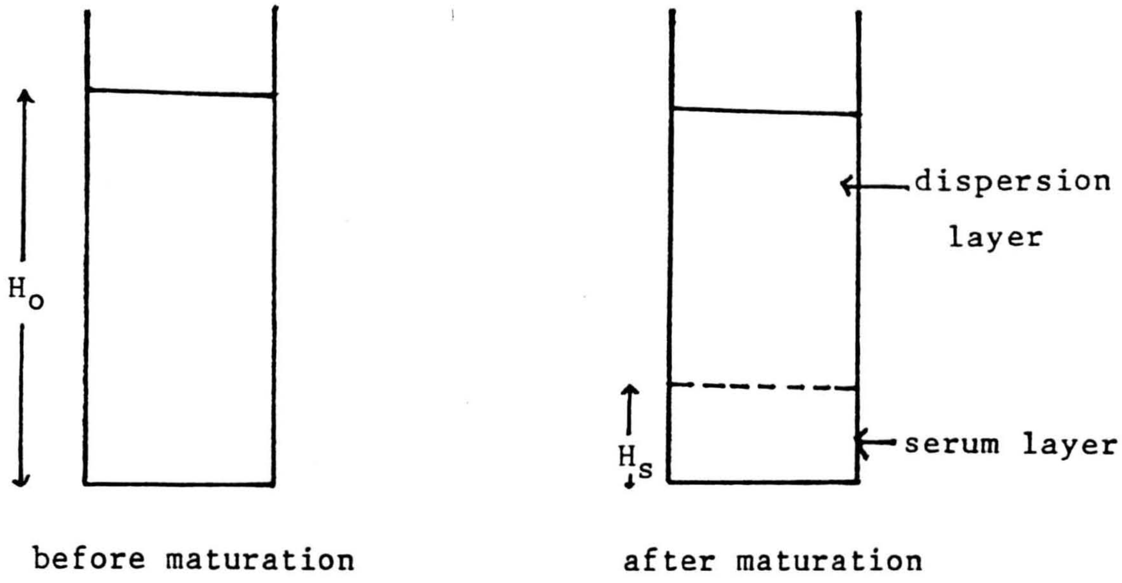


Fig. 4.7 : Illustrating method for determining effects of added polymer upon creaming of NR latex

H_o = height of the initial latex sample

H_s = height of the serum layer after maturation

CHAPTER FIVE

CHARACTERISTICS OF POLYMERS

5.1 Results of viscosity measurements on polymer solutions

The determination of intrinsic viscosity of each polymer was done by means of the Huggins equation, i.e.,

$$\eta_{sp}/C = [\eta] + K' [\eta]^2 C \qquad \text{....(5.1)}$$

where η_{sp} = specific viscosity of polymer solution at concentration C

$[\eta]$ = intrinsic viscosity

K' = Huggins constant

The intrinsic viscosities of polymers were obtained by extrapolatating plots of η_{sp}/C against C to C=0. The viscosity-average molecular weights, $\overline{M}_v$, of the polymethacrylic acids were calculated from the intrinsic viscosities using the Mark-Houwink relationship, i.e,

$$[\eta] = K \overline{M}_v^{\alpha} \qquad \text{....(5.2)}$$

where M_v = viscosity-average molecular weight and, K and α are constants for a given polymer-solvent pair.

In the calculations of M_v, the values of K and α were taken as $242 \times 10^{-3} cm^3 g^{-1}$ and 0.51 respectively.(127)

5.1.1 Results of viscosity measurements on polymers of Type 1

The results of viscosity measurements on polymer solutions of Type 1 are shown in Figs 5.1 to 5.5. The values of $[\eta]$ as obtained from these figures, and the corresponding values of $\bar{M}_v$ for the polymethacrylic acids are given, in Table 5.1

For all the groups of polymers for which results have been obtained, the intrinsic viscosities of the polymers were found to vary in the expected order, i.e., the intrinsic viscosity decreased as the concentration of initiator used to prepare the polymer increased. In each group of polymers, the intrinsic viscosities of the branched polymers were found to be less than that of the linear polymer prepared using the lowest concentration of initiator. However, this does not necessarily imply that the branched polymers are of low molecular weight as it is known that the intrinsic viscosity of a branched polymer is always less than that of a linear polymer of the same molecular weight because a branched polymer molecule is more compact than a linear polymer of the same molecular weight. Therefore the intrinsic viscosities obtained for branched polymers cannot be regarded as indications of

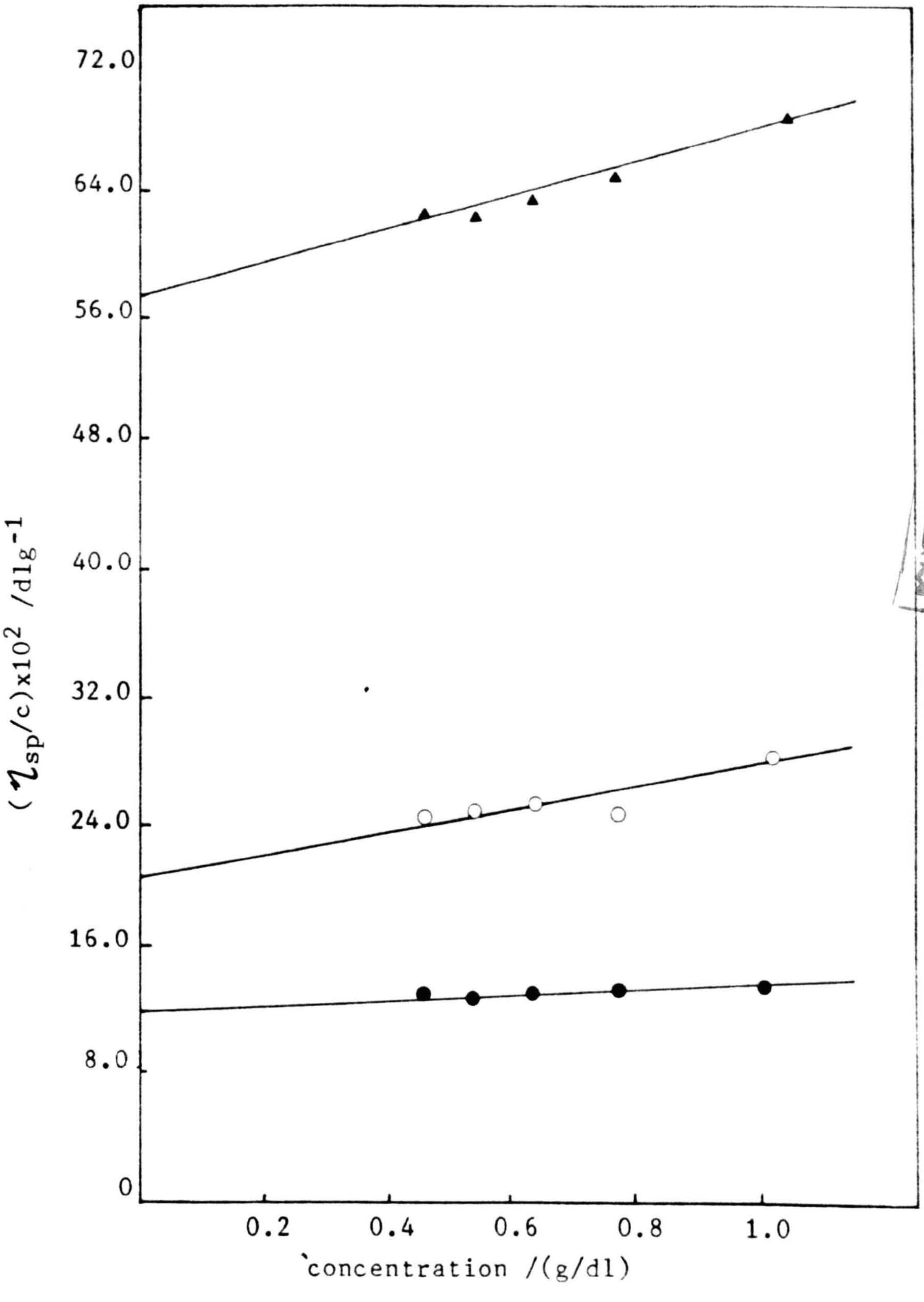


Fig. 5.1 : Viscosity results for some polymers of group MAA of Type 1

● MAA-B
○ MAA-C
▲ MAA-D

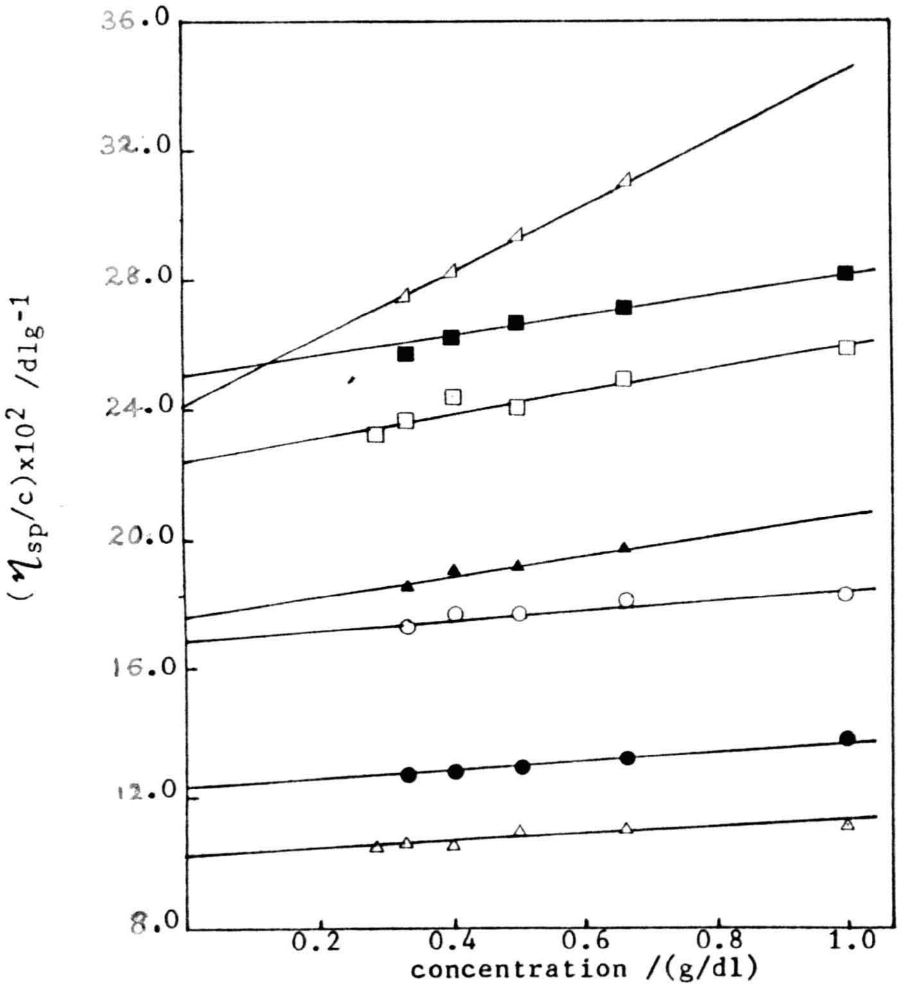


Fig. 5.2 : Viscosity results for polymers of group MAA/EHA(80:20) of Type 1

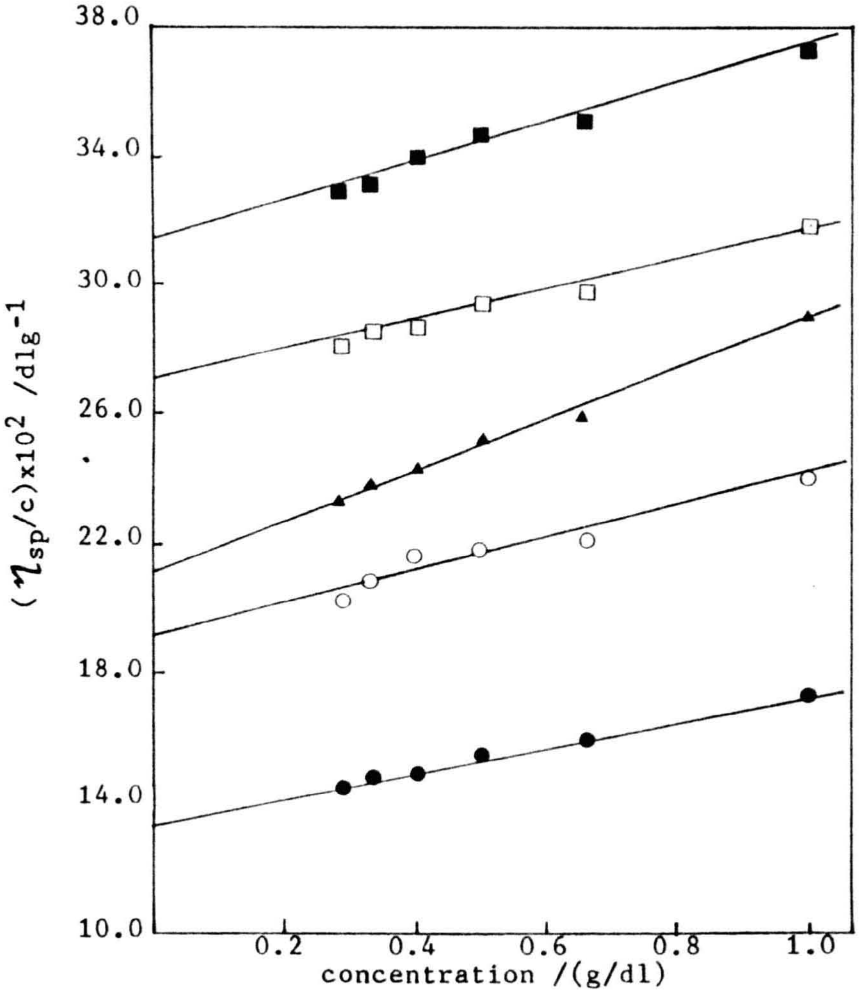


Fig. 5.3 : Viscosity results for polymers of group MAA/EHA(60:40) of Type 1

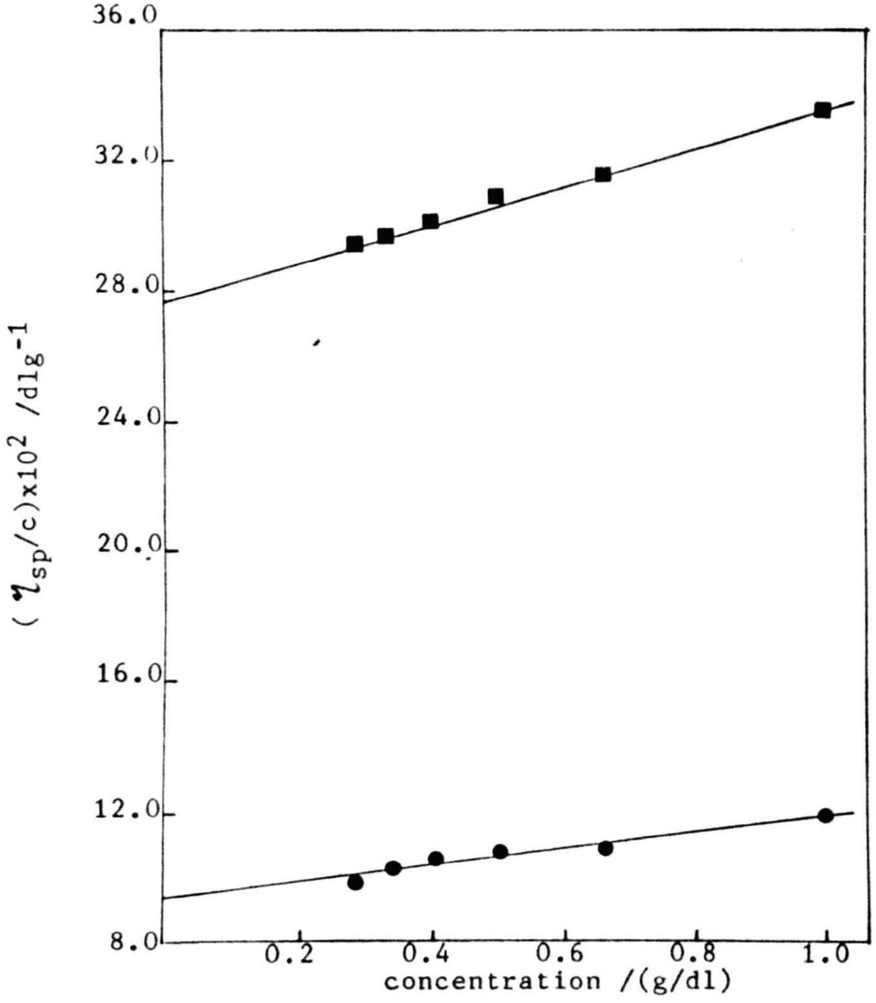


Fig. 5.4 : Viscosity results for polymers of group MAA/EHA(70:30) of Type 1

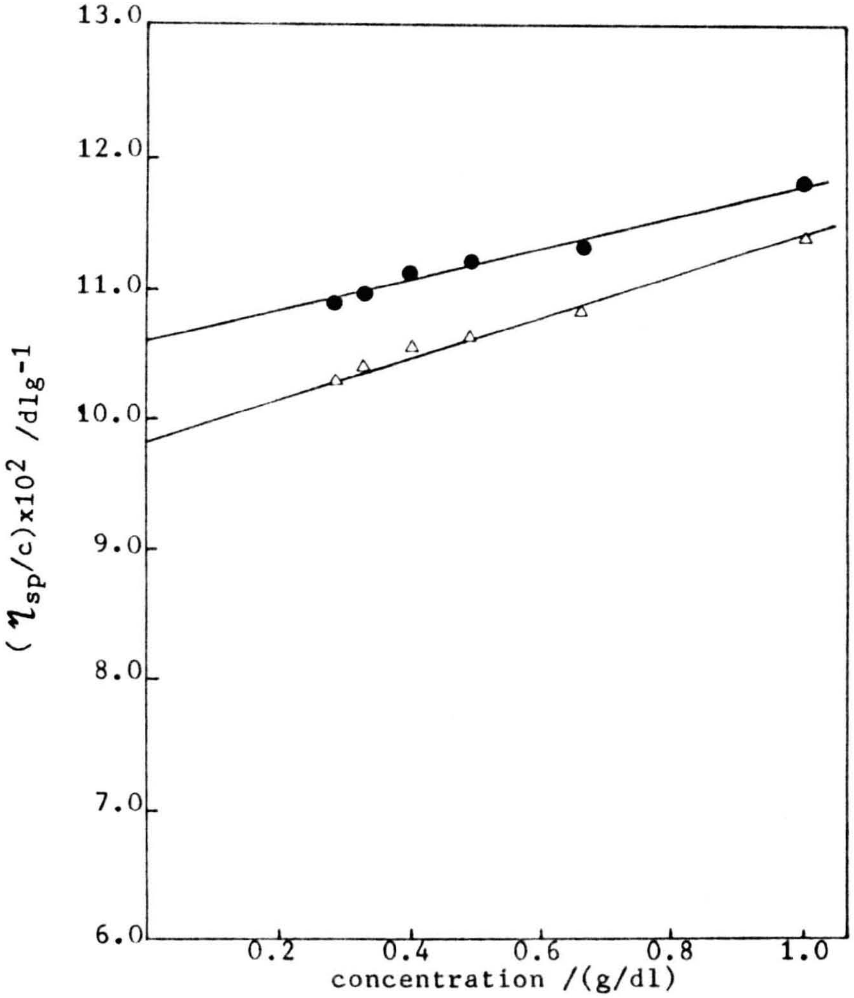


Fig. 5.5 : Viscosity results for polymers of group MAA/EHA(50:50) of Type 1

their molecular weight relative to those of linear polymers of the same type.

polymer	intrinsic viscosity /dlg^{-1}	$\bar{M}_v$
MAA-B	0.120	2458
MAA-C	0.205	7530
MAA-D	0.574	55447
MAA/EHA(80:20)A	0.102	-
MAA/EHA(80:20)B	0.122	-
MAA/EHA(80:20)C	0.168	-
MAA/EHA(80:20)Ca	0.176	-
MAA/EHA(80:20)Cb	0.225	-
MAA/EHA(80:20)D	0.242	-
MAA/EHA(80:20)E	0.251	-
MAA/EHA(70:30)B	0.094	-
MAA/EHA(70:30)D	0.278	-
MAA/EHA(60:40)B	0.132	-
MAA/EHA(60:40)C	0.192	-
MAA/EHA(60:40)Ca	0.212	-
MAA/EHA(60:40)Cb	0.270	-
MAA/EHA(60:40)D	0.315	-
MAA/EHA(50:50)A	0.098	-
MAA/EHA(50:50)B	0.106	-

Table 5.1 : Intrinsic viscosities of polymers of Type 1 at 25±1°C and calculated molecular weights for polymethacrylic acids

5.1.2 Results of viscosity measurements of polymers of Type 2

The results of viscosity measurements of polymers of Type 2 are shown in Figs. 5.6 to 5.12. The corresponding intrinsic viscosities are given in Table 5.2. Again the intrinsic viscosities were found to be in the expected order. However, the intrinsic viscosities of the polymers of Type 2 were found to be smaller than those of the polymers of Type 1. A possible explanation for this observation will be discussed in the following section.

5.2 Discussion of results of intrinsic viscosities of polymers of Type 1 and polymers of Type 2

The results given in Table 5.1 and 5.2 reveal that the intrinsic viscosities of the polymers of Type 2 are smaller than those of polymers of Type 1. This is undoubtedly a consequence of the differences between the reaction conditions of the two methods. There are two obvious differences between the reaction conditions of the two methods:

1. the initiator concentrations and their modes of variation with time of reaction were different in the two methods
2. the concentration of unreacted monomer was presumably much lower in Method 2 than in Method 1.

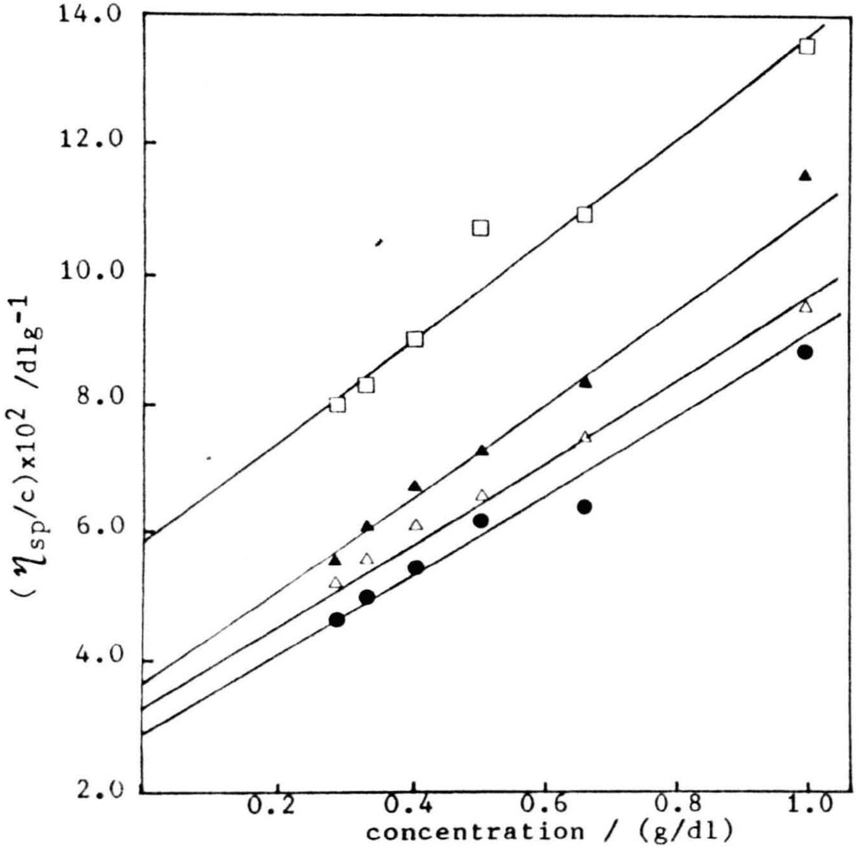


Fig. 5.6 : Viscosity results for polymers of group MAA/EHA(90:10) of Type 2

● MAA/EHA(90:10)A △ MAA/EHA(90:10)B
▲ MAA/EHA(90:10)C □ MAA/EHA(90:10)D

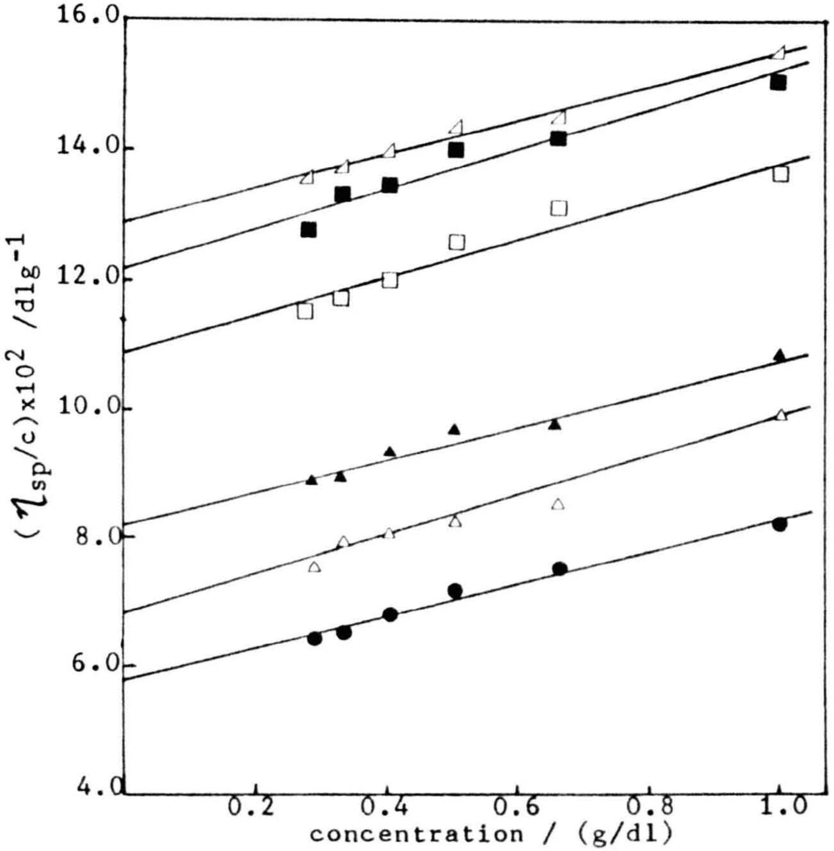


Fig. 5.7 : Viscosity results for polymers of group MAA/EHA(80:20) of Type 2

● MAA/EHA(80:20)A △ MAA/EHA(80:20)B
▲ MAA/EHA(80:20)C □ MAA/EHA(80:20)D
■ MAA/EHA(80:20)E ◿ MAA/EHA(80:20)F

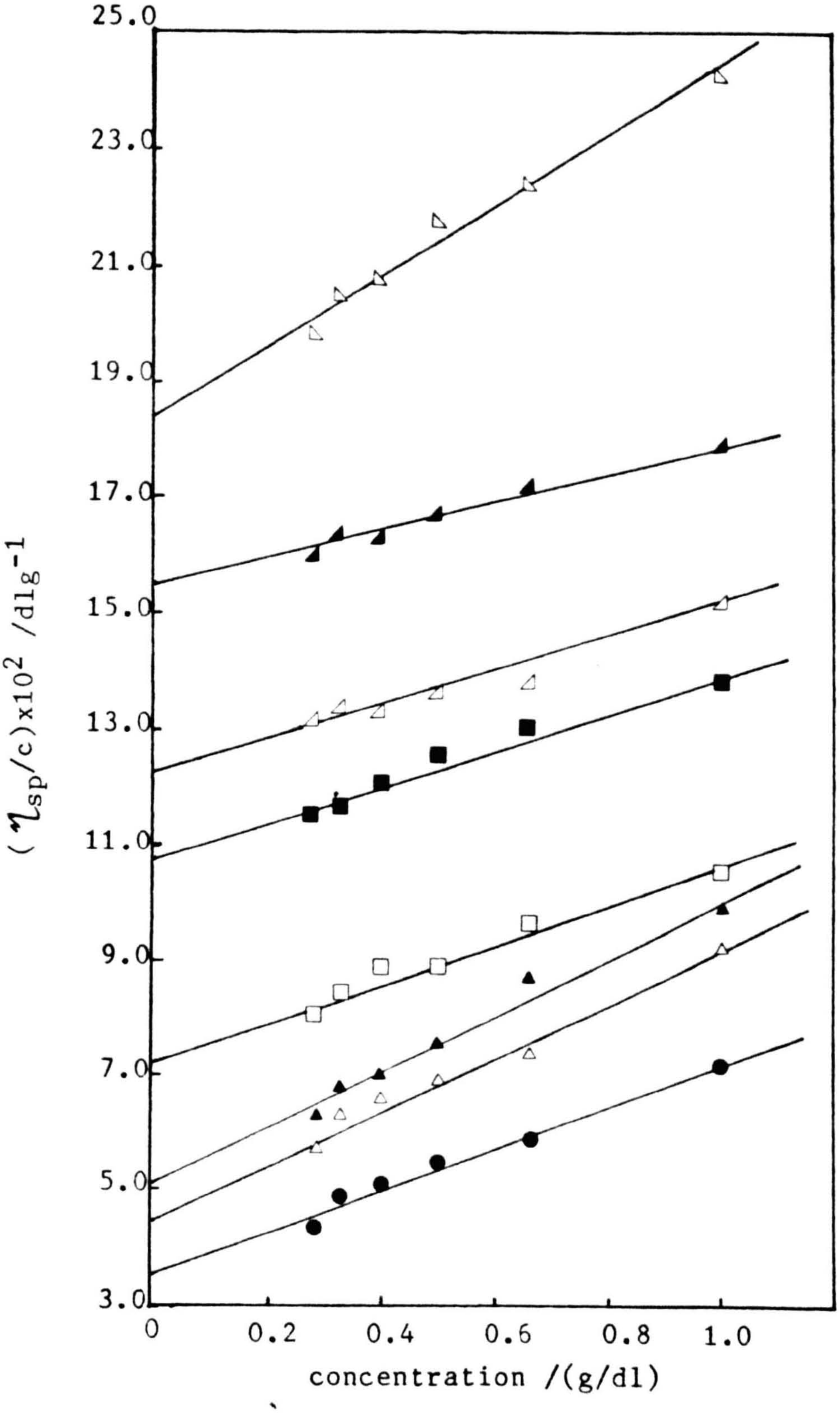


Fig. 5.8 : Viscosity results for polymers of group MAA/EHA(60:40) of Type 2

● MAA/EHA(60:40)A	■ MAA/EHA(60:40)E
△ MAA/EHA(60:40)B	◿ MAA/EHA(60:40)F
▲ MAA/EHA(60:40)C	◢ MAA/EHA(60:40)G
□ MAA/EHA(60:40)D	◺ MAA/EHA(60:40)H

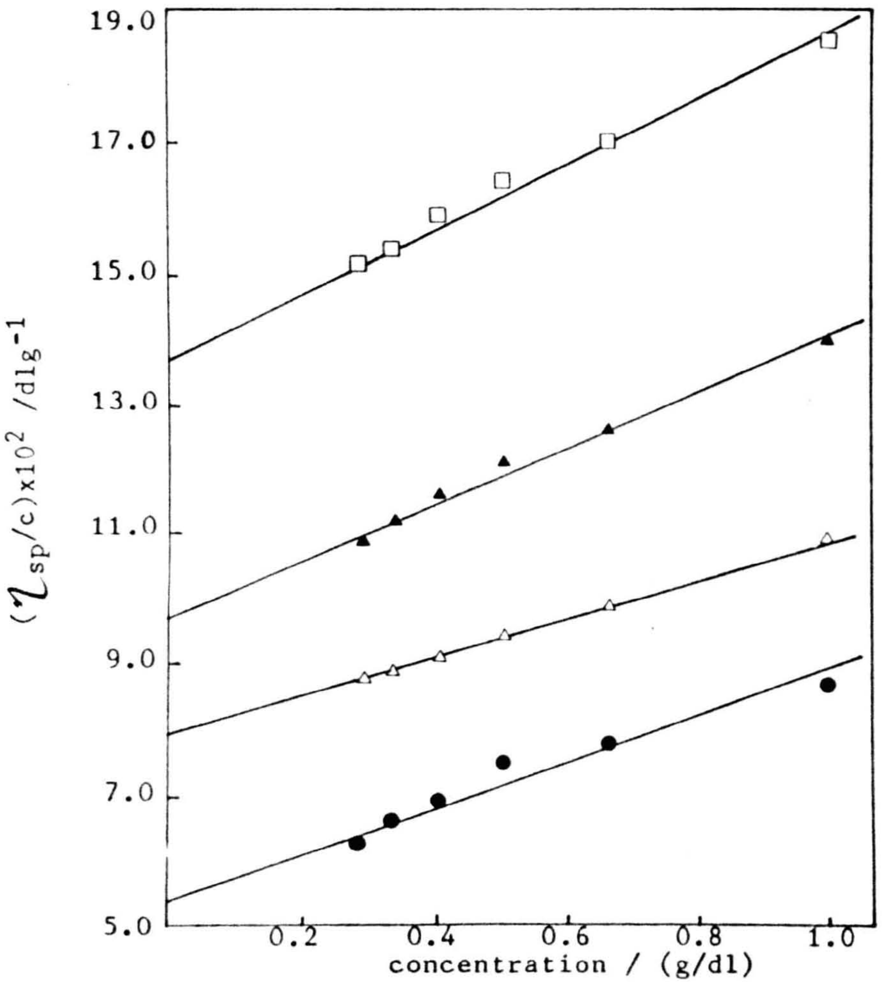


Fig. 5.9 : Viscosity results for polymers of group MAA/EHA(70:30) of Type 1

● MAA/EHA(70:30)A ▲ MAA/EHA(70:30)B
△ MAA/EHA(70:30)C □ MAA/EHA(70:30)D

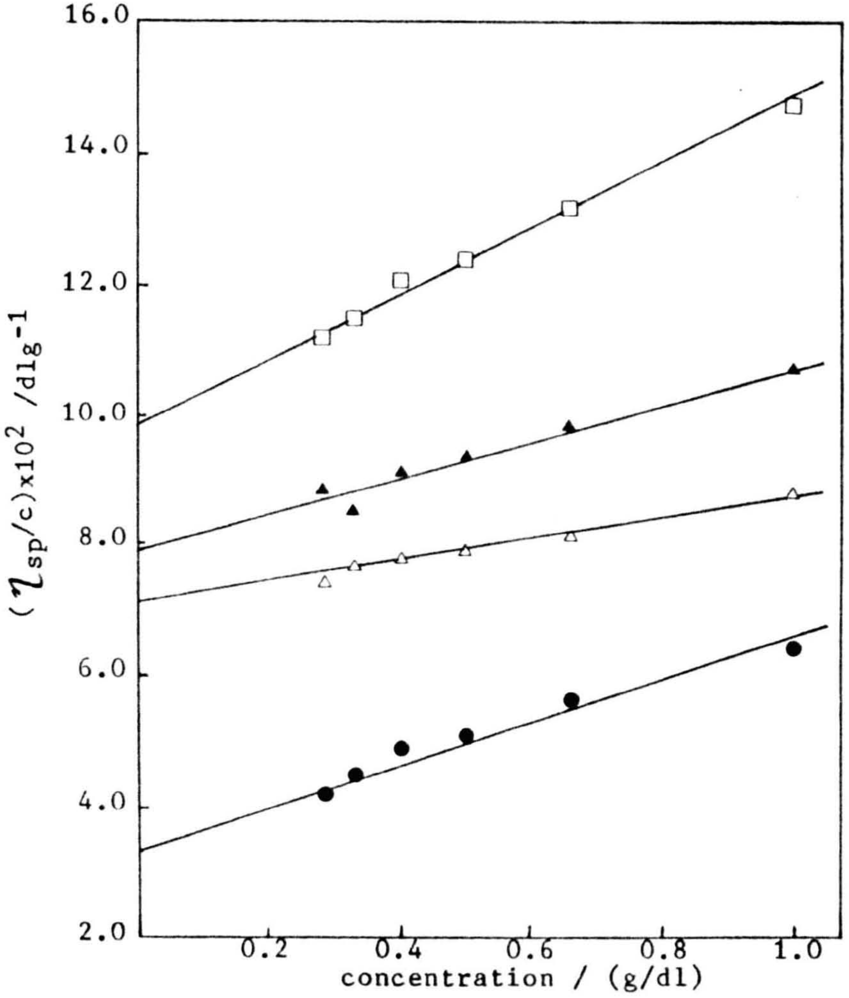


Fig. 5.10 : Viscosity results for polymers of group MAA/EHA(50:50) of Type 1

● MAA/EHA(50:50)A △ MAA/EHA(50:50)B
▲ MAA/EHA(50:50)C □ MAA/EHA(50:50)D

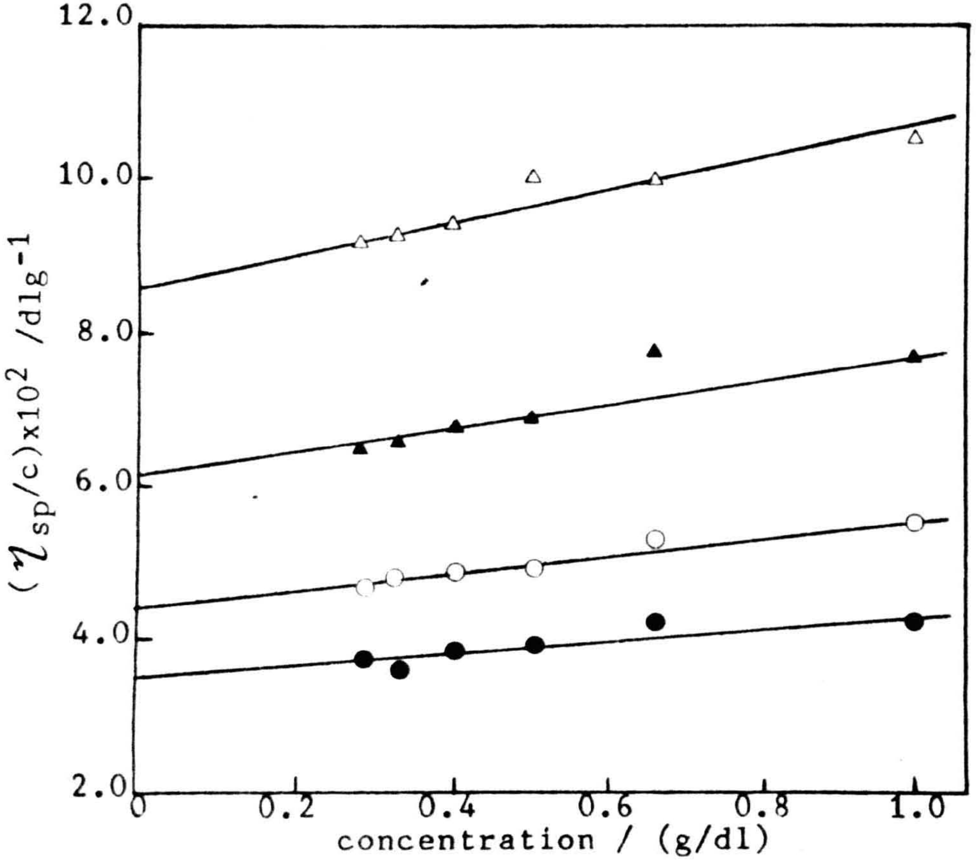


Fig. 5.11 : Viscosity results for polymers of group AA/EHA(80:20) of Type 2

● AA/EHA(80:20)A ○ AA/EHA(80:20)B
▲ AA/EHA(80:20)C △ AA/EHA(80:20)D

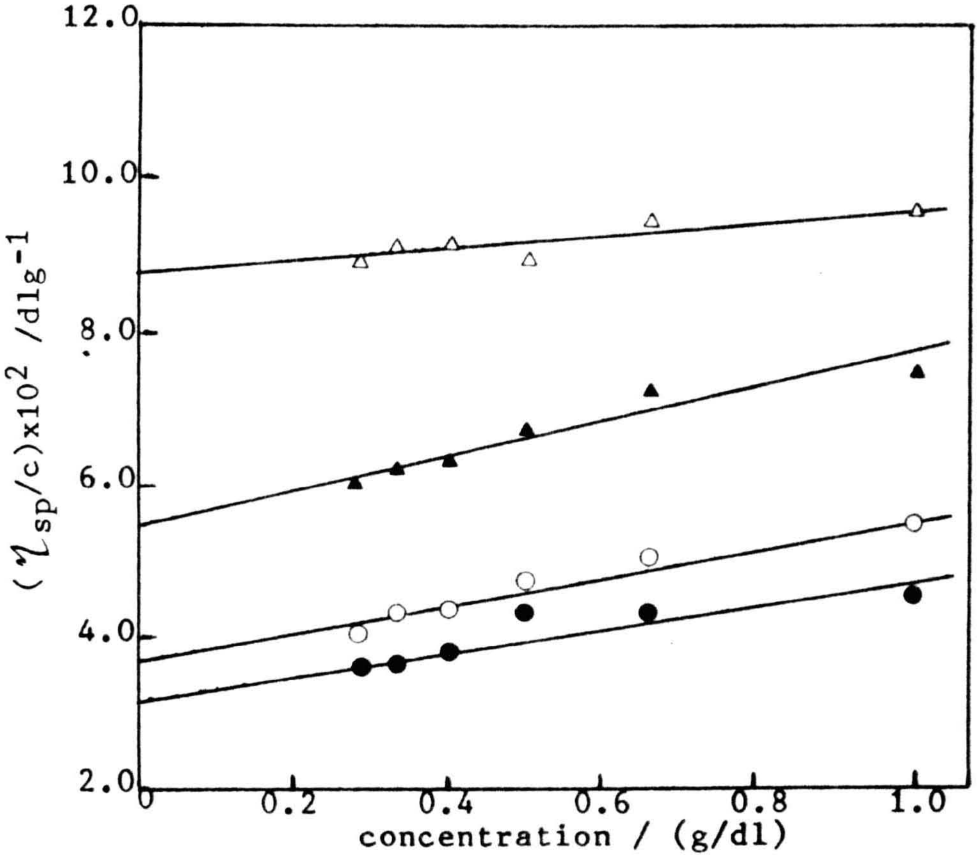


Fig. 5.12 : Viscosity results for polymers of group AA/EHA(60:40) of Type 2

● AA/EHA(60:40)A ○ AA/EHA(60:40)B
▲ AA/EHA(60:40)C △ AA/EHA(60:40)D

polymer	intrinsic viscosity /dlg^{-1}
MAA/EHA(90:10)A	0.029
MAA/EHA(90:10)B	0.034
MAA/EHA(90:10)C	0.037
MAA/EHA(90:10)D	0.059
MAA/EHA(80:20)A	0.058
MAA/EHA(80:20)B	0.068
MAA/EHA(80:20)C	0.082
MAA/EHA(80:20)D	0.109
MAA/EHA(80:20)E	0.122
MAA/EHA(80:20)F	0.129
MAA/EHA(70:30)A	0.054
MAA/EHA(70:30)B	0.080
MAA/EHA(70:30)C	0.097
MAA/EHA(70:30)D	0.137
MAA/EHA(60:40)A	0.036
MAA/EHA(60:40)B	0.045
MAA/EHA(60:40)C	0.052
MAA/EHA(60:40)D	0.073
MAA/EHA(60:40)E	0.109
MAA/EHA(60:40)F	0.124
MAA/EHA(60:40)G	0.156
MAA/EHA(60:40)H	0.184
MAA/EHA(50:50)A	0.033
MAA/EHA(50:50)B	0.072
MAA/EHA(50:50)C	0.080
MAA/EHA(50:50)D	0.099
AA/EHA(80:20)A	0.036
AA/EHA(80:20)B	0.044
AA/EHA(80:20)C	0.062
AA/EHA(80:20)D	0.087
AA/EHA(60:40)A	0.028
AA/EHA(60:40)B	0.037
AA/EHA(60:40)C	0.055
AA/EHA(60:40)D	0.089

Table 5.2 : Intrinsic viscosities of polymers of Type 2 at 25±1°C

The differences in initiator concentration and its mode of variation with time in two methods are important here because it is known that the rate of initiation (and hence the initiator concentration) is an important factor in determining the molecular weight (and hence the intrinsic viscosity) of the polymer formed. In order to examine this matter more closely variation of initiator concentration with time of reaction was calculated for two polymerisations carried out using the same overall recipe but by two different methods, one by Method 1 and the other by Method 2. These calculations were carried out for polymerisation reactions carried out using the following overall recipe:

MAA = 34.4g (33.89cm^3)
EHA = 18.4g (20.81cm^3)
AZDN = 0.528g (3.216x10^{-3} moles)
(polymerisation temperature = 70°C)

The variation of initiator concentration with time, t, in a conventional bulk polymerisation process such as that used in Method 1 can be calculated using the equation

$$C = C_o e^{-kt} \qquad ....(5.3)$$

where C = concentration of initiator when t = t

C_o= initial concentration of initiator, the concentration when $t = 0$

k = rate coefficient for the thermal decomposition of the initiator

The results of this calculation carried out using equation 5.3 are shown in Fig. 5.13. The value for k for 2,2'-azo bis-(2-methyl proprionitrile) decomposing in methanol at 70°C was taken as 1.5×10^{-4}.(128)

The variation of initiator concentration with time for the first 6 hours of reaction for Method 2, in which the mixture of initiator dissolved in IMS (100cm^3) and monomers is added to the reaction flask containing refluxing IMS (150cm^3), was calculated using the following equation:

$$C = Ae^{-kt} - (a\beta e^{\alpha}/U) + a\beta\alpha e^{-kt}\,[\log U + \alpha U + (\alpha^2U^2/2.2!) + \ldots\ldots$$
$$\ldots\ldots + (\alpha^nU^n/n.n!) \qquad \ldots.(5.4)$$

where C = concentration of initiator when $t = t$

k = rate coefficient for thermal decomposition of the initiator

a = rate of addition of the initiator/initial volume of the solvent in the reaction flask

α = k/(rate of addition of monomer mixture/ initial volume of the solvent in the reaction flask)

$\beta = e^{-\alpha}/(k/\alpha)$

$U = 1+(k/\alpha)t$

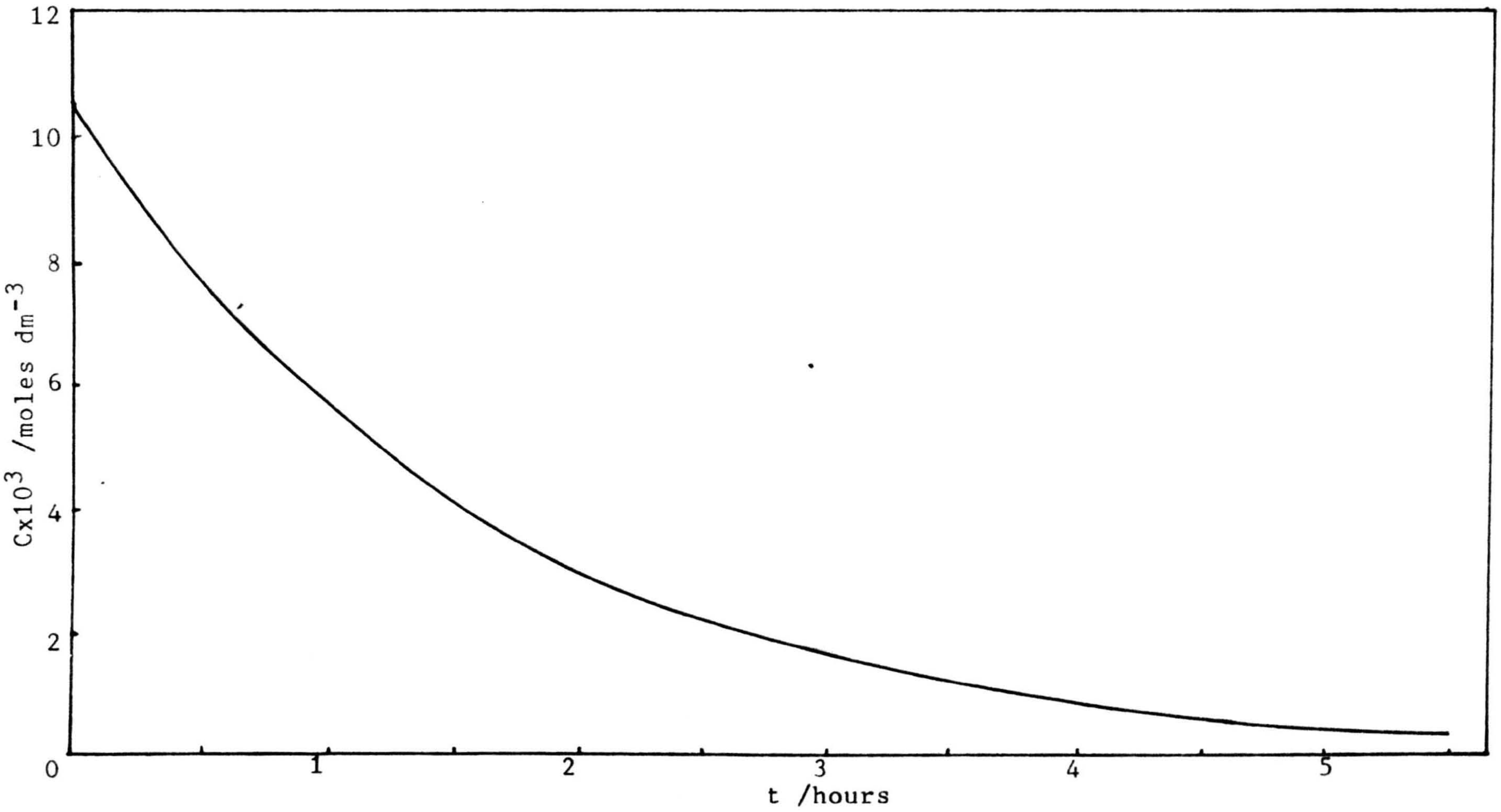


Fig. 5.13 : Typical variation of concentration of initiator(C) with time of reaction during polymerisatio **of polymers by Method 1** , MAA - 34.4g, EHA - 18.4g, AZDN - 0.528g, polymerisation temperature 70°C and $k = 1.5 \times 10^{-4}$(128)

The value of A was calculated using an equation derived from the equation 5.4 as follows:

when t = 0 the concentration of initiator, C, = 0

Thus,

$$A = a\beta e^{\alpha} + a\beta\alpha\,[\alpha + (\alpha^2/2.2!) + \ldots\ldots + (\alpha^n/n.n!) \qquad \ldots.(5.5)$$

The derivation of equation 5.4 is given in Appendix 1. The variation of initiator concentration with time of reaction after the completion of the addition of polymerisation reactants was calculated using the equation 5.3. The variation of the concentration of initiator with time of reaction for Method 2, predicted by equation 5.4 for the first 6 hours and by equation 5.3 for the rest of the reaction period, is given in Fig. 5.14. The value taken for k for 2,2'-azo bis-(2-methyl proprionitrile) decomposing in methanol at 70°C was taken as 1.5×10^{-4}.(128) The computer programme given in Appendix 2 was used to calculate A and, thereby C for the initial 6 hours of the polymerisation reaction.

In the conventional solution polymerisation process, <u>i.e.</u>, Method 1, as the polymerisation proceeded the initiator concentration decreased throughout the reaction (Fig. 5.13). In contrast, in Method 2, the initiator concentration increased for about 3 hours and then started to decrease (Fig. 5.14). A more clear

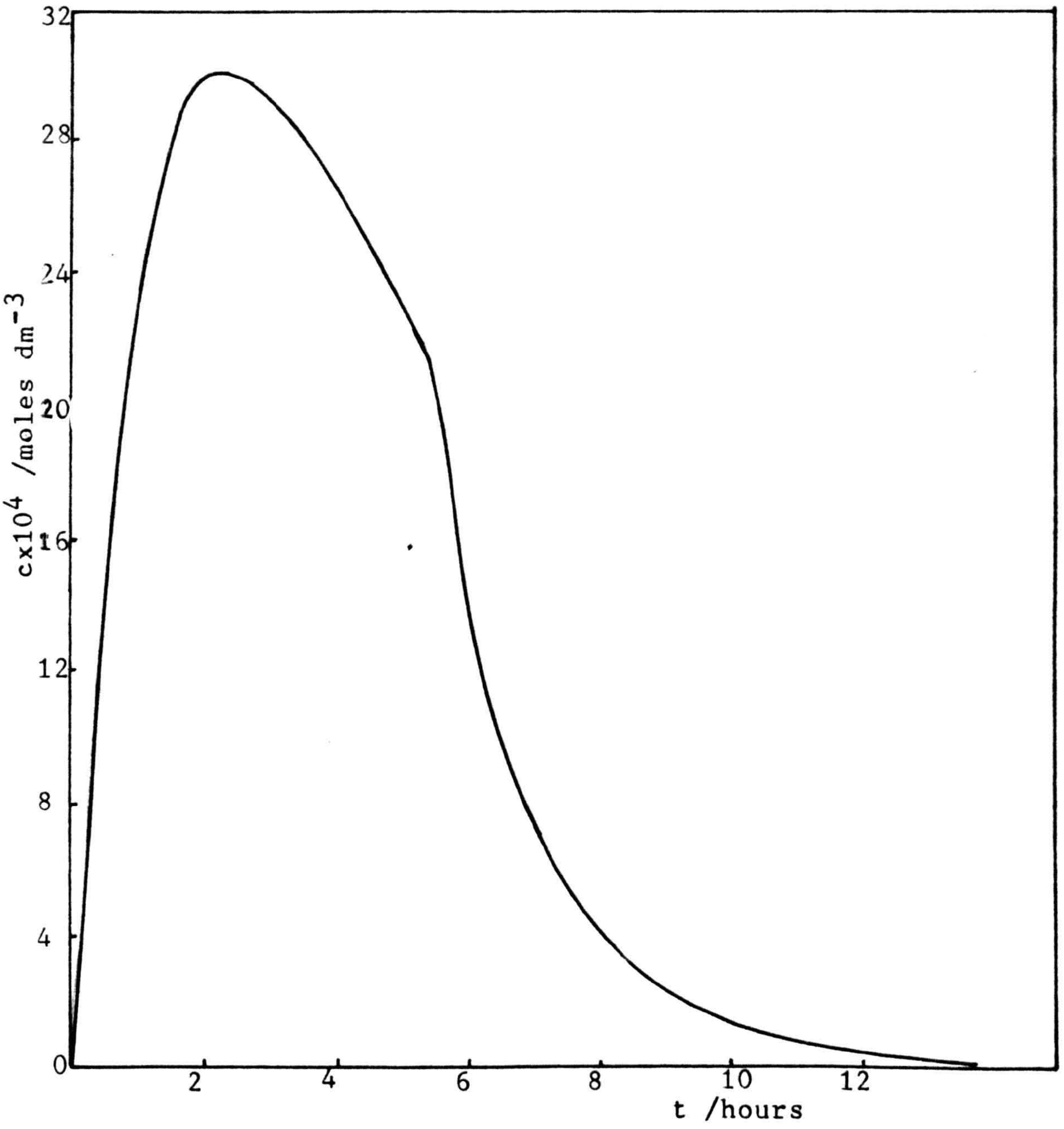


Fig. 5.14 : Typical variation of concentration of initiator (C) with time of reaction during polymerisation of polymers by Method 2 , MAA - 34.4g, EHA - 18.4g, AZDN - 0.528g, polymerisation temperature 70°C and $k = 1.5\times10^{-4}$(128)

illustration of this difference in variation of initiator concentraion with time of reaction for two methods is given in Fig. 5. 15 in which the Figs. 5.13 and 5.14 are combined. As is apparent from Fig. 5. 15, even though the initiator concentrations were much higher in Method 1 initially than in Method 2, in the later stages of the polymerisation the situation was reversed. This observation provides a possible reason for the lower intrinsic viscosities of the polymers prepared by Method 2 as compared to those of the polymers prepared by Method 1, as the degree of polymerisation and hence molecular weight of the polymer varies inversely with initiator concentration. However, it is not possible to state with certainty that the increase in the initiator concentration is the main cause for lower intrinsic viscosities of the polymers prepared by Method 2, since the degree of polymerisation also varies directly with the monomer concentration. In the absence of transfer reactions, the number-average degree of polymerisation, $\overline{P}_n$, of a polymer produced by free-radical addition polymerisation is given by

$$\overline{P}_n = k_p\,[M]/k_t^{\frac{1}{2}}(fk[I])^{\frac{1}{2}} \qquad \ldots.(5.6)$$

where k_p = rate coefficient for propagation reaction
$[M]$ = concentration of monomer
k_t = rate coefficient for termination reaction
f = initiator efficiency
k = rate coefficient for thermal decomposition of the initiator

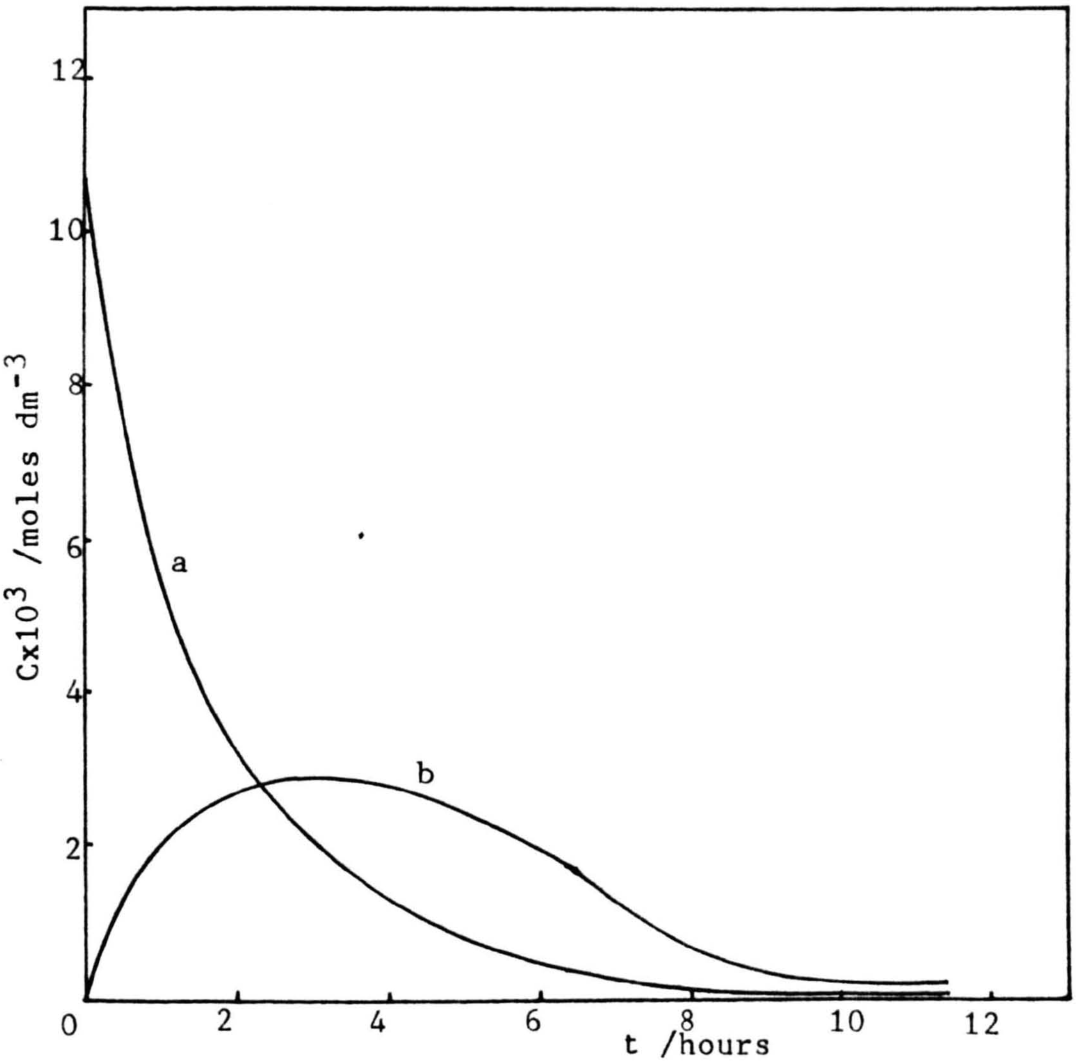


Fig. 5.15 : Typical variation of concentration of initiator (C) with time of reaction during polymerisation of polymers by Method 1 (a) and by Method 2 (b), MAA - 34.4g, EHA - 18.4g, AZDN - 0.528g, polymerisation temperature 70°C and $k = 1.5x10^{-4}$(128)

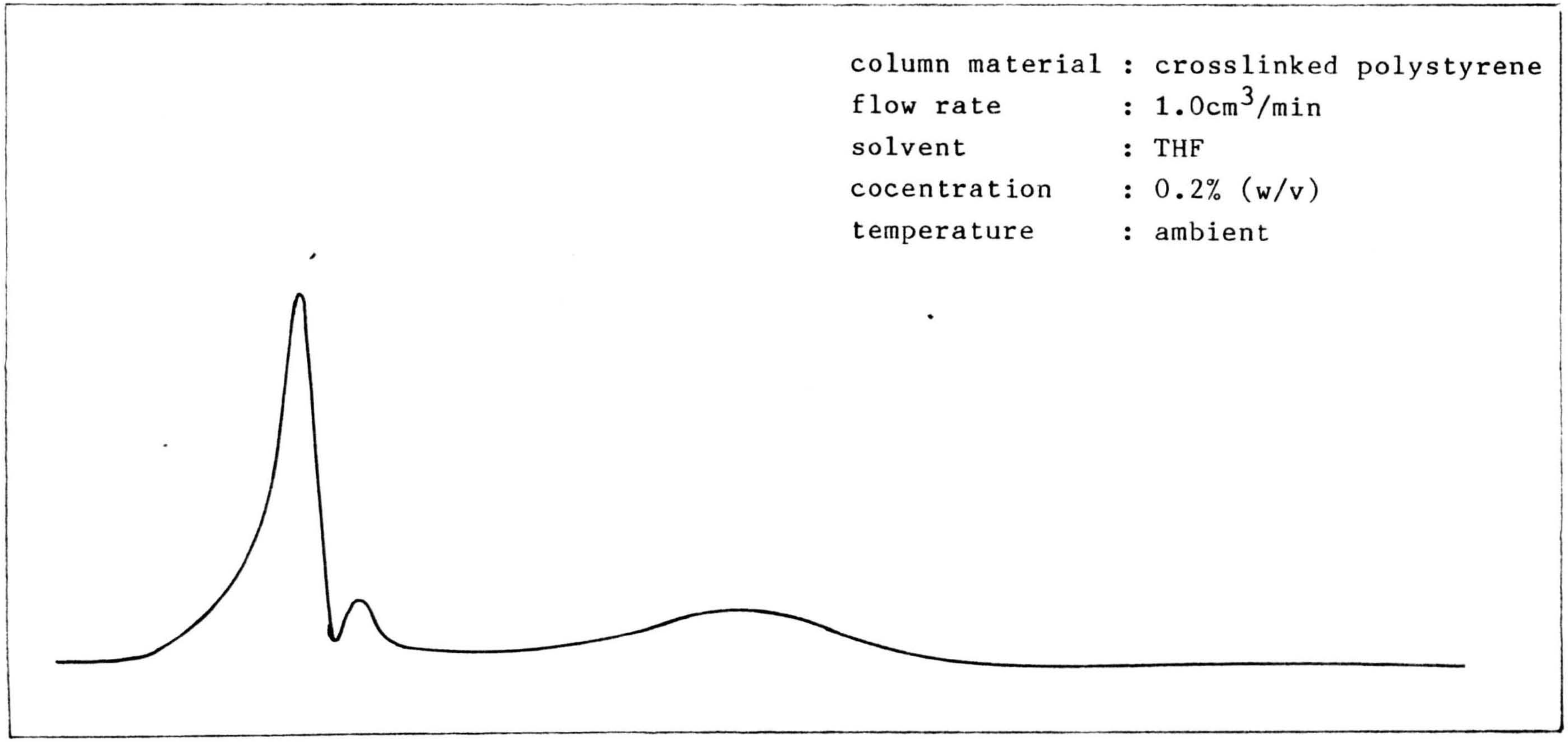
[I] = concentration of initiator

Therefore a more plausible explanation for the differences in intrinsic viscosities of the polymers prepared by these two methods would have been obtained if the variations of monomer concentration with time of reaction for both methods were also taken into consideration. The monomer concentration decreased with time during polymerisations carried out by Method 1. The nature of the variation of monomer concentration in the case of polymerisations carried out by Method 2 is uncertain, but the concentration undoubtedly increased somewhat during the initial stages stages of the addition.

5.3 Results of gel permeation chromatographic analyses (GPC) of polymers

The results of the GPC analyses of some polymers of Type 1 are given in Table 5.3. All the reported molecular weights are the "polystyrene equivalents". Two typical GPC chromatograms of polymers MAA/MA(80:20)C and MAA/EHA(80:20)C are shown in Figs. 5.16 and 5.17 respectively.

The weight-average molecular weight, $\bar{M}_w$, and number-average molecular weight, $\bar{M}_n$, of the linear polymers of each group were found to vary in the expected order. Amongst the polymethacrylic acids, only one sample, MAA-B, gave a detectable peak in the chromatogram. According to



column material : crosslinked polystyrene

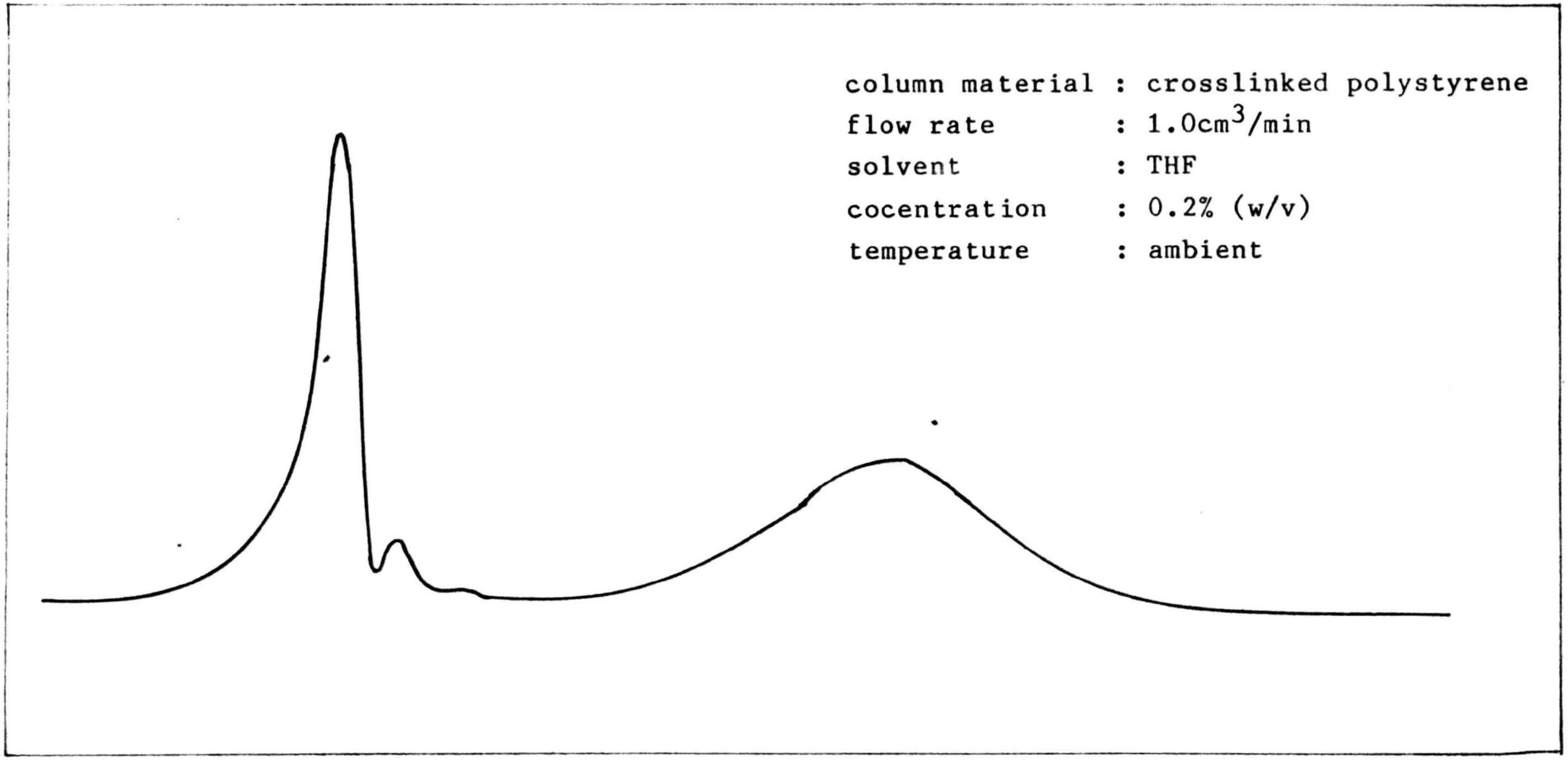
flow rate : 1.0cm^3/min

solvent : THF

cocentration : 0.2% (w/v)

temperature : ambient

Fig. 5.16 : Gel permeation chromatogram for polymer MAA/MA(80:20)C



column material : crosslinked polystyrene
flow rate : 1.0cm^3/min
solvent : THF
cocentration : 0.2% (w/v)
temperature : ambient

Fig. 5.17 : Gel permeation chromatogram for polymer MAA/EHA(80:20)C

Dr. Holding, the reason for this could have been the high polarity of these samples, which facilitates their adhesion to the GPC column. As regards to the molecular weights of branched polymers, the $\bar{M}_w$ values of polymers expected to have high degrees of branching were found to be higher than

polymer	$\bar{M}_w \mathrm{x} 10^{-3}$	$\bar{M}_n \mathrm{x} 10^{-3}$	polydispersity
MAA-B	2.7	0.7	3.7
MAA/MA(80:20)B	8.3	1.5	5.4
MAA/MA(80:20)C	13.5	2.1	6.5
MAA/MA(80:20)Ca	18.5	2.1	8.9
MAA/MA(80:20)Cb	18.9	4.2	4.5
MAA/MA(60:40)B	16.7	6.3	2.7
MAA/MA(60:40)C	33.7	11.4	2.9
MAA/MA(60:40)Ca	55.7	13.2	4.2
MAA/MA(60:40)Cb	98.0	13.8	7.1
MAA/MA(60:40)D	87.7	34.6	2.5
MAA/EHA(80:20)B	13.8	5.1	2.7
MAA/EHA(80:20)C	36.5	14.2	2.6
MAA/EHA(80:20)Ca	73.3	13.0	5.6
MAA/EHA(80:20)Cb	365	14.2	25.8
MAA/EHA(80:20)D	227	73.7	3.1
MAA/EHA(60:40)B	22.4	6.1	3.6
MAA/EHA(60:40)C	54.4	11.8	4.6
MAA/EHA(60:40)Ca	105	10.1	10.4
MAA/EHA(60:40)Cb	330	13.9	23.8
MAA/EHA(60:40)D	140	44.5	3.2

Table 5.3 : Results of GPC analyses of polymers of Type 1

those of the corresponding liner polymers of high molecular weight. Furthermore, the polydispersity of the branched polymers was found to be very high.

The intrinsic viscosity and the molecular weight of a polymer obtained by GPC are supposed to indicate the size of the polymer molecule, and this depends upon its conformation in a particular solvent. On this basis, it is difficult to explain the discrepancies between the results of viscosity measurements and GPC analyses obtained for branched polymers.

5.4 Results of assessment of hydrophilicity of polymers

5.4.1 Results of assessment of hydrophilicity of polymers of Type 1

The results of hydrophilicity assessment of some of the polymers of Type 1 are given in Table 5.4. For each group, it was expected that the hydrophilicity of the polymer would decrease as the molecular weight of the polymer increased. Contrary to expectation, the hydrophilicities of the polymers were found to increase as their molecular weights increased. The hydrophilicities of the branched polymers were found to be less than those of the linear polymers of high molecular weight. The hydrophilicity of the polymer was not found to be dependent upon the degree of branching, but, not surprisingly, it was found to be dependent upon the composition of the polymer.

As expected, hydrophilicity decreased with increasing EHA content.

polymer	volume of distilled water required to give first permanent turbid appearance of 10 cm^3 of 1% (w/v) polymer solution in IMS /cm^3
MAA/EHA(80:20)B	3.5
MAA/EHA(80:20)C	5.0
MAA/EHA(80:20)Ca	5.0
MAA/EHA(80:20)Cb	5.0
MAA/EHA(80:20)D	9.2
MAA/EHA(70:30)B	3.1
MAA/EHA(70:30)D	4.9
MAA/EHA(60:40)B	1.6
MAA/EHA(60:40)C	1.5
MAA/EHA(60:40)Ca	1.6
MAA/EHA(60:40)Cb	1.6
MAA/EHA(60:40)D	2.3
MAA/EHA(50:50)A	1.1
MAA/EHA(50:50)B	1.1

Table 5.4 : Results of hydrophilicity assessments of polymers of Type 1

5.4.2 Results of hydrophilicity assessments of polymers of Type 2

The results of hydrophilicity assessment of polymers of Type 2 are given in Table 5.5. The hydrophilicities of these polymers were found to be in the expected order, i.e., the hydrophilicity of the polymer was found to decrease with increasing molecular weight and increasing EHA content. Furthermore, the hydrophilicities of these polymers were found to be higher than those of similar polymers of Type 1.

5.5 Discussion of results of hydrophilicity assessment

As the hydrophilicity is an important characteristic of water-soluble polymers which are to be added to aqueous latices, the assessment of hydrophilicity was made in order to make sure that the hydrophilicity of the polymers varied in the expected order when their composition and molecular weight varied.

It is apparent from the results presented in Tables 5.4 and 5.5 that the variation of hydrophilicity with composition is in the expected order for both types of polymers. In other words, for a given initiator concentration, the hydrophilicity varies with composition as expected, i.e., the higher the EHA/MAA ratio, the lower the hydrophilicity.

As regards for the variation of hydrophilicity with molecular weight, for a given EHA/MAA ratio, the hydrophilicity of the polymers of Type 1 increases as

polymer	volume of distilled water required to give first permanent turbid appearance of 10 cm^3 of 1% (w/v) polymer solution in IMS /cm^3
MAA/EHA(90:10)0.029	17.2
MAA/EHA(90:10)0.034	16.5
MAA/EHA(90:10)0.037	16.2
MAA/EHA(90:10)0.059	15.5
MAA/EHA(80:20)0.058	7.5
MAA/EHA(80:20)0.068	7.0
MAA/EHA(80:20)0.082	6.2
MAA/EHA(80:20)0.109	6.0
MAA/EHA(80:20)0.122	5.8
MAA/EHA(80:20)0.129	5.5
MAA/EHA(70:30)0.054	4.8
MAA/EHA(70:30)0.080	4.5
MAA/EHA(70:30)0.097	4.0
MAA/EHA(70:30)0.137	3.4
MAA/EHA(60:40)0.036	3.9
MAA/EHA(60:40)0.045	3.3
MAA/EHA(60:40)0.052	3.0
MAA/EHA(60:40)0.073	2.7
MAA/EHA(60:40)0.109	2.3
MAA/EHA(60:40)0.124	2.1
MAA/EHA(60:40)0.156	2.0
MAA/EHA(60:40)0.184	1.8
MAA/EHA(50:50)0.033	2.1
MAA/EHA(50:50)0.072	1.8
MAA/EHA(50:50)0.080	1.6
MAA/EHA(50:50)0.099	1.4
AA/EHA(80:20)0.036	9.9
AA/EHA(80:20)0.044	9.3
AA/EHA(80:20)0.062	8.3
AA/EHA(80:20)0.087	8.1
AA/EHA(60:40)0.028	3.5
AA/EHA(60:40)0.037	3.3
AA/EHA(60:40)0.055	3.1
AA/EHA(60:40)0.089	2.9

Table 5.5 : Results of hydrophilicity assessment of polymers of Type 2

the initiator concentration decreases, i.e., as the molecular weight of the polymer increases. This observation was unexpected. It was expected that the hydrophilicity of the polymer would decrease as its molecular weight increased. The most likely explanation of this unexpected observation is that the MAA tends to copolymerise more rapidly than the EHA, so that, when the initiator concentration was low, and hence the conversion relatively low, a polymer of higher MAA content (and therefore higher hydrophilicity) was formed than when the initiator concentration was high and the conversion relatively high. This explanation will be confirmed subsequently by analytical results (see Section 5.8). Theoretical predictions for this drift of copolymer composition with conversion in the case of EHA and MAA will be discussed in detail subsequently (see Section 5.10).

5.6 Results of acidimetric titrations

The results of acidimetric titrations for some polymers of Type 1 are given in Table 5.6. Also given in Table 5.6 are results obtained by this method for acid contents of two homopolymers, namely, polymethacrylic acid and polyacrylic acid. These latter determinations were carried out in order to assess the accuracy of this method. The acid content of all the polymers investigated were found to be less than would be expected on the basis of their nominal composition. Furthermore, the acid contents of polymers of high molecular weight were found to be higher than those of the corresponding polymers of low molecular weight. The comparisons between the results for polymers of high molecular weight and those for polymers of low molecular weight having the same nominal composition are consistent with the results for the assessment of the hydrophilicities of those polymers, and support the view that the unexpected differences in hydrophilicity are a consequence of differences in composition.

polymer	Carboxylic content of polymer
MAA/EHA(80:20)B	67
MAA/EHA(80:20)C	70
MAA/EHA(80:20)D	74
MAA/EHA(70:30)B	62
MAA/EHA(70:30)D	66
MAA/EHA(60:40)B	52
MAA/EHA(60:40)C	52
MAA/EHA(60:40)D	55
MAA/EHA(50:50)A	44
MAA/EHA(50:50)B	44
MAA-D	75
*CARBOPOL	85

Table 5.6 : Results of acidimetric titrations of polymers of Type 1

* a commercial sample of polyacrylic acid

As this method was not found to give accurate results for the acid content of the polymers, no attempt was made to characterise the polymers of Type 2 by this method.

5.7 Discussion of results of acidimetric titrations

The results in Table 5.6 demonstrate the unsuitability of this titrimetric method for the determination of the acid contents of polymers of the type used in this work. The results obtained for the homopolymers confirm that their acid contents, as determined by this method , are lower than would be expected on the basis of their composition. The acid contents of EHA/MAA copolymers prepared using a given concentration of initiator, as determined by this method, decrease as the EHA/MAA ratio increases-this is as expected.

The acid contents of EHA/MAA copolymers of given monomer feed ratio increases as the initiator concentration decreases, i.e., as the molecular weight of the polymer increases. This observation is unexpected and accords with the results of the hydrophilicity assessments, and supports the explanation tentatively proposed above for the unexpected trend of hydrophilicity with polymer molecular weight. Theoretical predictions for this drift of copolymer composition with conversion in the case of EHA and MAA will be discussed in detail subsequently (see

Section 5.10).

5.8 Results of infra-red analyses

5.8.1 Results of infra-red analyses of polymers of Type 1

The results of infra-red analyses of polymers of Type 1 are given in Table 5.7. Two typical infra-red spectra of MAA/EHA copolymers are given in Figs. 5.18 and 5.19. These are for polymers MAA/EHA(70:30)B and MAA/EHA(50:50)A respectively. The acid content of the polymers of low molecular weight were found to vary in the

polymer	$L = \dfrac{\log_{10} h_o/h \text{ at } 1710\text{cm}^{-1}}{\log_{10} h_o/h \text{ at } 1740\text{cm}^{-1}}$	methacrylic acid content of polymer /mole%
MAA/EHA(80:20)B	1.58	81
MAA/EHA(80:20)C	1.60	82
MAA/EHA(80:20)D	1.98	88
MAA/EHA(70:30)B	1.29	70
MAA/EHA(70:30)D	1.48	76
MAA/EHA(60:40)B	1.09	61
MAA/EHA(60:40)C	1.09	61
MAA/EHA(60:40)D	1.26	70
MAA/EHA(50:50)A	0.76	50
MAA/EHA(50:50)B	0.81	51

Table 5.7 : Results of infra-red analyses of polymers of Type 1

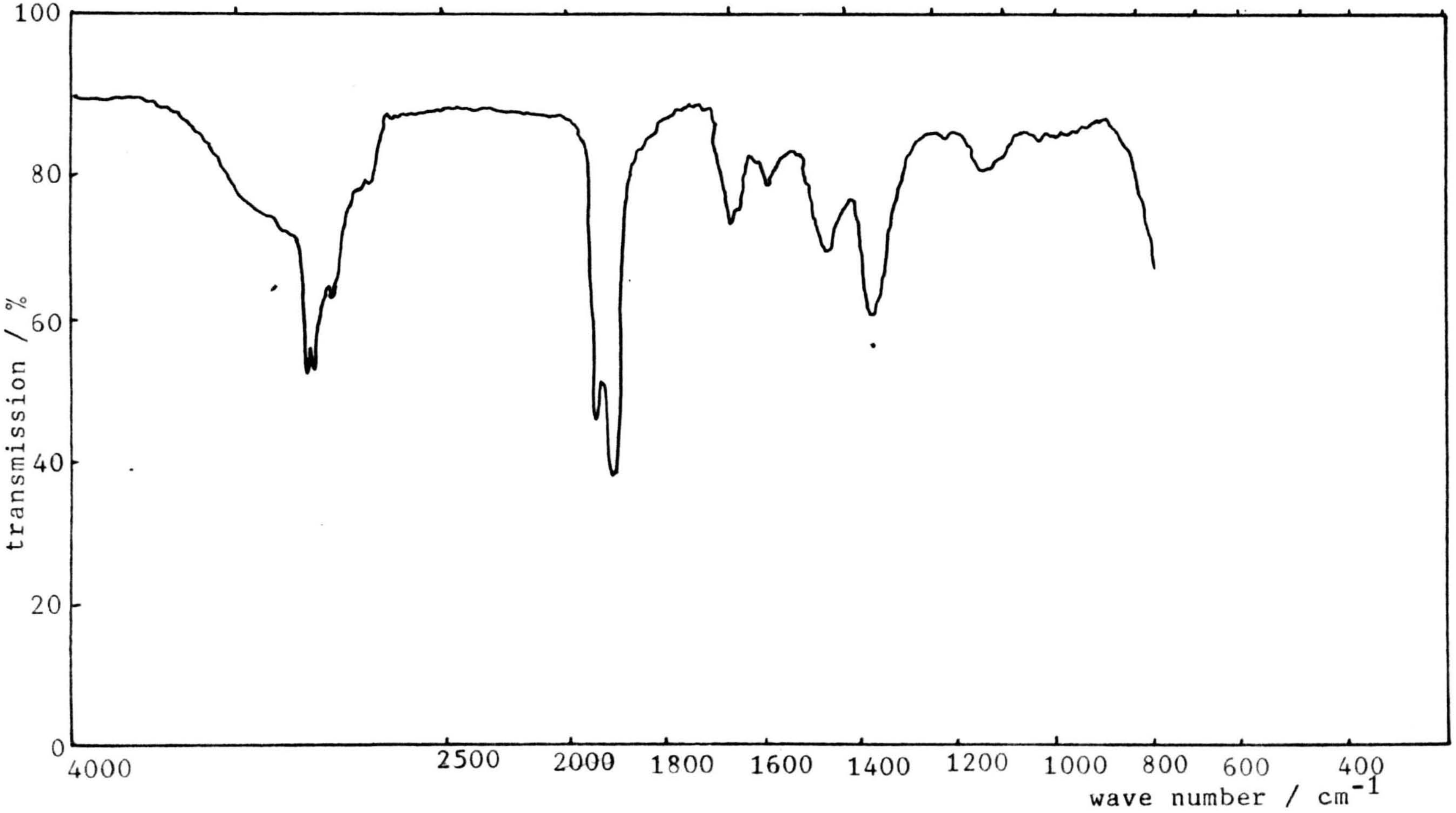


Fig. 5.18 : IR spectrum of polymer MAA/EHA(70:30)B

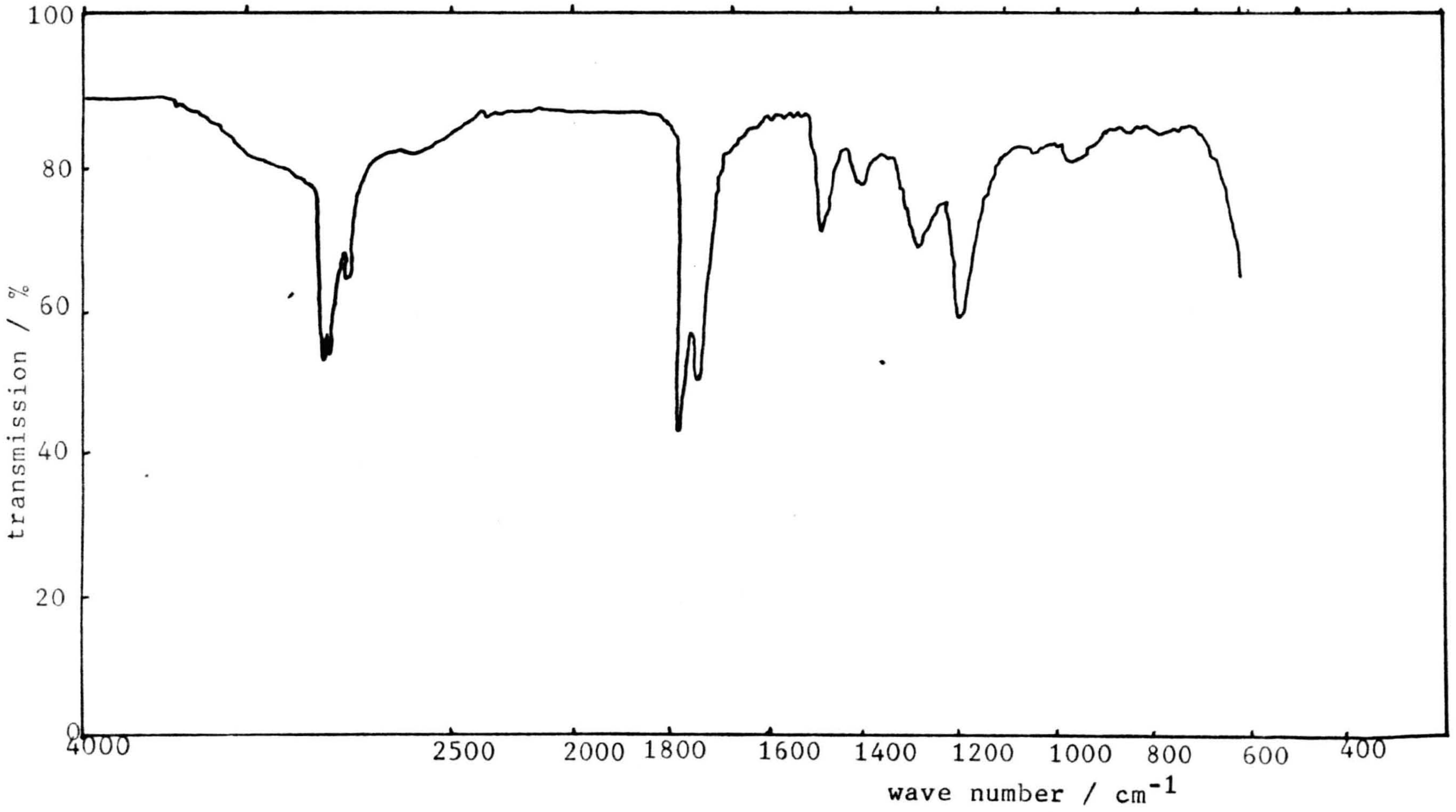


Fig. 5.19 : IR spectrum of polymer MAA/EHA(50:50)A

expected order with MAA/EHA ratio. Furthermore, the acid contents of these polymers given by this method were found to be very close to the values expected on the basis of their nominal composition. However, the acid contents of the polymers of high molecular weight were found to be higher than those expected on the basis of their nominal composition. Nevertheless the comparisons between the results for polymers of high molecular weight and those for polymers of low molecular weight having the same nominal composition are consistent with the results for the assessment of hydrophilicity for these polymers, and support the view that the unexpected differences in hydrophilicity are a consequence of differences in composition.

5.8.2 Results of infra-red analysis of polymers of Type 2

The results of the infra-red analyses of the polymers of Type 2 are given in Table 5.8. The acid content of all the polymers, as determined by this method, were found to be in good agreement with those expected on the basis of their nominal composition. Furthermore, as in the case of polymers of Type 1, the results for the assessment of the hydrophilicities of these polymers accord with the compositions given by this IR analyses. There was no variation of the composition with the initiator concentration used in the preparation of the polymers.

polymer	$L = \dfrac{\log_{10} h_o/h \text{ at } 1710\text{cm}^{-1}}{\log_{10} h_o/h \text{ at } 1740\text{cm}^{-1}}$	methacrylic acid content of polymer /mole%
MAA/EHA(90:10)0.029	2.15	90
MAA/EHA(90:10)0.034	2.20	91
MAA/EHA(90:10)0.037	2.18	90
MAA/EHA(90:10)0.059	2.20	91
MAA/EHA(80:20)0.058	1.57	81
MAA/EHA(80:20)0.068	1.58	81
MAA/EHA(80:20)0.082	1.57	81
MAA/EHA(80:20)0.109	1.59	82
MAA/EHA(80:20)0.122	1.60	82
MAA/EHA(80:20)0.129	1.60	82
MAA/EHA(70:30)0.054	1.29	70
MAA/EHA(70:30)0.080	1.29	70
MAA/EHA(70:30)0.097	1.31	71
MAA/EHA(70:30)0.137	1.30	70
MAA/EHA(60:40)0.036	1.07	60
MAA/EHA(60:40)0.045	1.07	60
MAA/EHA(60:40)0.052	1.07	60
MAA/EHA(60:40)0.073	1.08	60
MAA/EHA(60:40)0.109	2.00	61
MAA/EHA(60:40)0.124	1.09	61
MAA/EHA(60:40)0.156	1.08	60
MAA/EHA(60:40)0.184	1.09	61
MAA/EHA(50:50)0.033	0.76	50
MAA/EHA(50:50)0.072	0.78	50
MAA/EHA(50:50)0.080	0.78	50
MAA/EHA(50:50)0.099	0.79	51

Table 5.8 : Results of infra-red analyses of polymers of Type 2

5.9 Discussion of results of IR analyses of polymers

It is apparent from the results presented in Table 5.8 that these IR analyses provide accurate results for the acid content of the polymers. The results of hydrophilicity assessment for polymers of both types accord with their composition as determined by the IR analyses. Furthermore, the results of IR analyses for the polymers of Type 2 indicate that there is no variation of compositions of the polymers with initiator concentration used in their preparation and that the use of Method 2 to prepare the polymers overcame the problem of composition drift with conversion.

5.10 Theoretical consideration of predicted composition drift of polymers prepared by Method 1

The IR analyses of the polymers of Type 1 revealed that in each group, the MAA contents of the polymers of high molecular weight were significantly higher than those of the corresponding feeds. As has been suggested in Section 5.5, the most likely reason for this deviation of composition from expectation is incomplete conversion during the polymerisation reactions used to prepare those polymers together with differences in the reactivity of the two monomers. In order to predict how the composition of a copolymer of MAA and EHA varies with conversion, the instantaneous composition of two copolymers, namely, MAA/EHA(80:20)B and MAA/EHA(80:20)D, at the end of the polymerisation were calculated theoretically as a function of conversion.

The weight conversion for each polymerisation reaction was determined experimentally according to the procedure given in Section 4.2.1. The resultant weight conversions for polymers MAA/EHA(80:20)B and MAA/EHA(80:20)D were found to be 97% and 80% respectively. The instantaneous copolymer composition corresponding to each conversion was predicted by calculating the variation of mole fraction of MAA, f_1, in the feed, with mole conversion using the following equation:(129)

$$1 - \frac{M}{M_o} = 1 - \left(\frac{f_1}{(f_1)_o}\right)^{\alpha} \left(\frac{f_2}{(f_2)_o}\right)^{\beta} \left(\frac{(f_1)_o - \delta}{f_1 - \delta}\right)^{\gamma} \quad \ldots\ldots(5.6)$$

where M_o = total mole concentration of MAA and EHA in the initial feed

M = total mole concentration of unreacted MAA and EHA in the final reaction mixture

$(f_1)_o$ = mole fraction of MAA in the initial feed

$(f_2)_o$ = mole fraction of EHA in the final feed

f_1 = mole fraction of unreacted MAA in the final reaction mixture

f_2 = mole fraction of unreacted EHA in the final reaction mixture

$\alpha = r_2/1-r_2$ $\qquad\qquad \beta = r_1/1-r_1$

$\gamma = (1-r_1r_2)/[(1-r_1)(1-r_2)]$

$\delta = 1-r_2/(2-r_1-r_2)$

r_1 = monomer reactivity ratio of MAA

r_2 = monomer reactivity ratio of EHA

$1 - M/M_o$ = fractional mole conversion

The fractional weight conversions corresponding to fractional mole conversions were calculated using the equation 5.7.$^{(129)}$

$$1 - \frac{W}{W_o} = 1 - \frac{[M]_o \, (f_1\mu_1 + f_1\mu_2) \, [M]}{[M_1]_o\mu_1 + [M_2]_o\mu_2 \quad [M]_o} \qquad \ldots.(5.7)$$

where W_o = total weight concentration of MAA and EHA in the initial feed

W = total weight concentration of unreacted MAA and EHA in the final reaction mixture

μ_1 = molecular weight of MAA

μ_2 = molecular weight of EHA

$[M_1]_o$ = mole concentration of MAA in the initial feed

$[M_2]_o$ = mole concentration of EHA in the final feed

A problem was encountered in that no values of the monomer reactivity ratios for the pair MAA/EHA could be found in the literature. However, Paxton$^{(130)}$ has reported that the monomer reactivity ratios for the copolymerisation of MAA and BA initiated by benzoyl peroxide in ethanol at 50°C are 1.31 and 0.35 respectively. In the absence of the required monomer reactivity ratios, this pair of monomers were taken as a good model for the MAA/EHA comonomer pair. Therefore in the calculations of the variation of f_1 with conversion, the monomer reactivity ratios of MAA and EHA were taken as 1.31 and 0.35 respectively.

The predicted variations of f_1 with mole conversion (curve a) and with weight conversion (curve b) are shown in Fig. 5.20. It appears that an appreciable change in f_1 does not occur until about 80% weight conversion. When the weight conversion exceeds approximately 90%, a dramatic decrease in f_1 appears to occur. Thus the polymer molecules which are formed at the final stages of the polymerisation should contain very high mole percentage of EHA, and if the polymerisation reaction reaches 100% conversion, the resultant polymer may contain a very small percentage of copolymer molecules which almost entirely comprise EHA units.

The values for f_1 and mole conversions corresponding to the weight conversions 97% and 80%, as obtained from Fig. 5.20 are given in Table 5.9. For each conversion the mole fraction of MAA in the polymer being formed at that conversion, F_1, was calculated using the equation(129)

weight conversion /%	mole conversion /%	f_1
80	68.4	0.730
97	96.9	0.525

Table 5.9 : Predicted values of f_1 and mole conversions corresponding to experimentally-observed weight conversions

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad \ldots.(5.8)$$

On this basis the values of F_1 at 80% and 97% weight

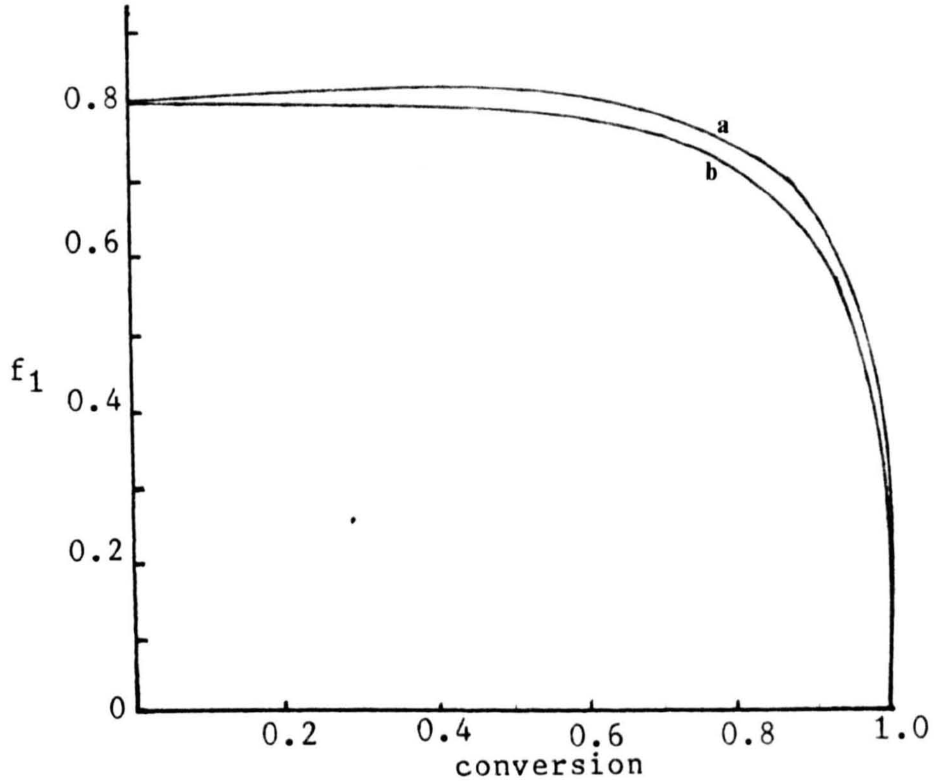


Fig. 5.20 : Predicted variation of f_1 with conversion for copolymerisation of MAA and EHA where $(f_1)_o$ = 0.80 and $(f_2)_o$ = 0.20 (r_1 and r_2 taken as 1.31 and 0.35 respectively)

a - mole conversion

b - weight conversion

conversions were predicted to be 0.80 and 0.65 respectively. At 2% weight conversion the value of F_1 was predicted to be 0.84. These theoretical predictions support the proposed composition drift with conversion in the case of MAA/EHA copolymers.

5.11 Further experimental evidence for copolymer composition drift with conversion for MAA/EHA copolymers prepared by Method 1

The results shown in Figs. 5.20 and 5.21 are the variation of conversion and hydrophilicity with reaction time, respectively, for polymers of sub-group MAA/EHA(80:20)B of Type 1. Figs. 5.22 and 5.23 shows how the hydrophilicity and MAA content of these polymers, as determined by IR analyses, vary with the conversion. The hydrophilicity and MAA content decreased dramatically with conversion. These results further supports the suggested copolymer composition drift with conversion for MAA/EHA copolymers of Type 1. Therefore a similar explanation is proposed to that which has been proposed for the similar variation in results for hydrophilicity assessment of the polymers of Type 1 (see Section 5.5).

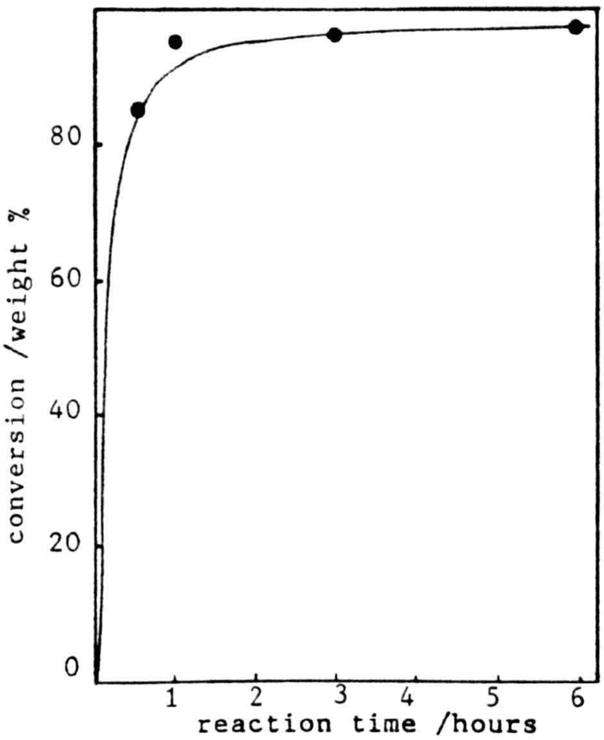


Fig. 5.20 : Variation of conversion with reaction time

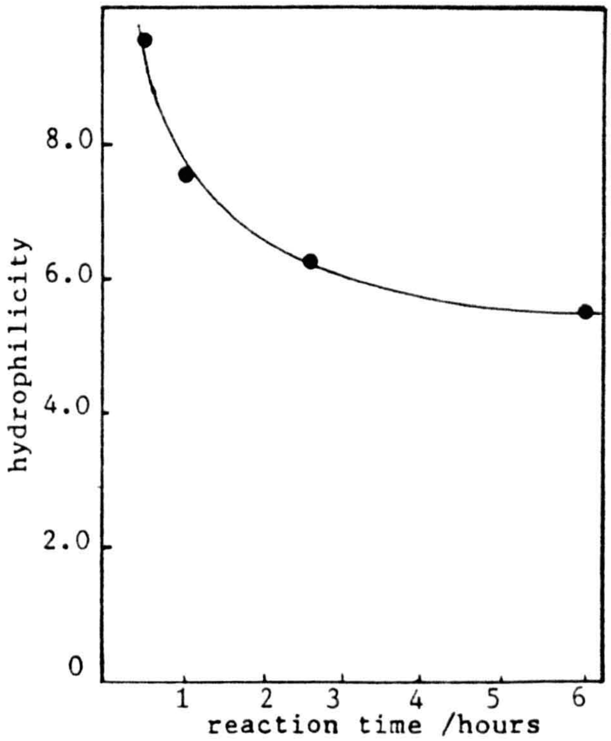


Fig. 5.21 : Variation of hydrophilicity of the polymer with reaction time

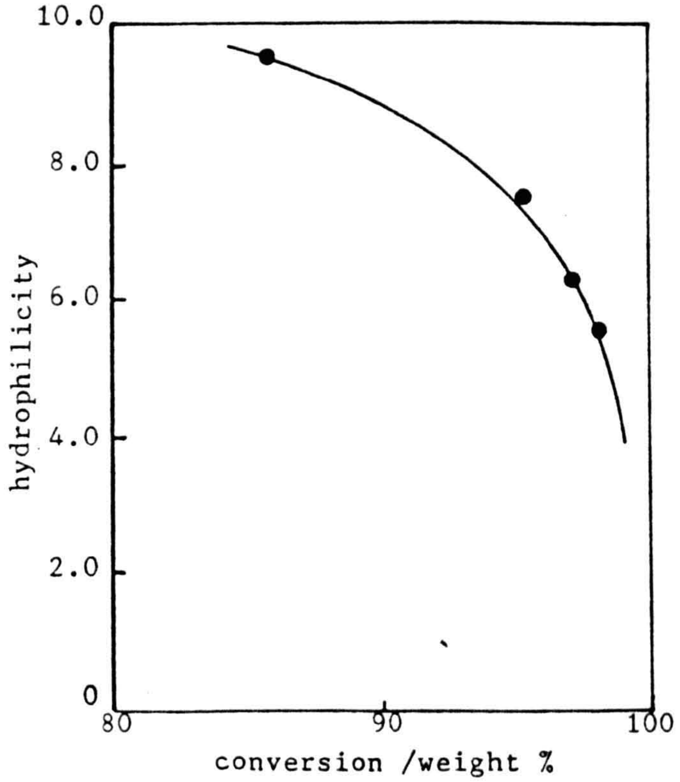


Fig. 5.22 : Variation of hydrophilicity of the polymer with conversion

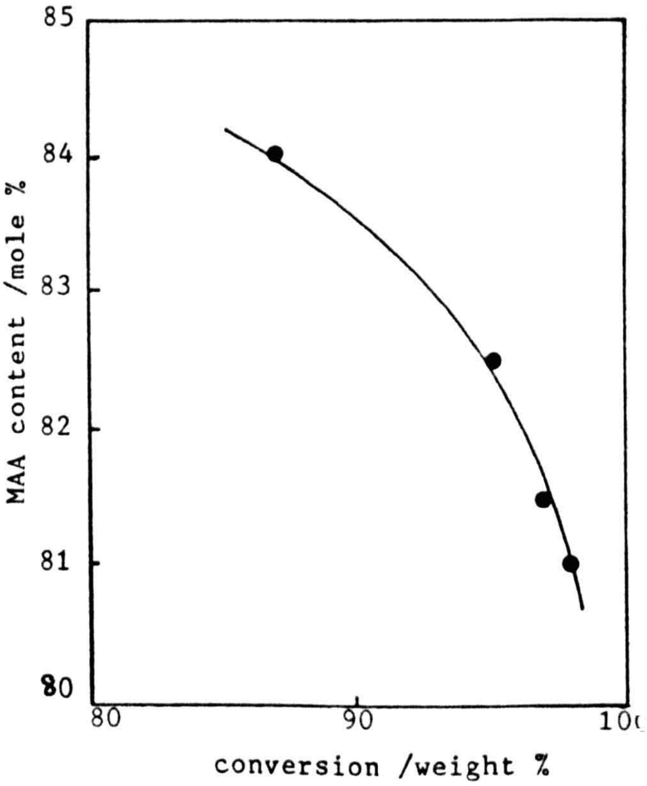


Fig. 5.23 : Variation of MAA content of the polymer with conversion

5.12 Results of assessment of tendency of polymers to form insoluble products by interaction with zinc ions and zinc-ammine ions

5.12.1 Results of assessment of polymers of Type 1

The results of the assessment of tendency of polymers of Type 1 to form insoluble products by interaction with zinc ions and with zinc-ammine ions are given in Table 5.10. These experiments were carried out in order to investigate the possibility that interactions might occur between the various polymers and zinc-ammine ions, with the formation of insoluble products. All the polymers investigated formed gelatinous precipitates when they were mixed as aqueous solutions of pH=7 with aqueous solutions of zinc sulphate. But with aqueous solutions of zinc ammonium sulphate, none of the polymers gave insoluble products.

5.12.2 Results of assessment of polymers of Type 2

The results of the assessment of the tendency of polymers of Type 2 to form insoluble products by interaction with zinc ions and with zinc-ammine ions are given in Table 5.11. The reactions of these polymers with zinc ions and with zinc-ammine ions were found to be identical to those of polymers of Type 1.

polymer (as an aqueous solution of pH=7)	reaction with zinc sulphate solution	reaction with zinc ammonium sulphate solution
MAA/EHA(80:20)A	white precipitate	clear solution
MAA/EHA(80:20)B	white precipitate	clear solution
MAA/EHA(80:20)C	white precipitate	clear solution
MAA/EHA(80:20)Ca	white precipitate	clear solution
MAA/EHA(80:20)Cb	white precipitate	clear solution
MAA/EHA(80:20)D	white precipitate	clear solution
MAA/EHA(80:20)E	white precipitate	clear solution
MAA/EHA(70:30)B	white precipitate	clear solution
MAA/EHA(70:30)D	white precipitate	clear solution
MAA/EHA(60:40)B	white precipitate	clear solution
MAA/EHA(60:40)C	white precipitate	clear solution
MAA/EHA(60:40)Ca	white precipitate	clear solution
MAA/EHA(60:40)Cb	white precipitate	clear solution
MAA/EHA(60:40)D	white precipitate	clear solution
MAA/EHA(50:50)A	white precipitate	clear solution
MAA/EHA(50:50)B	white precipitate	clear solution

Table 5.10 : Results of assessment of tendency of polymers of Type 1 to form insoluble products by interaction with zinc ions and with zinc-ammine ions

5.13 Discussion of results of assessment of tendency of polymers to form insoluble products by interaction with zinc ions and with zinc-ammine ions

The purpose of carrying out these experiments was to clarify whether or not the formation of insoluble

polymer (as an aqueous solution of pH=7)	reaction with zinc sulphate solution	reaction with zinc ammonium sulphate solution
MAA/EHA(90:10)0.029	white precipitate	clear solution
MAA/EHA(90:10)0.034	white precipitate	clear solution
MAA/EHA(90:10)0.037	white precipitate	clear solution
MAA/EHA(90:10)0.059	white precipitate	clear solution
MAA/EHA(80:20)0.058	white precipitate	clear solution
MAA/EHA(80:20)0.068	white precipitate	clear solution
MAA/EHA(80:20)0.082	white precipitate	clear solution
MAA/EHA(80:20)0.109	white precipitate	clear solution
MAA/EHA(80:20)0.122	white precipitate	clear solution
MAA/EHA(80:20)0.129	white precipitate	clear solution
MAA/EHA(70:30)0.054	white precipitate	clear solution
MAA/EHA(70:30)0.080	white precipitate	clear solution
MAA/EHA(70:30)0.097	white precipitate	clear solution
MAA/EHA(70:30)0.137	white precipitate	clear solution
MAA/EHA(60:40)0.036	white precipitate	clear solution
MAA/EHA(60:40)0.045	white precipitate	clear solution
MAA/EHA(60:40)0.052	white precipitate	clear solution
MAA/EHA(60:40)0.073	white precipitate	clear solution
MAA/EHA(60:40)0.109	white precipitate	clear solution
MAA/EHA(60:40)0.124	white precipitate	clear solution
MAA/EHA(60:40)0.156	white precipitate	clear solution
MAA/EHA(60:40)0.184	white precipitate	clear solution
MAA/EHA(50:50)0.033	white precipitate	clear solution
MAA/EHA(50:50)0.072	white precipitate	clear solution
MAA/EHA(50:50)0.080	white precipitate	clear solution
MAA/EHA(50:50)0.099	white precipitate	clear solution

Table 5.11 : Results of assessment of tendency of polymers of Type 2 to form insoluble products by interaction with zinc ions and zinc-ammine ions

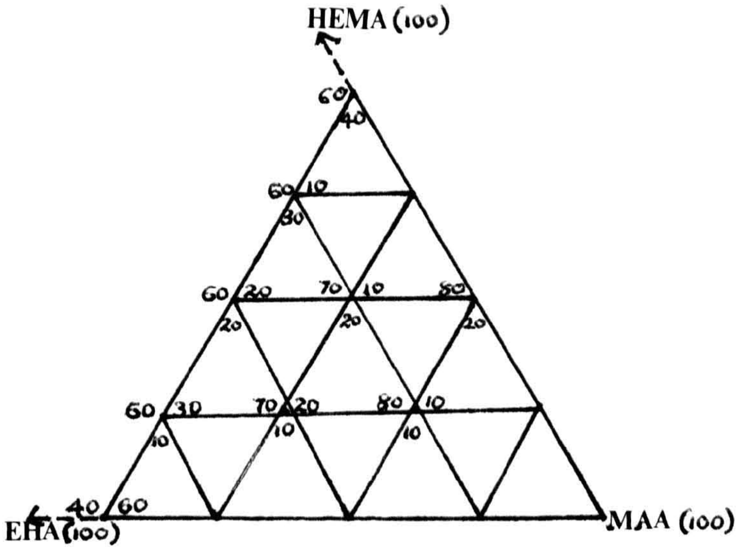
reaction products between the added polymers and zinc ions or zinc-ammine ions was a factor which had to be taken into account when interpreting the effects of the polymers upon NR latex to which zinc compounds had been added. In particular, it was desired to clarify whether the formation of insoluble polymer zinc salts was a factor which had to be taken into account when interpreting results for the effects of added polymers upon the zinc-oxide thickening of NR latex. The results of these assessments indicate that insoluble products are formed with zinc ions, but not with zinc-ammine ions. This observation was expected because zinc-ammine salts are generally more soluble in water than are the corresponding zinc salts, in cases where the latter have low solubilities.

CHAPTER SIX

EFFECTS OF POLYMERS OF TYPE 1 UPON SOME PROPERTIES OF NR LATEX

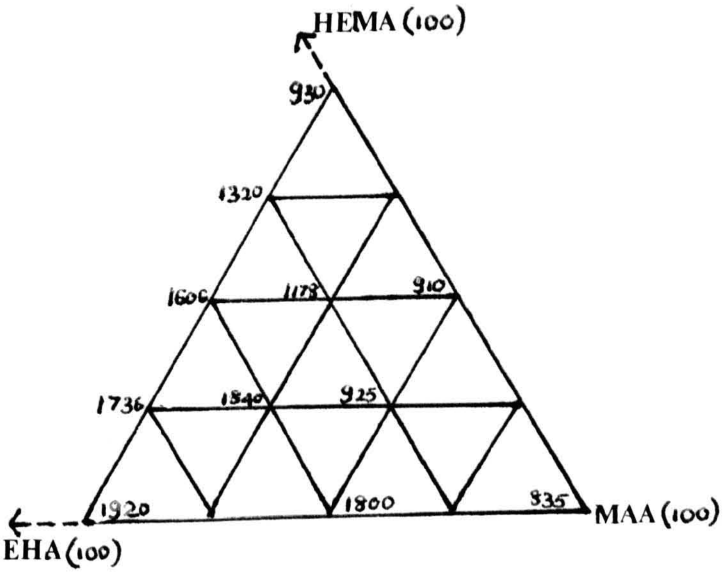
6.1 Results of preliminary investigation of effects of various polymers upon mechanical stability of NR latex

The results of the preliminary investigation of the effects of various polymers upon the MST of NR latex (Batch 1) at the 0.50 pphls level of addition are shown in Fig. 6.1. The polymers used in this investigation were those prepared by Bradbury. The composition of the polymers used in this preliminary investigation are given in Fig. 6.1 (a) and the corresponding MST values are given in Fig. 6.1 (b). The polymethacrylic acid and MAA/HEMA copolymers were not found to be effective in enhancing the MST of NR latex, whilst the copolymers of MAA/EHA were found to be very effective. The magnitude of the enhancement of MST brought about by the MAA/EHA copolymers was found to increase as the EHA content of the polymer was increased. The terpolymers of MAA/HEMA/EHA were also found to enhance the MST, and the variation of the magnitude of the enhancement with the EHA content of the polymer was found to be more pronounced than that with the HEMA content of the polymer. This observation suggested that it would be of interest to investigate correlations between the various characteristics of an added polymer and its



(a)

compsoition of polymers/ mole %



(b)

MST /sceonds

Fig. 6.1 : Effects of various added polymers upon MST of NR latex (Batch 1) at the 0.50 pphls level of addition

influence upon the properties of NR latex using the copolymers of such monomers as MAA and EHA.

6.2 Results of effects of various groups of polymers of Type 1 upon mechanical stability and viscosity of NR latex

6.2.1 Effects of polymers of group MAA

The effects of various levels of added polymers of group MAA upon the MST and viscosity of NR latex (Batch 1) are shown in Figs. 6.2 and 6.3 respectively. In each case, the added polymer caused the MST of the latex to be slightly enhanced, and the extent of the enhancement depended upon the molecular weight of the polymer, being apparently greatest for the polymer of highest molecular weight. This observation is in contrast to that observed in the preliminary investigation, where polymethacrylic acid was found to decrease the MST of latex. The efficiency of branched polymers in enhancing MST was found to be slightly higher than that of the linear polymers of low molecular weight, and this efficiency was found to increase slightly as the degree of branching was increased.

As regards the effects of these polymers upon the viscosity of NR latex, all the polymers enhanced the viscosity at all the levels investigated, and the extent of the enhancement was found to depend upon the molecular

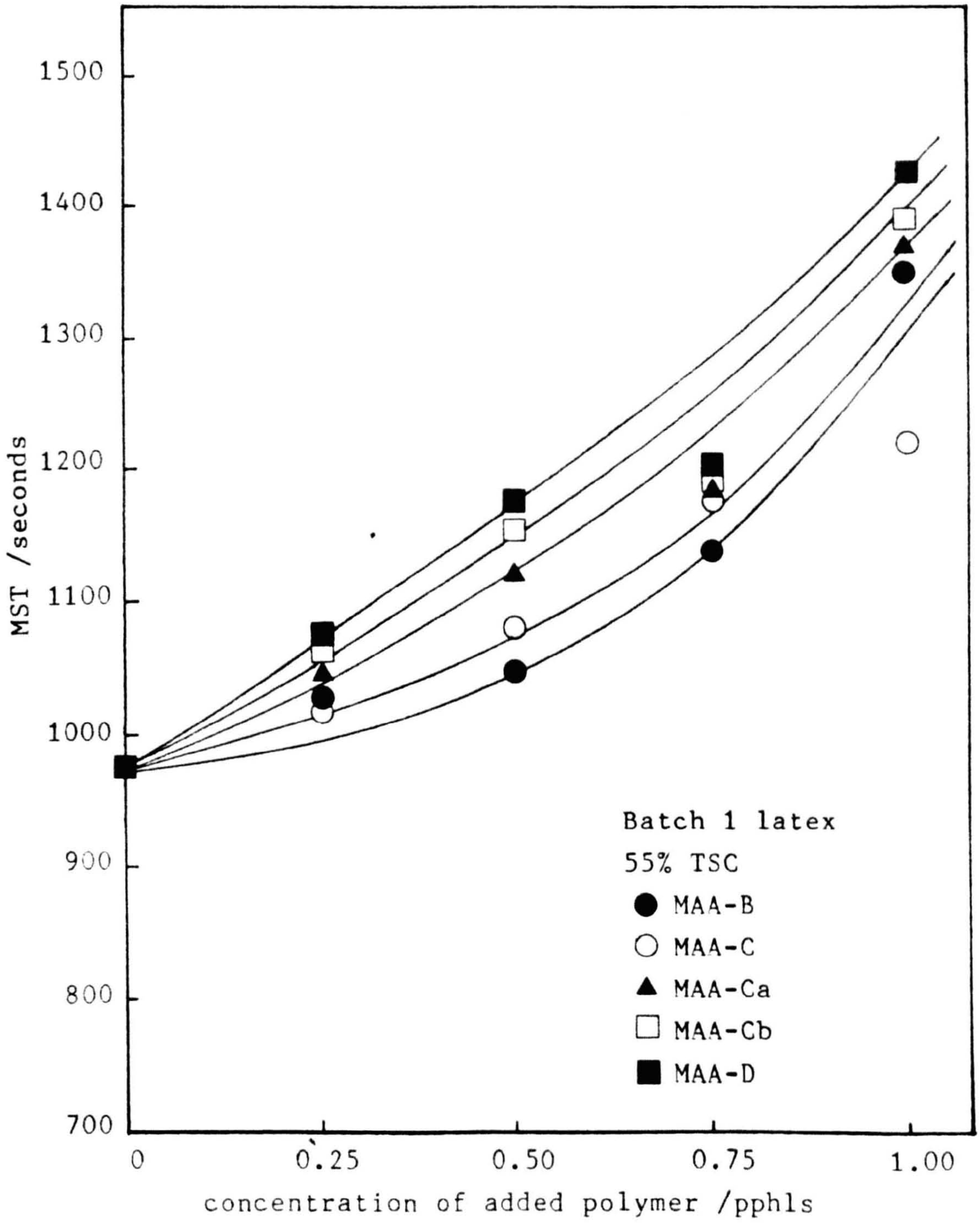


Fig. 6.2 : Effects of polymers of Type 1 group MAA upon MST of NR latex

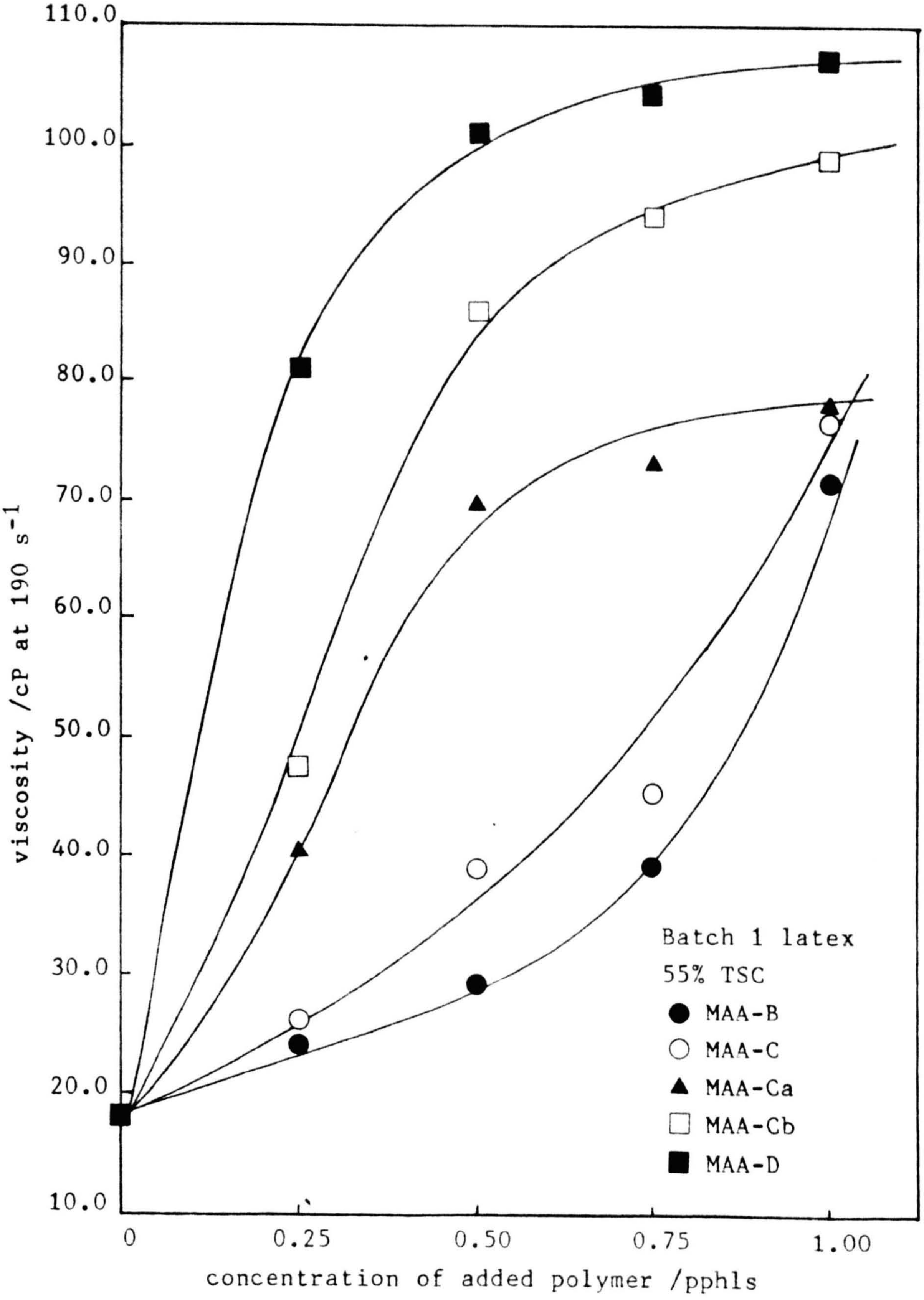


Fig. 6.3 : Effects of polymers of Type 1 group MAA upon viscosity of NR latex

weight of the polymer. The polymer of highest molecular weight brought about a sharp enhancement of viscosity over a fairly narrow range of addition, whereas the polymers of low molecular weight caused the viscosity to be enhanced at an increasing rate with increasing level of addition. The branched polymers were found to be more effective in enhancing the viscosity than linear polymers of low molecular weight, and this efficiency was found to increase with degree of branching.

6.2.2 Effects of polymers of group MAA/MA(80:20)

The effects of various levels of added polymers of group MAA/MA(80:20) upon the MST and viscosity of NR latex (Batch 1) are shown in Figs. 6.4 and 6.5 respectively. The effects polymers of this group upon the MST and viscosity were found to be similar to those of the polymers of group MAA. However, the abilities of these polymers to enhance the MST were found to be slightly greater than those of the polymers of group MAA, whilst their abilities to enhance the viscosity was found to be slightly less than those of the polymers of group MAA.

6.2.3 Effects of polymers of group MAA/MA(60:40)

The effects of various levels of added polymers of group MAA/MA(60:40) upon the MST and viscosity of NR latex (Batch 1) are shown in Figs. 6.6 and 6.7

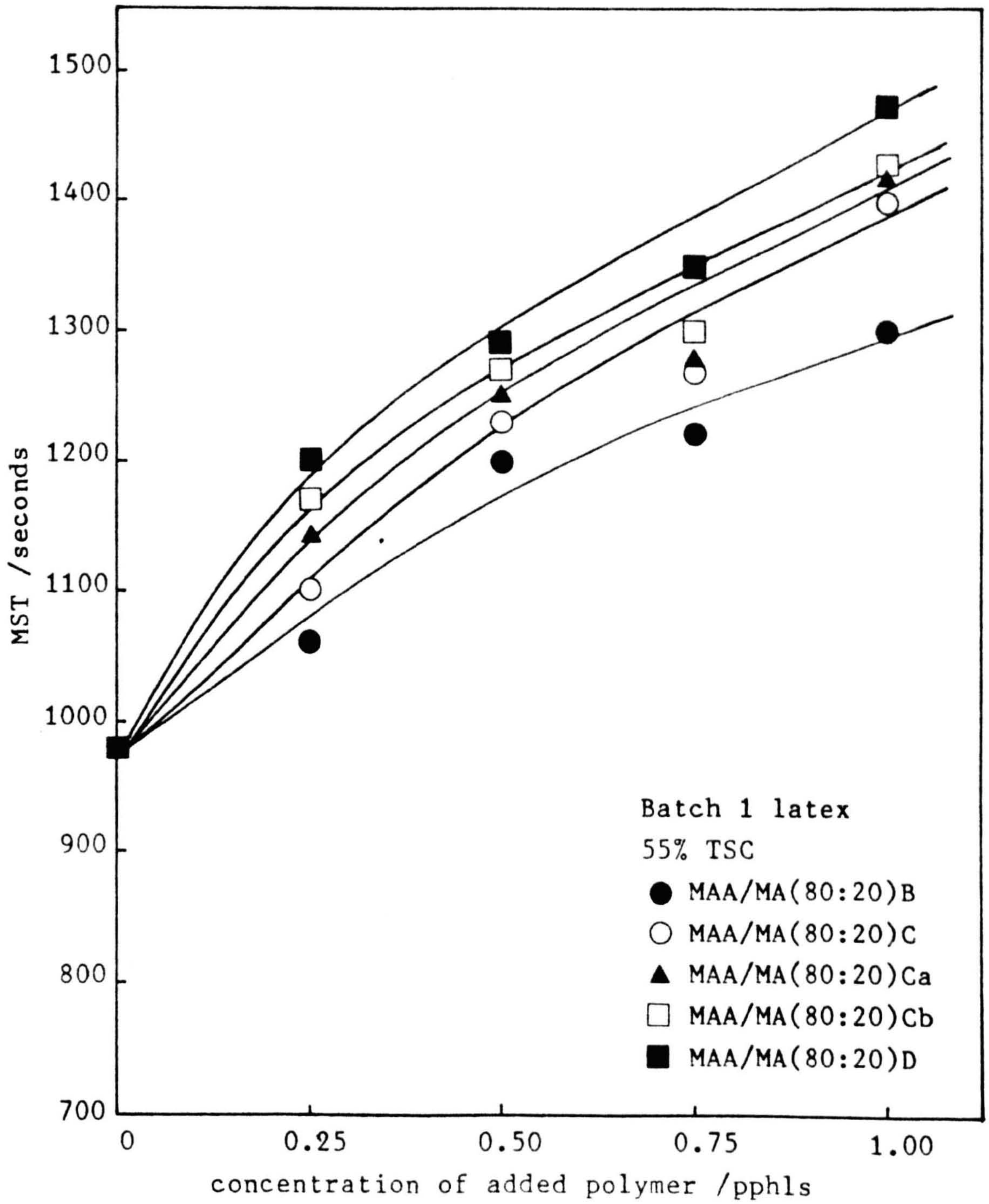


Fig. 6.4 : Effects of polymers of Type 1 group MAA/MA(80:20) upon MST of NR latex

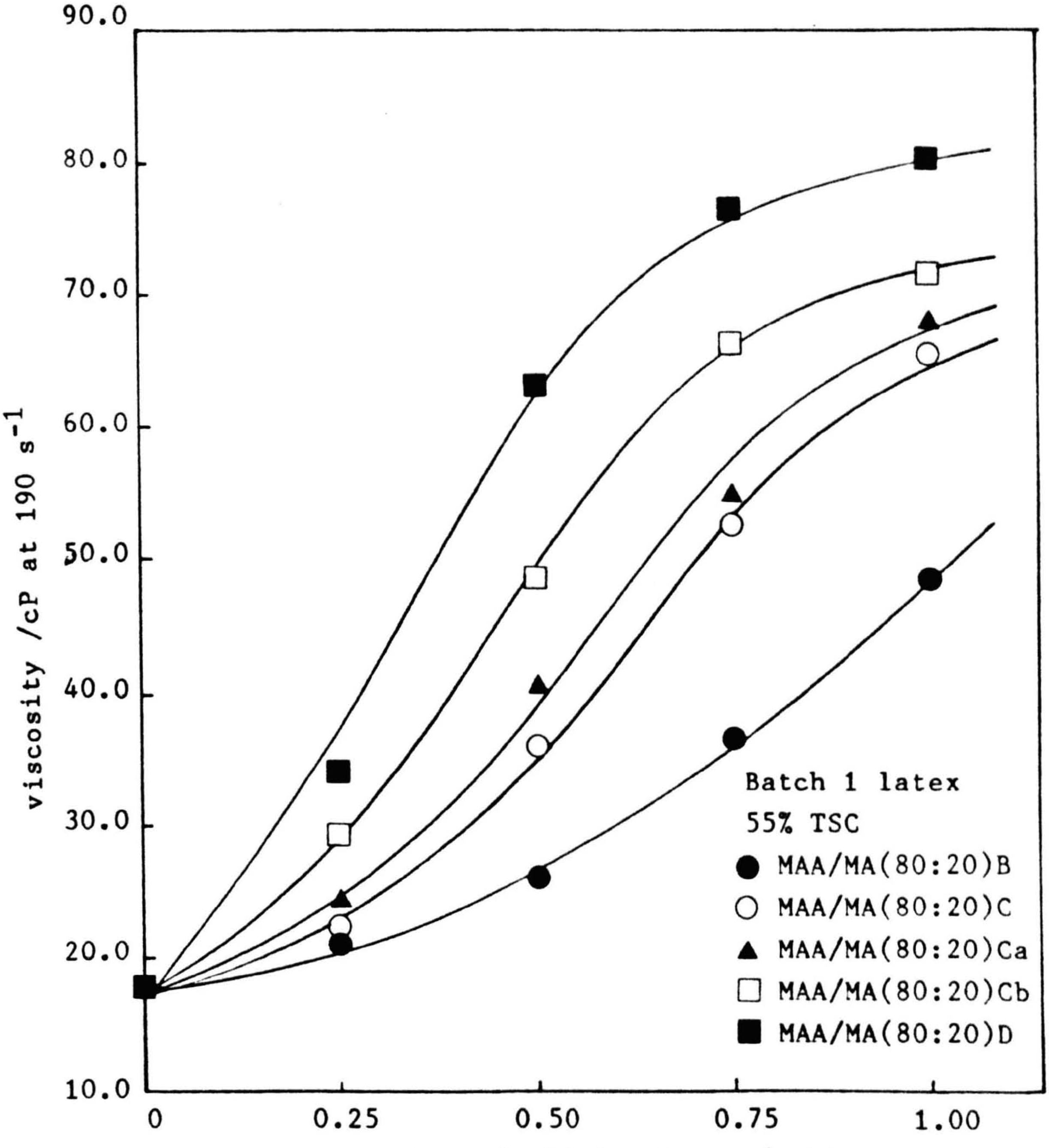


Fig. 6.5 : Effects of polymers of Type 1 group MAA/MA(80:20) upon viscosity of NR latex

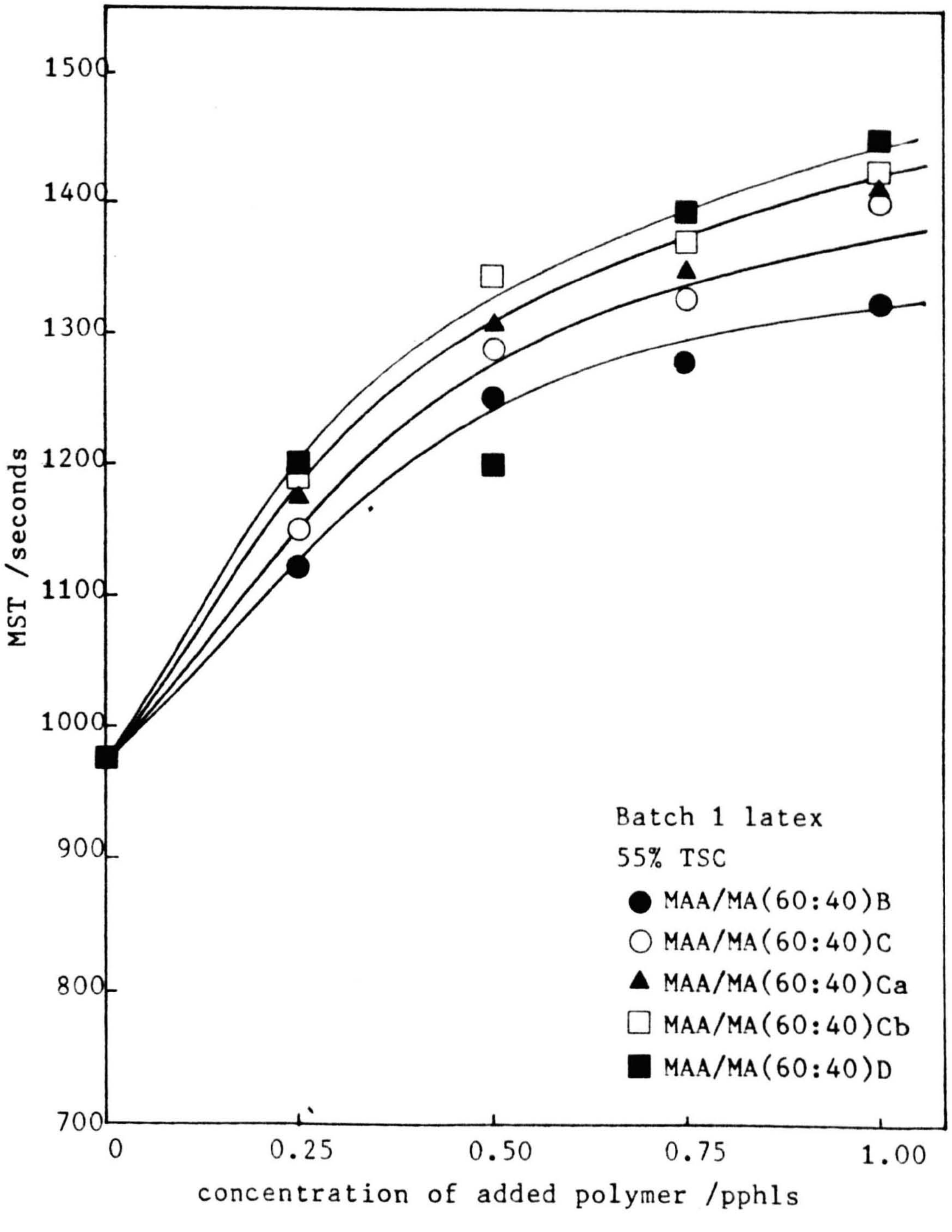


Fig. 6.6 : Effects of polymers of Type 1 group MAA/MA(60:40) upon MST of NR latex

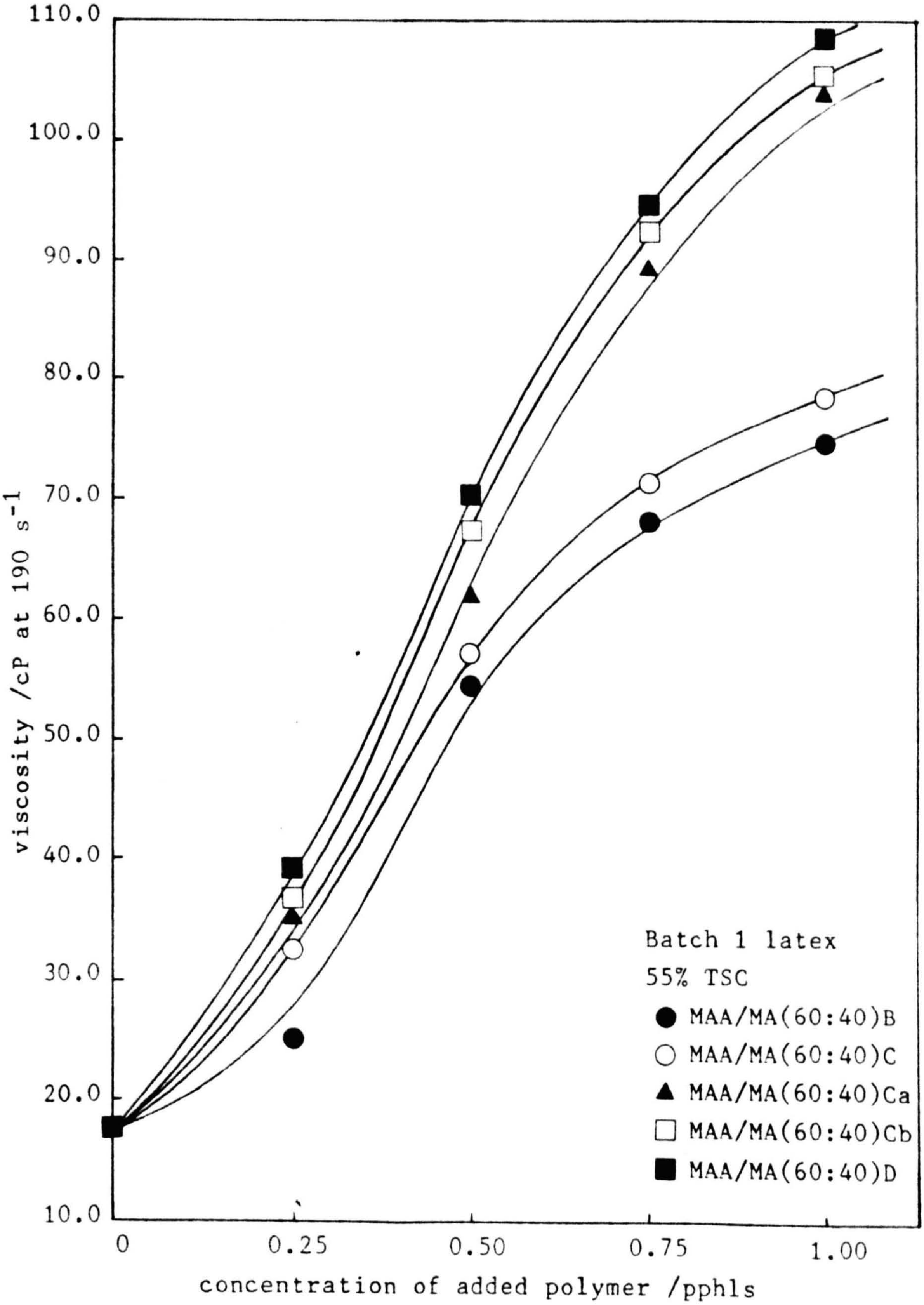


Fig. 6.7 : Effects of polymers of Type 1 group MAA/MA(60:40) upon viscosity of NR latex

respectively. The effects of polymers of this group upon the MST and viscosity were found to be similar to those of the polymers of group MAA and group MAA/MA(80:20). But the abilities of these polymers to enhance the MST were found to be greater those of the polymers of groups MAA and MAA/MA(80:20).

As regards the effects of these polymers upon viscosity, they were found to be more effective in enhancing the viscosity of NR latex than were the polymers of group MAA/MA(80:20). Furthermore, in general, these polymers were as effective as polymers of group MAA in enhancing the viscosity of NR latex. The abilities of branched polymers of this group to enhance the viscosity were found to be higher than those of the branched polymers of group MAA at high levels of addition.

6.2.4 Effects of polymers of group MAA/EHA(80:20)

The effects of various levels of added polymers of group MAA/EHA(80:20) upon the MST and viscosity of NR latex (Batch 1) are shown in Figs. 6.8 and 6.9 respectively. The of polymers of this group brought about much greater enhancements of MST than the polymers of groups MAA, MAA/MA(80:20) and MAA/MA(60:40), but similar enhancements of viscosity. However, the relationship between the molecular weight of the linear polymers of this group were found to be different from that observed for the

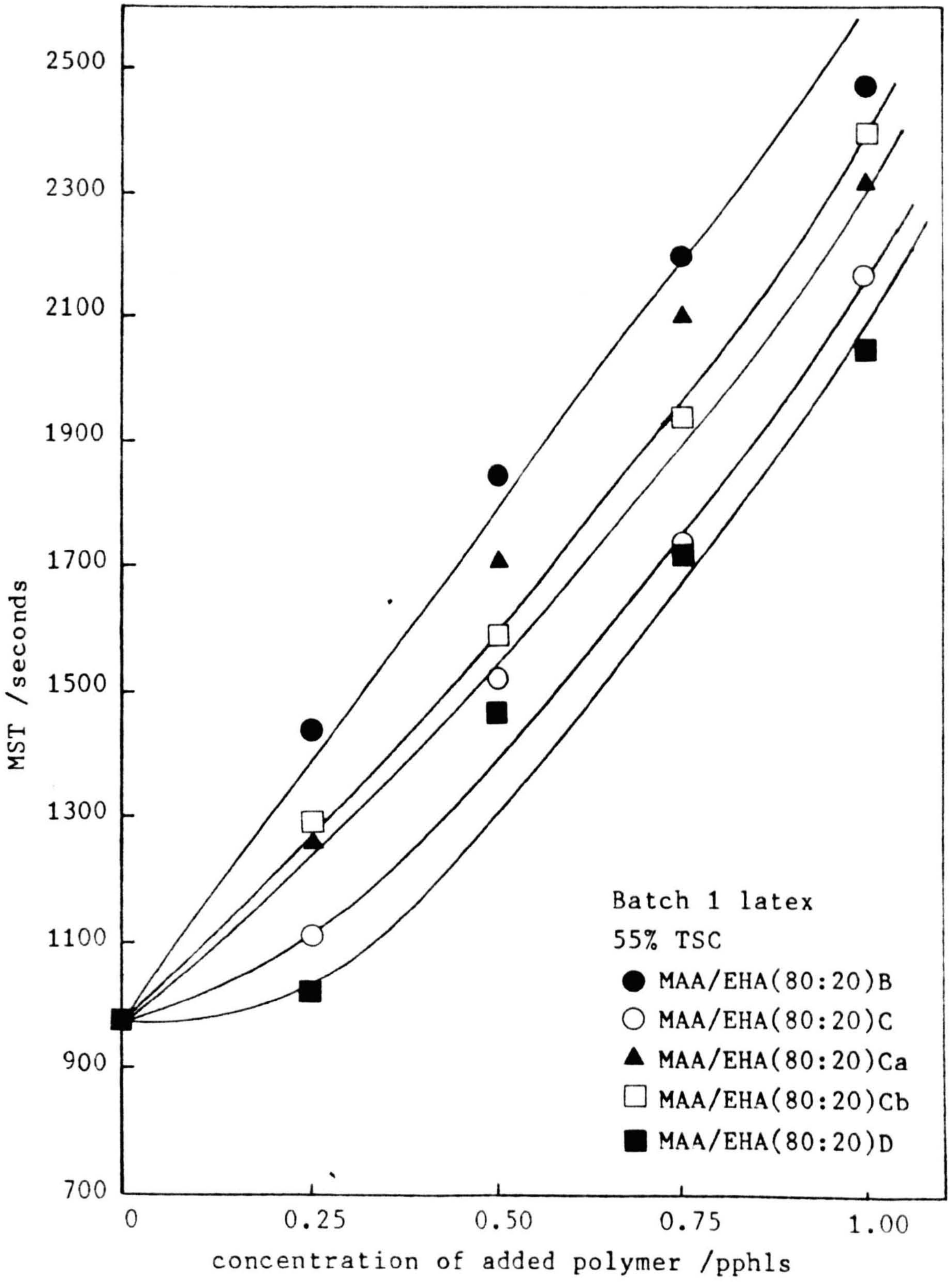


Fig. 6.8 : Effects of polymers of Type 1 group MAA/EHA(80:20) upon MST of NR latex

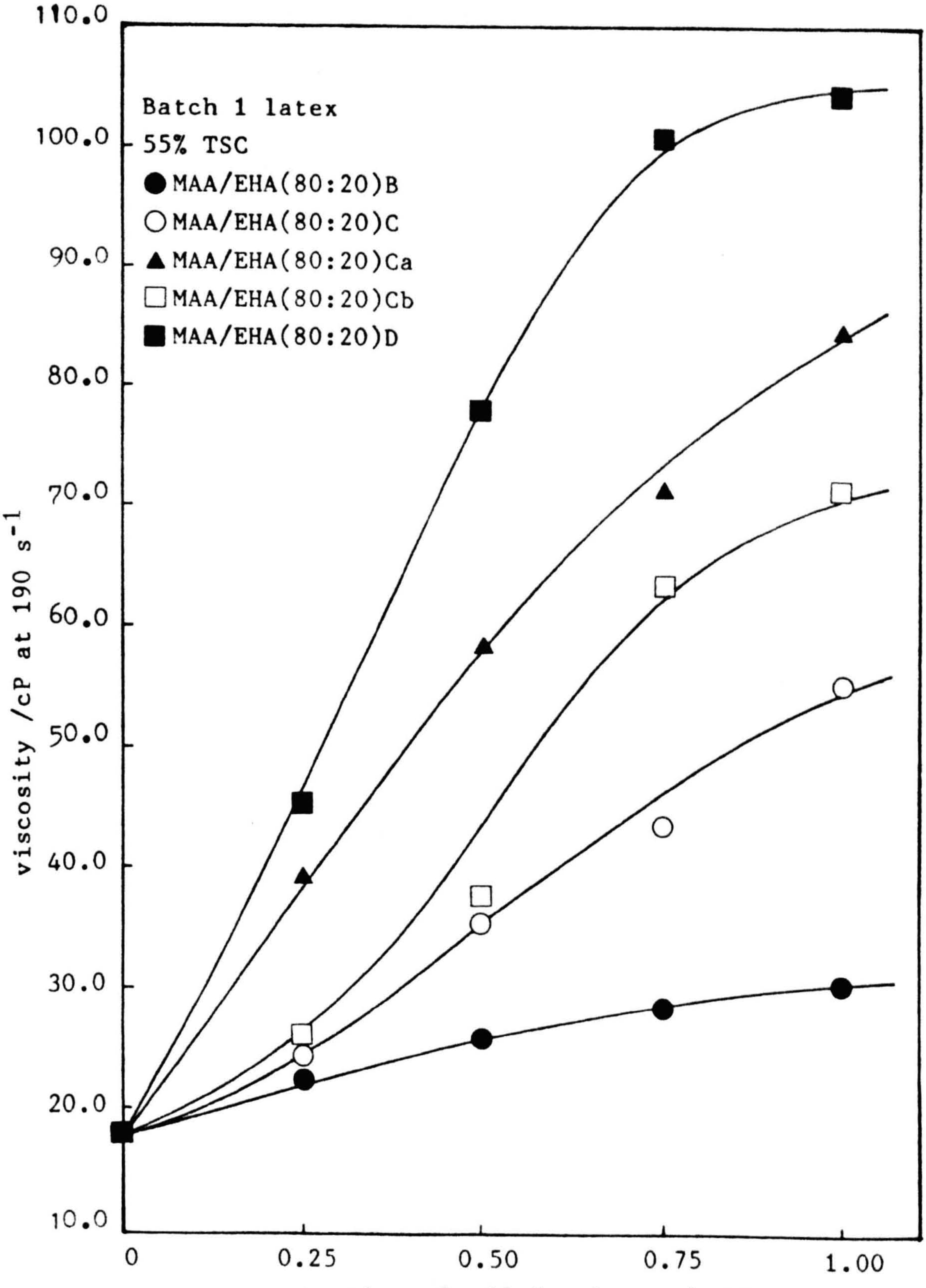


Fig. 6.9 : Effects of polymers of Type 1 group MAA/EHA(80:20) upon viscosity of NR latex

polymers of all the other groups investigated. Amongst the linear polymers investigated, the polymer of highest molecular weight brought about the least enhancement of MST, whilst the polymer of lowest molecular weight brought about the greatest enhancement of MST within the group. The efficiency of branched polymers in enhancing the MST was found to be higher than that of the linear polymer of highest molecular weight, but this efficiency was found to be decreased with increasing degree of branching.

The effects of linear polymers upon the viscosity of NR latex were found to be similar to those of the polymers of group MAA, group MAA/MA(80:20), and group MAA/MA(60:40). The branched polymers also enhanced the viscosity of the latex, but unlike all the other cases, the extent of the enhancement of viscosity decreased with increasing the degree of branching.

In view of the unexpected results obtained for the relationship between the molecular weight of the added polymers of group MAA/EHA(80:20) and its influence upon the enhancement of MST, it was thought that further experiments with polymers of same composition but of different molecular weights should be carried out. This further set of experiments was carried out using two linear polymers namely, MAA/EHA(80:20)A and MAA/EHA(80:20)E both of the same nominal composition but of different molecular weights. Their effects upon the MST and viscosity of NR latex (Batch 1) were investigated at the 0.50 pphls level of addition. The results of these further experiments, together with the results of effects of other linear polymers of the same group at the same level of addition are given in Table 6.1. The polymer of lowest molecular weight, i.e., MAA/EHA(80:20)A, brought about the highest enhancement of MST, whilst the polymer of highest molecular weight, i.e., MAA/EHA(80:20)E, brought about the lowest enhancement of MST. Indeed, the polymer MAA/EHA(80:20)E had virtually no significant effect upon MST.

polymer	intrinsic viscosity of polymer/(dlg^{-1})	MST/s	viscosity/cP
MAA/EHA(80:20)A	0.102	1920	18.69
MAA/EHA(80:20)B	0.122	1845	26.02
MAA/EHA(80:20)C	0.168	1520	35.77
MAA/EHA(80:20)D	0.242	1476	78.07
MAA/EHA(80:20)E	0.251	1040	94.31

Table 6.1: Effects of linear polymers of group MAA/EHA(80:20) upon MST and viscosity of NR latex at the 0.50 pphls levels of addition

MST of unmodified latex = 975 seconds
viscosity of unmodified latex = 17.89 cP

The effects of these polymers upon the viscosity of NR latex were found to be similar to those of all the other polymers investigated thus far.

6.2.5 Effects of polymers of group MAA/EHA(70:30)

The effects of various levels of added polymers of group MAA/EHA(70:30) upon the MST and viscosity of NR latex (Batch 2) are shown in Figs. 6.10 and 6.11 respectively. The investigation of the effects of these polymers were confined to linear polymers because of the complexity of the results of branched polymers of group MAA/EHA(80:20) and group MAA/EHA(60:40).

Both linear polymers enhanced the MST of latex at all the levels investigated, but the efficiency of the polymer of high molecular weight in enhancing the MST was found to be much greater than that of the polymer of low molecular weight. The MST of latex samples containing the polymer of high molecular weight was found to be unmeasurably high at high levels of addition.

As regards the effects of these polymers upon viscosity of latex, both polymers were found to increase the viscosity, the efficiency of the polymer of high molecular weight being very much greater than that of the polymer of low molecular weight.

6.2.6 Effects of polymers of group MAA/EHA(60:40)

The effects of various levels of added polymers of group MAA/EHA(60:40) upon the MST and viscosity of NR

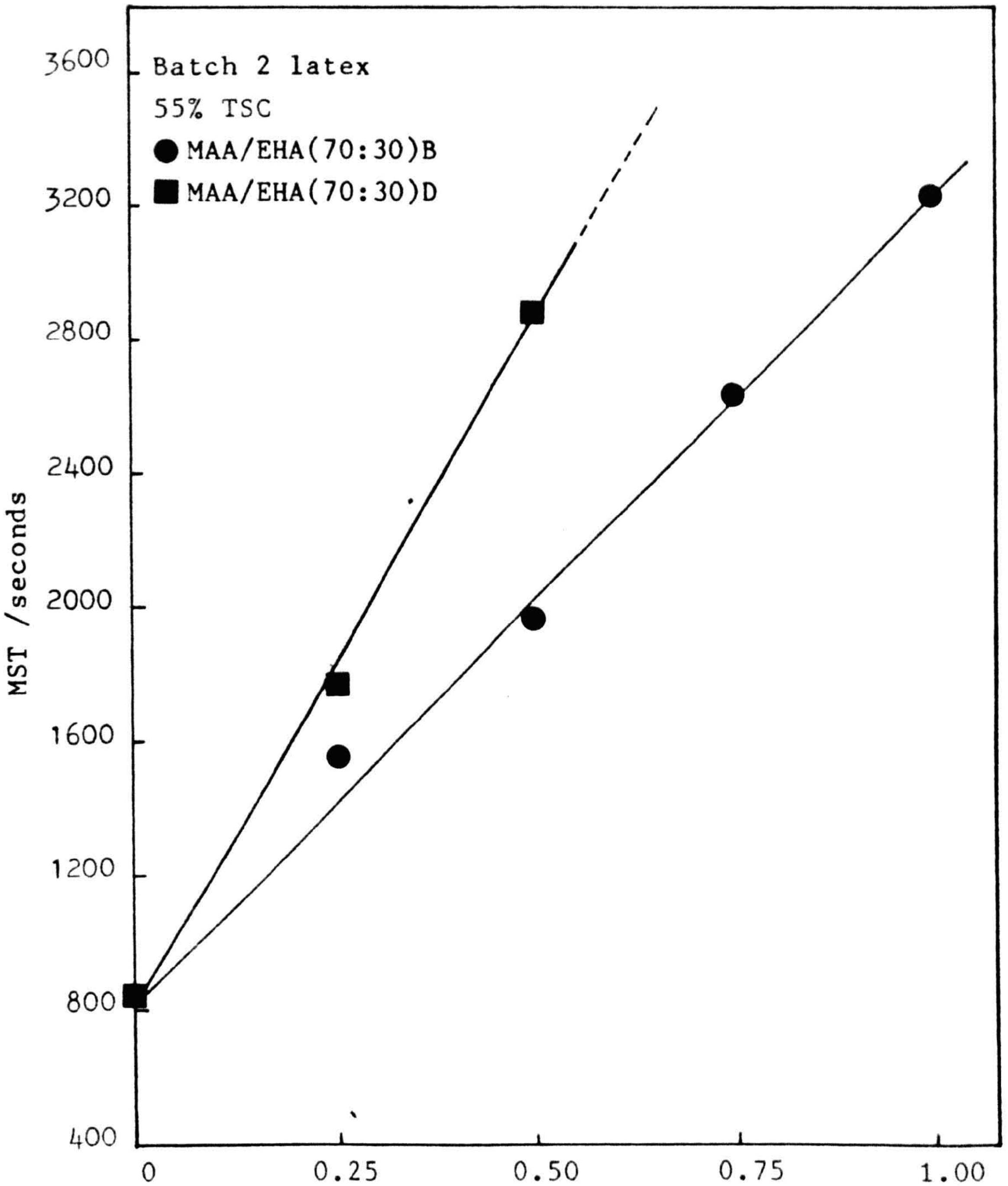


Fig. 6.10 : Effects of polymers of Type 1 group MAA/EHA(70:30) upon MST of NR latex

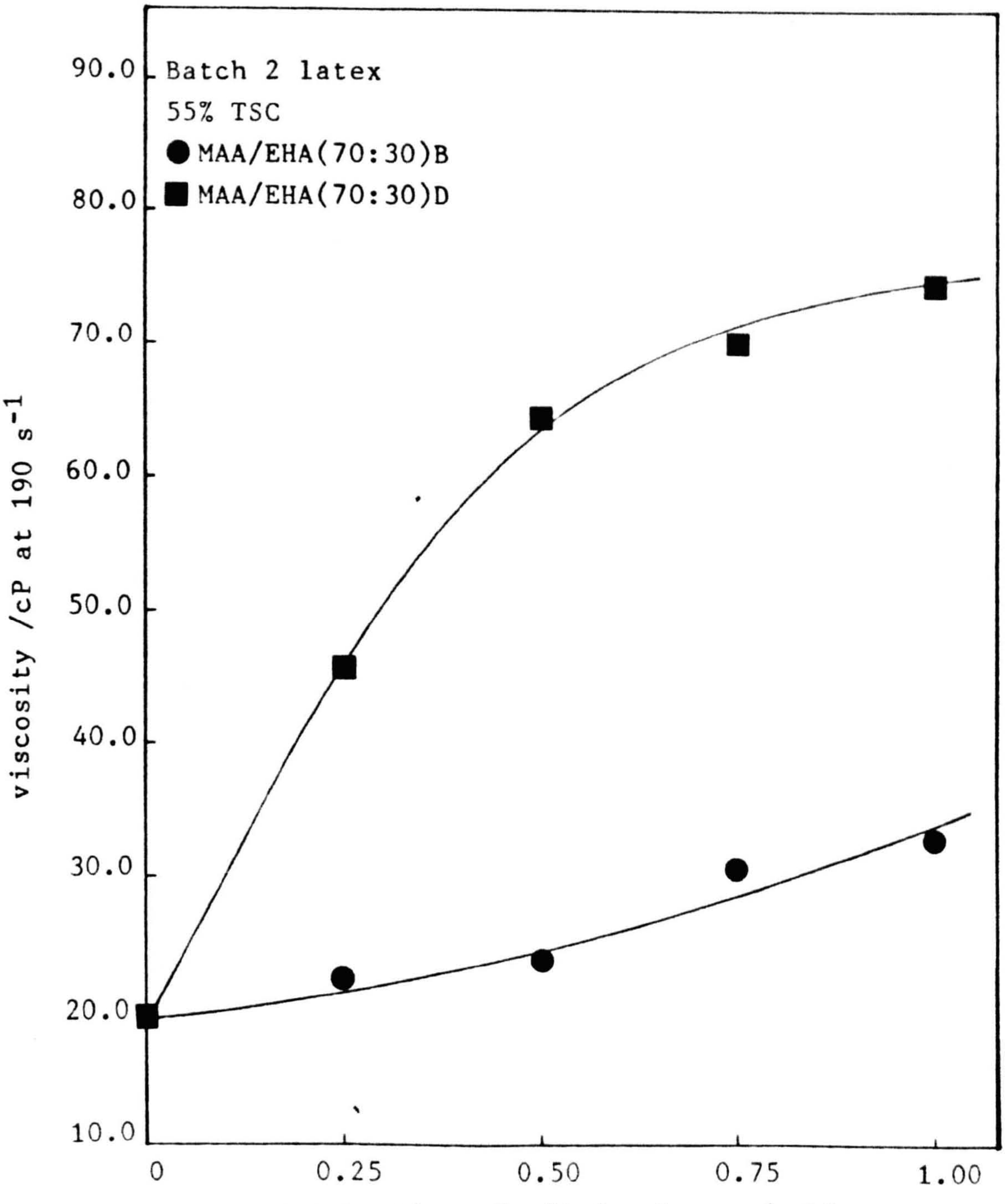


Fig. 6.11 : Effects of polymers of Type 1 group MAA/EHA(70:30) upon viscosity of NR latex

latex are shown in Figs. 6.12 and 6.13 respectively. All the polymers of this group brought about considerable enhancements of MST but, again, the extent of the enhancement depended upon the molecular weight of the polymer. The greatest enhancement of MST was brought about by the linear polymer of highest molecular weight, and the MST of latex sample containing this polymer was found to be unmeasurably high at high levels of addition. The efficiency of branched polymers in enhancing the MST were found to be less than that of the linear polymers of high molecular weight, and the extent of the enhancement of MST was found to increase with increasing degree of branching.

The effects of polymers of this group upon the viscosity of NR latex were found to be relatively less marked than those of those of the polymers described in the preceding sections. The branched polymers were found to be more effective in enhancing the viscosity of NR latex than all the linear polymers of the group, and their efficiency in enhancing the viscosity was found to be increased with increasing degree of branching.

6.2.7 Effects of polymers of group MAA/EHA(50:50)

The effects of various levels of added polymers of group MAA/EHA(50:50) upon the MST and viscosity of NR latex are shown in Figs. 6.14 and 6.15 respectively. The investigation of the effects of polymers of this group was

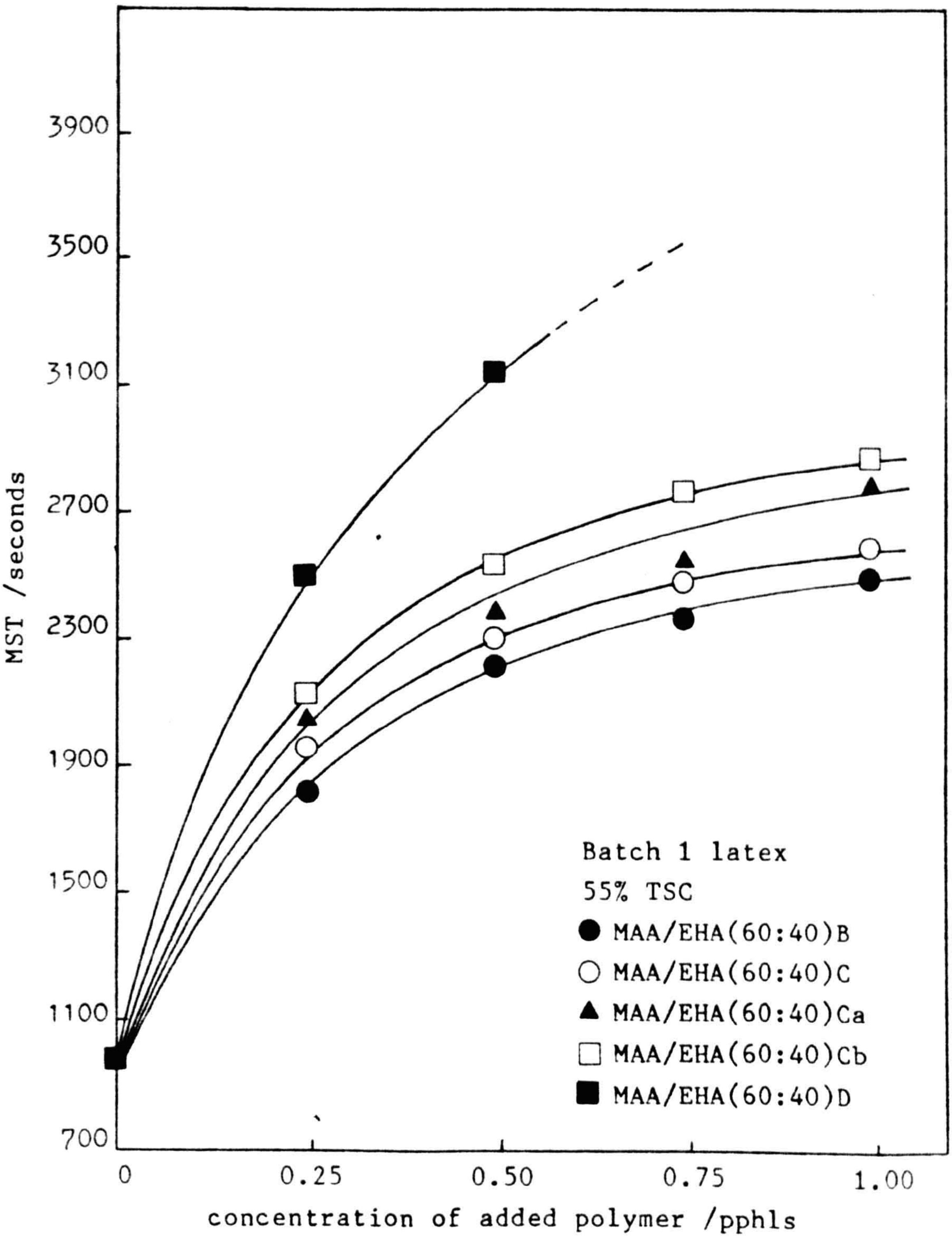


Fig. 6.12 : Effects of polymers of Type 1 group MAA/EHA(60:40) upon MST of NR latex

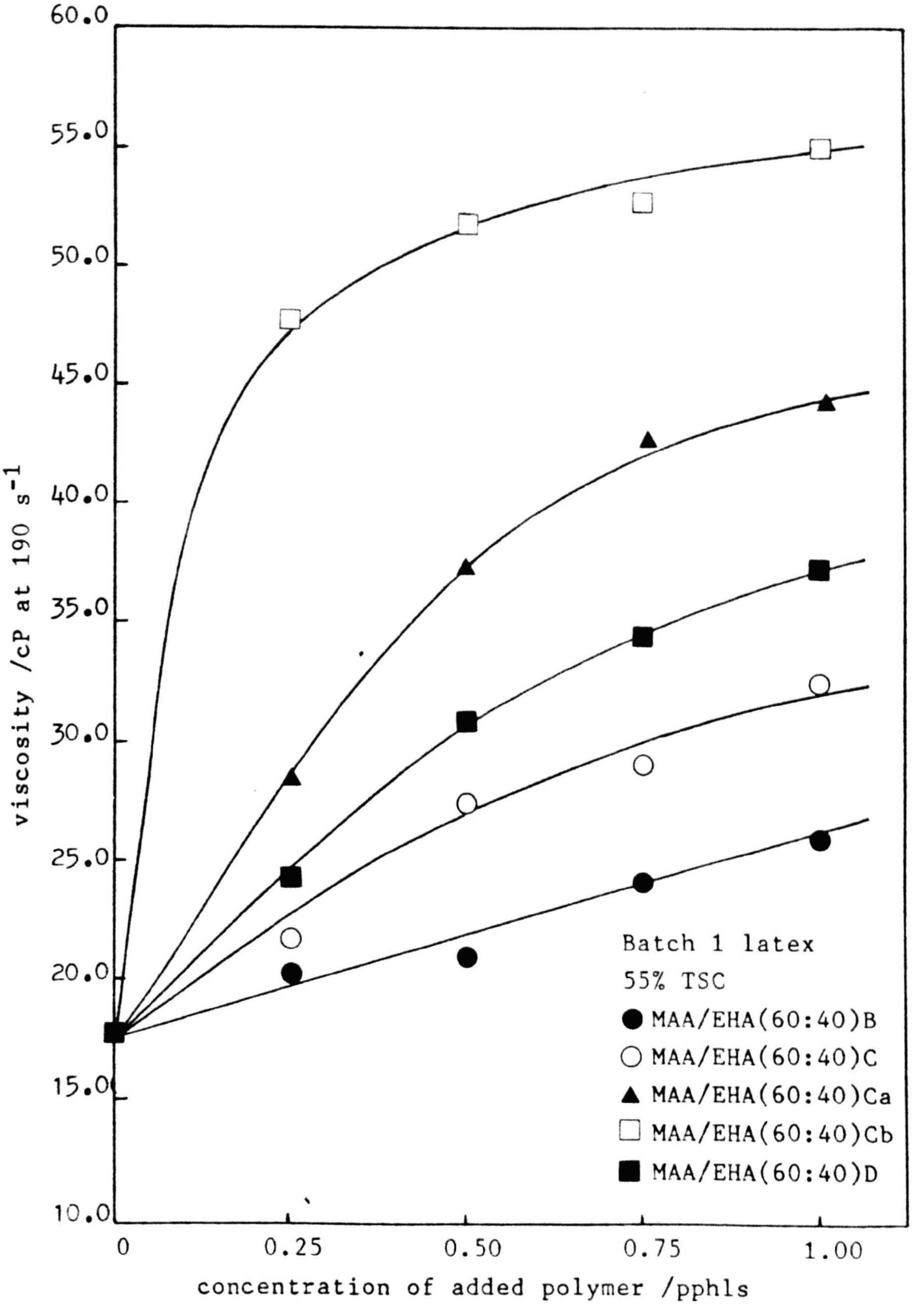


Fig. 6.13 : Effects of polymers of Type 1 group MAA/EHA(60:40) upon viscosity of NR latex

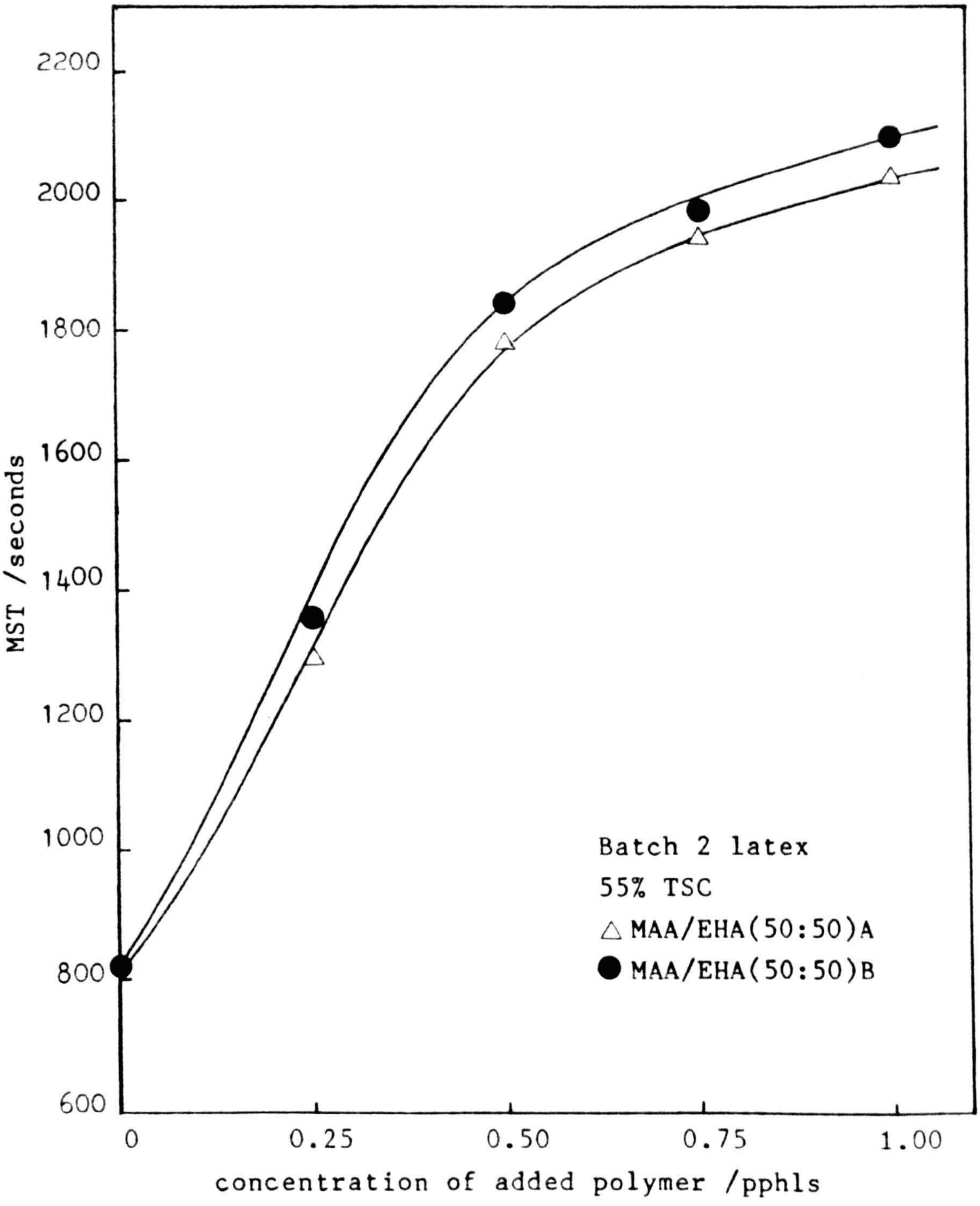


Fig. 6.14 : Effects of polymers of Type 1 group MAA/EHA(50:50) upon MST of NR latex

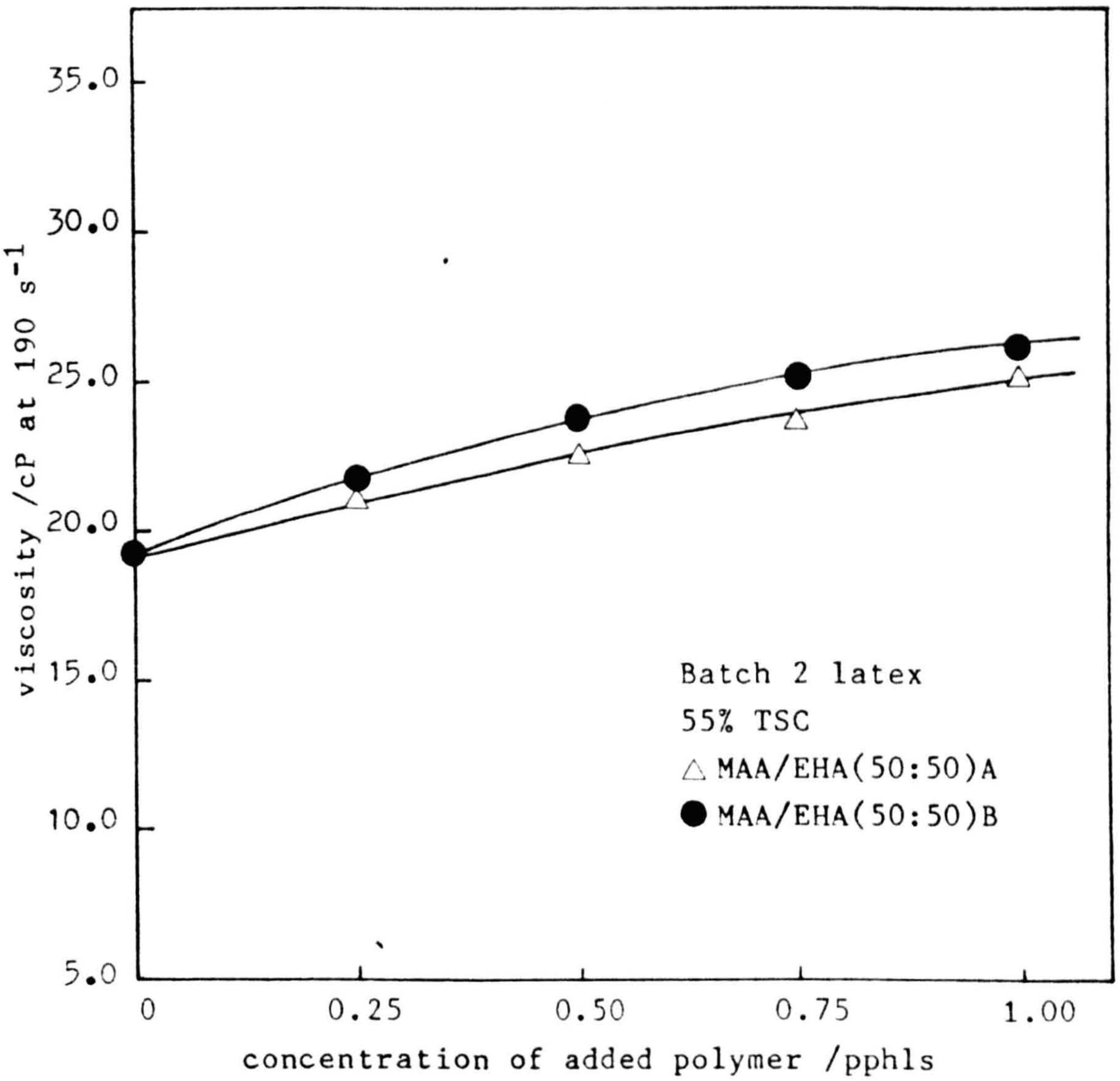


Fig. 6.15 : Effects of polymers of Type 1 group MAA/EHA(50:50) upon viscosity of NR latex

confined to linear polymers again for the same reason as has been given in Section 6.2.5. The efficiencies of both polymers in enhancing the MST and viscosity of NR latex were found to be relatively small. Amongst all the groups of polymers of Type 1 investigated the polymers of this group were found to be the least effective in enhancing viscosity. The dependence of the extent of the enhancement of both MST and viscosity upon the molecular weight of the polymer was found to be insignificant.

6.3 Discussion of the effects of various characteristics of the polymers of Type 1 upon mechanical stability and viscosity of NR latex

It is apparent from the results presented in the preceding sections that the MST and viscosity of NR latex can be enhanced by the addition of various polymers, and that the extent of the enhancement of both MST and viscosity is dependent upon characteristics of the polymer such as molecular weight, degree of branching, composition, and composition distribution. In this section the correlations between the characteristics of the polymer and the influence of the polymer upon the MST and viscosity of the latex are discussed.

6.3.1 Effects of molecular weight

All the polymers of Type 1 investigated were found to enhance both the MST and the viscosity of NR latex although in some cases the enhancements were small. In almost all cases, the ability of the added polymer to enhance MST and viscosity was found to increase as the molecular weight of the polymer increased. This observation suggests that the ability of an added polymer to enhance MST and viscosity is dependent upon its tendency to be adsorbed at the rubber/water interface.

As shown in the literature review, several workers have reported that the adsorption of an added polymer at the solid/liquid interface increases as its molecular weight is increased. Therefore the observed increase in efficiency of added polymer in enhancing MST with increasing molecular weight may be due in part to the increased tendency to be adsorbed at the rubber/water interface. The opposite pattern of behaviour observed with the polymers of group MAA/EHA(80:20) may be due to the variation in composition of the polymer with increasing molecular weight, as revealed by IR analysis of the polymers. Although, a similar variation in composition was also observed for the polymers of other groups, it appears that the polymers of high molecular weight in these groups may still have sufficient hydrophobic monomer units to facilitate adequate anchoring of the polymer on to the particle surface.

As regards the effects of the molecular weight of the added polymer upon its ability to enhance viscosity, it is reasonable to suppose that an added polymer can enhance the viscosity of NR latex at least three possible ways.

1. The polymer may dissolve in the dispersion medium, and thereby increase the viscosity of the dispersion medium, and hence the viscosity of the latex.
2. The polymer chains may become adsorbed at the surface of the latex particles, and may promote the bridging of the latex particles as illustrated in Fig. 6.16, and thereby increase the viscosity of the latex. But in this case one would expect the latex to develop a "structure" and for the viscosity to become shear-dependent.

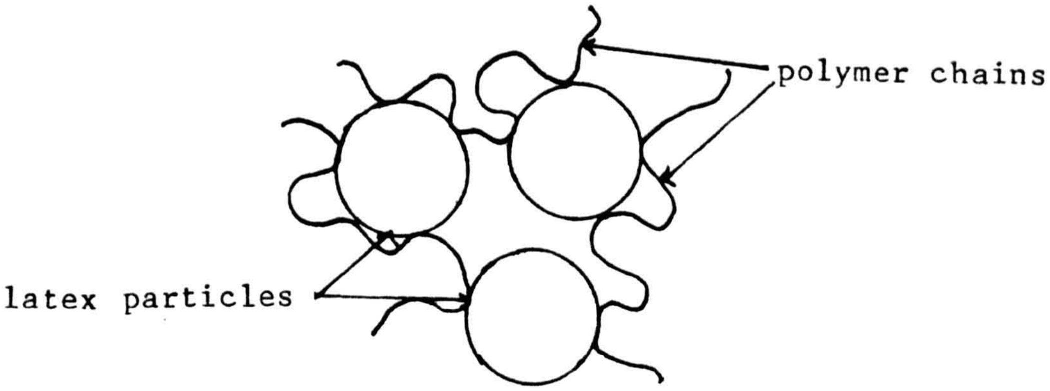


Fig. 6.16: Schematic representation of bridging of latex particles by added polymer chains

3. The polymer may become adsorbed at the surface of the latex particles without promoting interparticle

bridging, but with consequent increase in the thickness of the hydration layer and hence in the effective hydrodynamic size of the particles.

It is reasonable to expect that the contribution to viscosity of latex by each of these factors increases as the molecular weight of the polymer is increased.

6.3.2 Effects of degree of branching

In almost all cases, the branched polymers were found to be less effective than the corresponding linear polymers of high molecular weight, in enhancing the MST of NR latex. This may be a consequence of the differences in the degree of extension of these two types of polymers into the dispersion medium. As shown in Fig. 6.17 the degree of extension of branched polymers is lower than that of linear

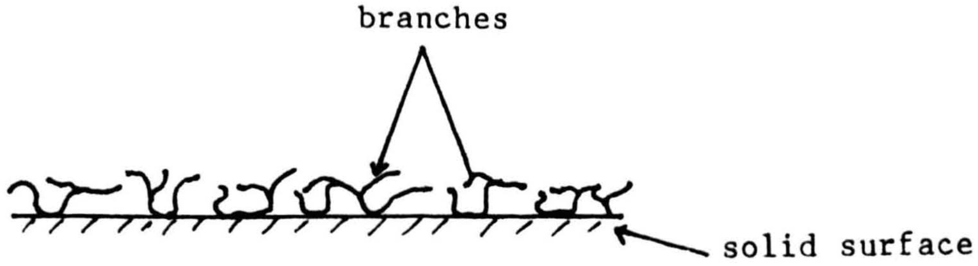


Fig. 6.17 : Schematic representation of the conformation of a branched polymer at the rubber/water interface

polymers of similar molecular weight. On this basis it would be expected that the efficiency of branched polymers in enhancing the MST would decrease as the degree of branching and the hydrophobicity of the polymer are increased.

That the opposite pattern of behaviour is observed for the branched polymers of groups MAA, MAA/MA(80:20) and MAA/MA(60:40) is not surprising, because of the weak hydrophobicity of the hydrophobic units in their polymer chains. In these groups, polymers of high degree of branching were more effective in enhancing the MST than the corresponding polymers of low degree of branching, possibly because of the higher adsorption tendency of the former at the rubber/water interface due to their relatively high molecular weight. Therefore in these cases it is not possible to distinguish the effects arising from branching itself and those arising from the concomitant increase in the molecular weight. The branched polymers of group MAA/EHA(80:20) were found to enhance the MST of latex in the expected order. However, the branched polymers of group MAA/EHA(60:40) were found to enhance the MST of latex in the opposite order. It appears, for the polymers of the group MAA/EHA(60:40), the effect of the molecular weight of the polymer in determining the extent of the enhancement of MST outweighs that of the degree of branching.

As regards the effects upon viscosity, the results of the effects of polymers of groups MAA, MAA/MA(80:20) and MAA/MA(60:40) indicate that the branched polymers are more effective in enhancing the viscosity of NR latex than are the corresponding linear polymers of low molecular weight, and that the efficiency of branched polymers in enhancing the viscosity increases with increasing the degree of branching. But, again, it is not clear whether these effects are due to the branching itself or due to the concomitant increase in molecular weight. The efficiencies of branched polymers of group MAA/EHA(80:20) in enhancing the viscosity of NR latex were found to be decreased with increasing degree of branching. This might be a consequence of the decrease in the degree of extension of the polymer molecules into the dispersion medium with increasing degree of branching. Unlike the branched polymers of all the other groups investigated, the branched polymers of the group MAA/EHA(60:40) were more effective in enhancing the viscosity of NR latex than were the corresponding linear polymer of highest molecular weight. Furthermore, the polymer of high degree of branching was found to be more effective in enhancing the viscosity of latex than was the corresponding polymer of low degree of branching. It is not clear from these results what factors are responsible for this behaviour.

6.3.3 Effects of composition

It is apparent from the results for the effects of polymers of various composition upon the MST of latex that the efficiency of an added polymer in enhancing the MST depends very much upon its composition. Polymethacrylic acids are less effective in enhancing the MST than are the copolymers of MAA and EHA. This might be a consequence of the relatively weak adsorption tendency of the former. It is interesting to examine how the ability of an added polymer to enhance MST varies with the EHA content of the polymer. This is illustrated in Fig. 6.18, which shows the effects of mole percentage of EHA in the added polymer upon its ability to influence the MST of NR latex at various levels of addition. In this comparison, the effects of the polymers of lowest molecular weight in each group upon the MST were considered. The effects upon the MST are expressed in terms of "mechanical stability ratio", this being defined as the ratio of the MST in the presence of added polymer to the MST of same batch of latex without added polymers. As shown in Fig.6.18, at any given level of addition, as the mole percentage of EHA in the added polymer is increased, the enhancement of MST rises to a maximum and then falls with further increase in EHA content. It appears that, at any given level of addition, the polymer MAA/EHA(70:30)B is the most effective enhancer of MST of NR latex amongst the polymers of low molecular weight investigated. This observation is consistent with the hypothesis that an effective steric stabiliser must contain sufficient hydrophobic units to anchor the polymer on to the particle surfaces, and sufficient hydrophilic units to impart colloid stability by mixing with the dispersion medium. Fig. 6.18 also reveals that the efficiency of the polymer MAA/EHA(70:30)B in enhancing the MST of NR latex relative to the other polymers increases as the level of addition is increased.

The effects of composition of the added polymer upon its ability to enhance the viscosity of NR latex are also interesting. In Fig. 6.19 the effects of the mole percentage of EHA in the added polymer upon its ability to influence the viscosity of NR latex are shown. Again the results for the polymers of lowest molecular weight in each group were considered for this comparison. It appears, that as the EHA content of the polymer is increased, the extent of the enhancement of viscosity decreases. This might be a consequence of decrease in both the solubility of the polymer in the dispersion medium and the effective hydrodynamic size of the particles containing adsorbed polymers with increasing the EHA content of the added polymer. The marked ability of polymethacrylic acid to enhance the viscosity of latex indicates that the enhancement of viscosity of latex is mainly due to increase in the viscosity of the dispersion medium. The relatively poor abilities of MAA/EHA copolymers to enhance the viscosity of NR latex indicate that the adsorption of

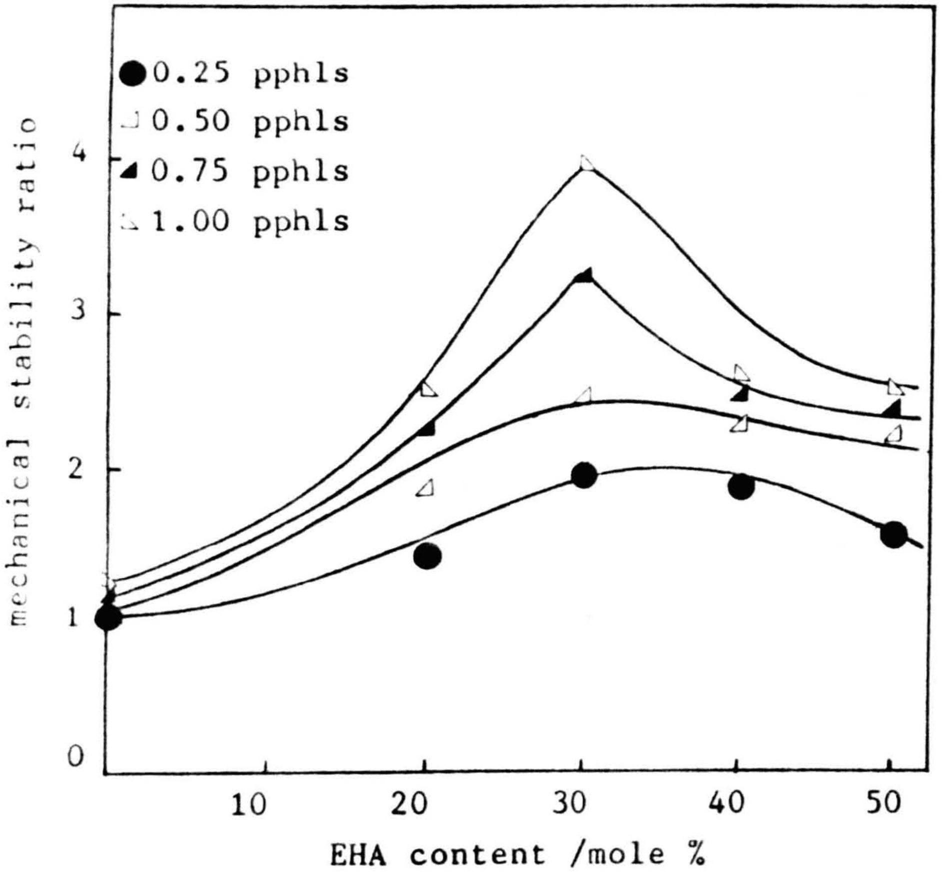


Fig. 6.18 : **Effects of EHA content of added polymer upon enhancement of MST of NR latex at various levels of addition**

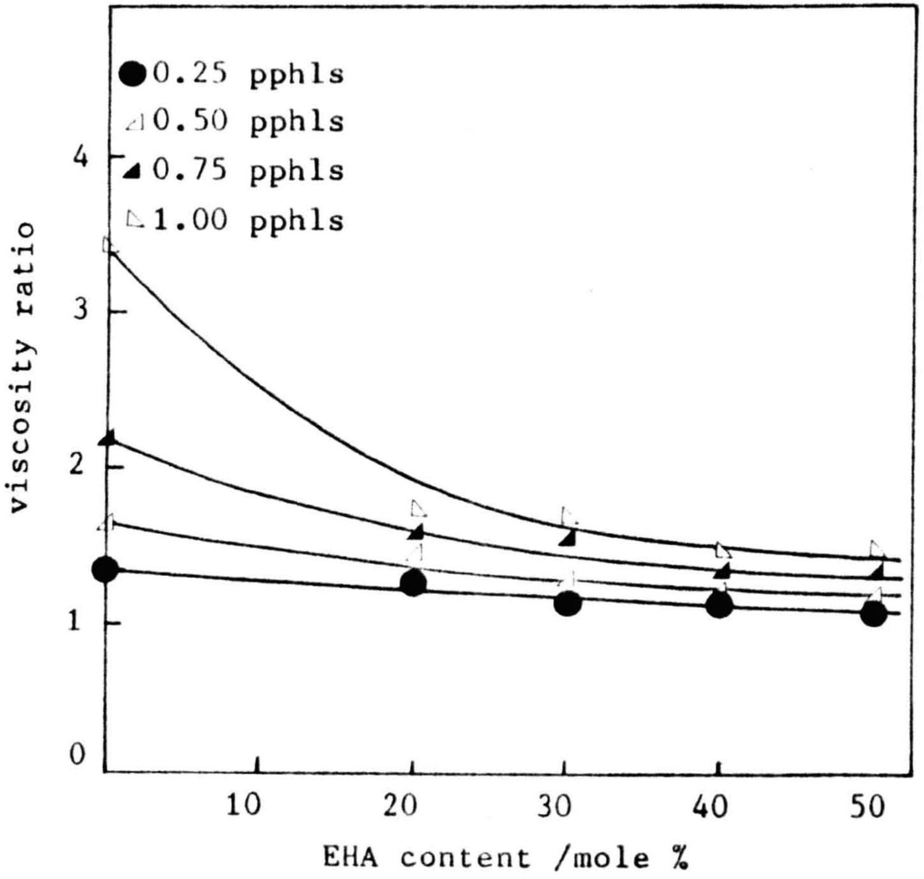


Fig. 6.19 : **Effects of EHA content of adde polymer upon enhancement of viscosity of NR latex at various level of addition**

polymer at the particle surfaces may reduce the extent to which viscosity is enhanced.

6.3.4 Effects of composition distribution

It is reasonable to expect that the composition distribution of an added polymer also affects its ability to influence the MST and viscosity of NR latex. The adsorption tendencies of polymer molecules of a polymer with a narrow compositional distribution would be expected to be uniform, whereas, those of polymer molecules of a polymer with a wide compositional distribution would not be expected to be uniform. Therefore the effects of a polymer with a wide compositional distribution would not necessarily demonstrate effects related to the overall composition of the polymer. So it is interesting to examine how the compositional distribution of a polymer of Type 1 varies with the feed composition. The predicted variation, of f_1, the mole fraction of unreacted MAA in the reaction mixture, with conversion for different feed compositions is shown in Fig. 6.20. These calculations were performed according to the procedure given in Section 5.10 and assuming that $r_1=1.31$ and $r_2=0.35$. It is apparent from these curves, that depending upon the feed composition, the compositional distribution of a polymer varies. The possible effects of compositional distribution of the added polymer upon the extent of the enhancement of MST and viscosity of NR latex will be

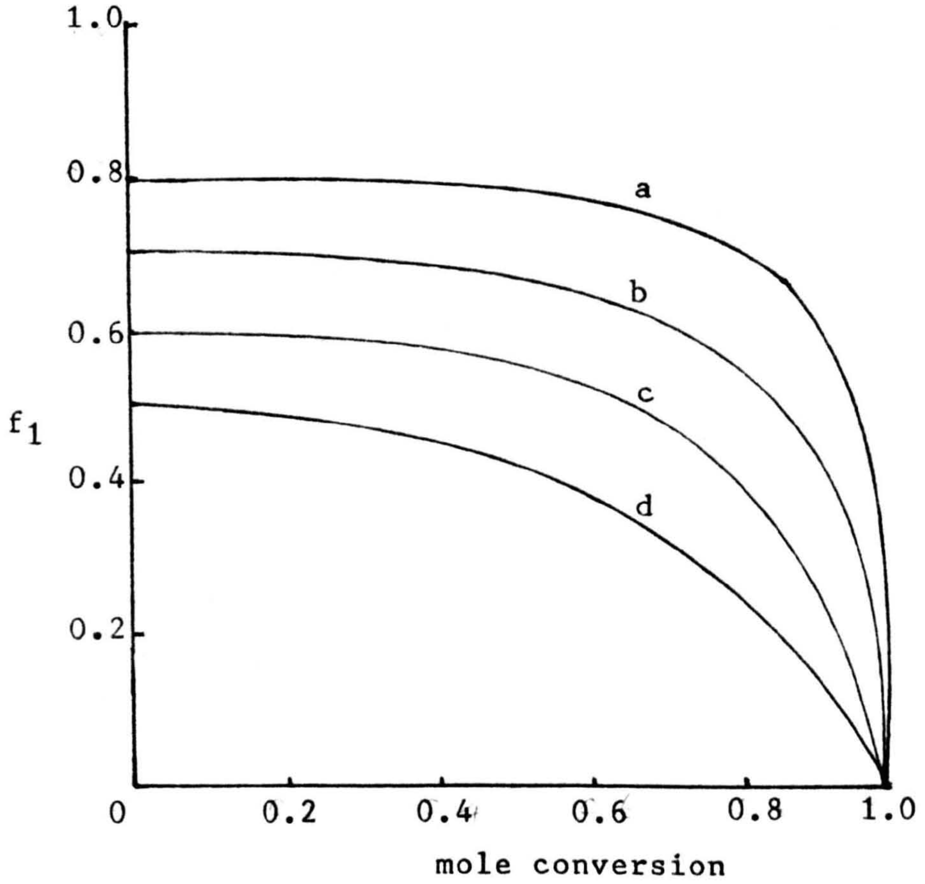


Fig. 6.20 : Predicted variation of f_1, with mole conversion for copolymerisation of MAA and EHA of different feed compositions assuming r_1=1.31 and r_2=0.35

a - $(f_1)_0$ = 0.80 b - $(f_1)_0$ = 0.70

c - $(f_1)_0$ = 0.60 d - $(f_1)_0$ = 0.50

discussed after the results for the effects of polymers of Type 2 upon the MST and viscosity of NR latex have been presented.

6.3.4 Effects of nature of anchor group

It is apparent from the results for the effects of added polymers upon MST and viscosity of NR latex that the ability of the added polymer to influence MST and viscosity also depends upon the nature of the anchor groups of the added polymer. The ability of the added polymer to enhance the MST increased remarkably as the MA anchor groups were replaced by EHA groups. This is surely a consequence of the increase in the adsorption tendency of the added polymer at the rubber/water interface due to the higher hydrophobicity of EHA groups when compare with that of MA groups. The ability of the added polymer to enhance MST of NR latex does not vary appreciably when the mole percentage of MA groups in the polymer increased from 20% to 40%. On the other hand the ability of the added polymer to enhance the MST dependent markedly upon the mole percentage of EHA in the polymer, see Fig.6.18. This observation shows the importance of the nature of the anchor groups in determining the ability of the added polymer to modify the properties of NR latex

6.4 Results for effects of polymers of Type 1 upon chemical stability of NR latex

The purpose of conducting these experiments was to ascertain if the effects of polymers upon the MST of NR latex are paralleled by similar effects upon the chemical stability of NR latex. Two groups of polymers, namely, group MAA/EHA(80:20) and group MAA/EHA(60:40) were chosen for these experiments. The group MAA/EHA(80:20) was selected because the correlation between the molecular weight of the polymers of this group and its ability to enhance MST was found to be different from that of the polymers of all the other groups investigated. The group MAA/EHA(60:40) was selected because of the marked efficiency of the polymers of this group to enhance the MST.

The results of the effects of added polymers of groups MAA/EHA(80:20) and MAA/EHA(60:40) upon the chemical stability of NR latex at the 0.50 pphls level of addition, as determined by measuring the MST of NR latex which had been destabilised by the addition of potassium chloride, are given in Table 6.2. As expected, the effects of these polymers upon the MST of latex were paralleled by similar effects upon the chemical stability of NR latex. Therefore a similar explanation is proposed for the results of the effects of these polymers upon the chemical stability of NR latex to that which has been proposed for the similar effects upon the MST of NR latex (see Section 6.3).

polymer	MST/s	MST/MST$_0$	MST/s	MST/MST$_0$
	(KCl present)		(KCl absent)	
MAA/EHA(80:20)B	1110	2.71	1845	1.89
MAA/EHA(80:20)C	780	1.90	1520	1.56
MAA/EHA(80:20)Ca	825	2.01	1710	1.75
MAA/EHA(80:20)Cb	765	1.87	1590	1.63
MAA/EHA(80:20)D	690	1.68	1476	1.51
MAA/EHA(60:40)B	960	2.34	2220	2.28
MAA/EHA(60:40)C	1130	2.75	2315	2.37
MAA/EHA(60:40)Ca	1160	2.83	2380	2.44
MAA/EHA(60:40)Cb	1485	3.62	2520	2.58
MAA/EHA(60:40)D	1560	3.80	3125	3.20

Table 6.2 : Effects of polymers of groups MAA/EHA(80:20) and MAA/EHA(60:40) upon MST of NR latex in the presence and abesnce of 1.00 part of potassium chloride per 100 parts of latex solids

MST of latex containing no added polymer = 410 s
(KCl present)

MST of latex containing no added polymer = 975 s
(KCl absent)

6.5 Results of effects of polymers of Type 1 upon zinc-oxide thickening of NR latex

The groups of polymers whose effects upon the MST of NR latex were found to be significant, namely, MAA/EHA(80:20), MAA/EHA(70:30), MAA/EHA(60:40) and MAA/EHA(50:50), were chosen for this investigation. The effects of the polymer of lowest molecular weight and the polymer of highest molecular weight in each group upon the zinc-oxide thickening of NR latex (Batch 2) were investigated at various levels of addition. The polymers of lowest molecular weight and the polymers of highest molecular weight will be referred to as the polymers of low molecular weight and the polymers of high molecular weight in the forthcoming sections, respectively. It should be noted that these definitions were given considering the relative values of intrinsic viscosities of the polymers. The effects of branched polymers of group MAA/EHA(80:20) and group MAA/EHA(60:40) were also investigated. In each case the rate of zinc-oxide thickening was observed over a period from 0 to 16 days.

6.5.1 Effects of polymers of low molecular weight

The effects of polymers of low molecular weight and various compositions upon the zinc-oxide thickening of NR latex at the 0.25 pphls level of addition are shown in Fig. 6.21. At the 0.25 level of addition, all the polymers

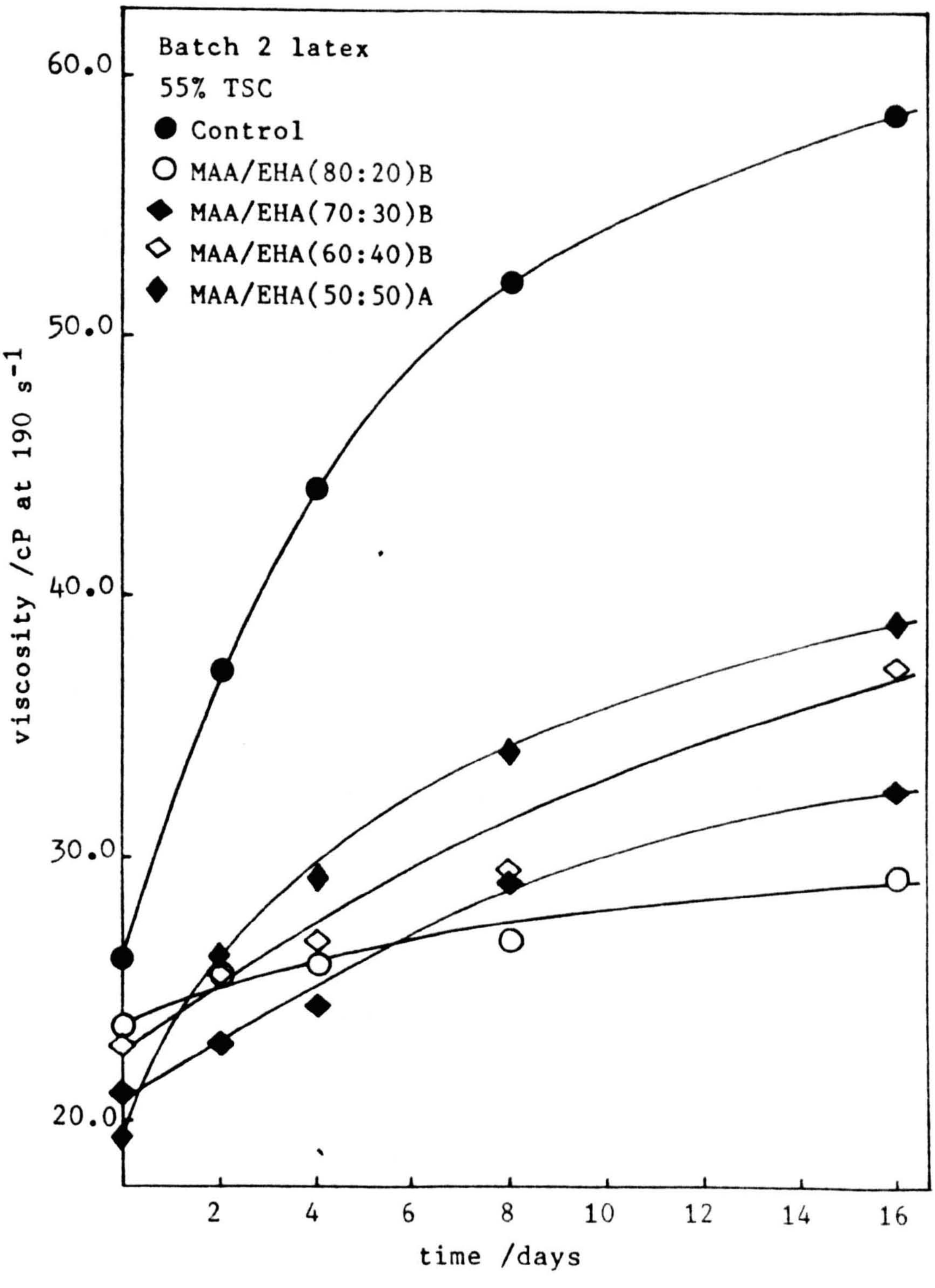


Fig. 6.21 : Effects of polymers of low molecular weight of Type 1 upon zinc-oxide thickening of NR latex at 0.25 pphls level of addition

of low molecular weight investigated retarded zinc-oxide thickening. Furthermore, the ability of the polymer to retard zinc-oxide thickening increased as the hydrophobicity of the polymer decreased.

The effects of the polymers upon the zinc-oxide thickening, at the 0.50 pphls levels of addition are shown in Fig. 6.22. The polymer MAA/EHA(50:50)A caused a marked acceleration of zinc-oxide thickening, whilst the other polymers caused the zinc-oxide thickening to be retarded. The latex compound containing polymer MAA/EHA(50:50)A was found to be gelled after 8 days. The effects of hydrophobicity of the polymer upon the rate of zinc-oxide thickening was found to be similar, but not identical, to that observed at the 0.25 pphls level of addition. The most hydrophilic polymer in the series, the polymer MAA/EHA(80:20)B, was less effective in retarding zinc-oxide thickening than was the polymer MAA/EHA(70:30)B.

The effects of polymers MAA/EHA(80:20)B and MAA/EHA(60:40)B upon the zinc-oxide thickening at the 0.75 pphls level of addition are shown in Fig. 6.23. The effects of polymer MAA/EHA(70:30)B were not investigated at this level of addition, as the difference between the rates of zinc-oxide thickening of the latex compound containing polymer MAA/EHA(80:20)B and that containing polymer MAA/EHA(70:30)B, at both 0.25 pphls and 0.50 pphls of addition was not found to be significantly large. The

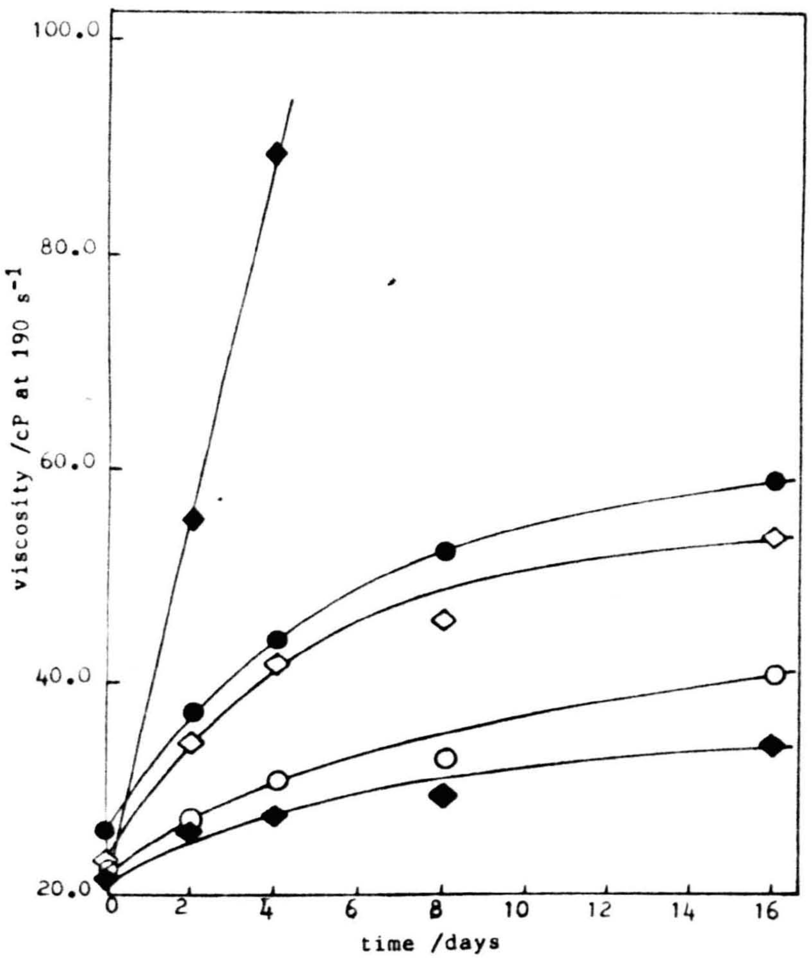


Fig. 6.22 : Effects of polymers of low molecular weight of Type 1 upon zinc-oxide thickening of NR latex at 0.50 pphls level of addition

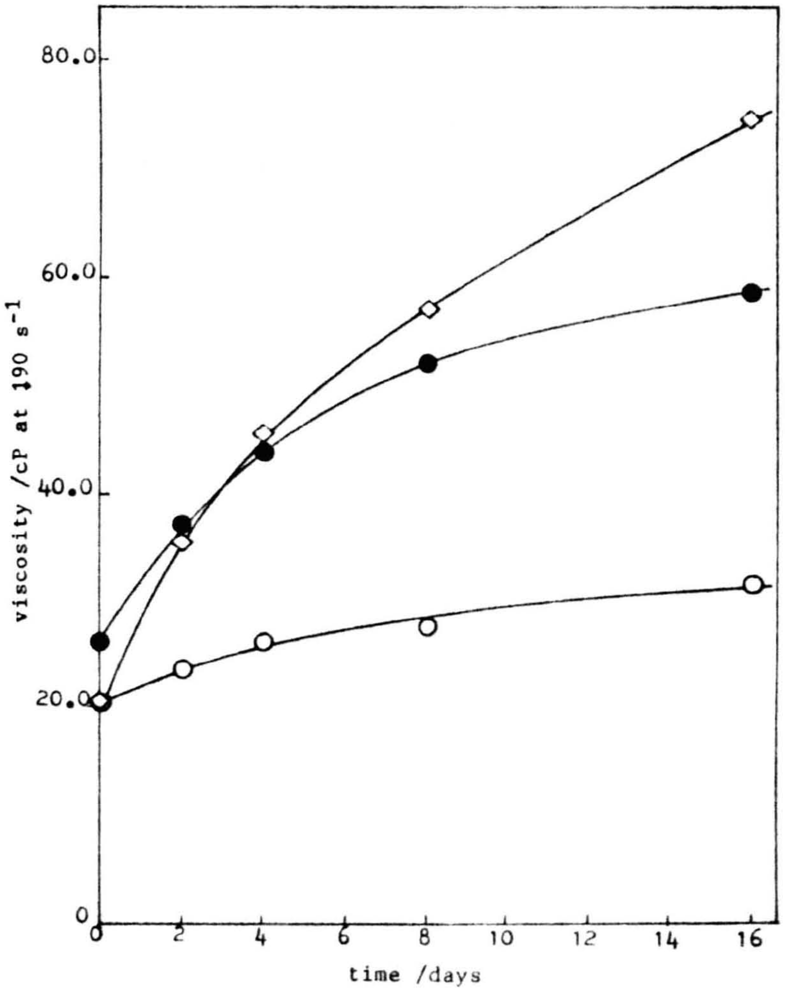


Fig. 6.23 : Effects of polymers of low molecular weight of Type 1 upon zinc-oxide thickening of NR latex at 0.75 pphls level of addition

latex compound containing polymer MAA/EHA(50:50)A was found to have gelled soon after compounding with zinc-oxide and ammonium acetate. The polymer MAA/EHA(60:40)B accelerated zinc-oxide thickening, whereas the polymer MAA/EHA(80:20)B retarded zinc-oxide thickening.

6.5.2 Effects of polymers of high molecular weight

The effects polymers of high molecular weight and various compositions upon the rate of zinc-oxide thickening of NR latex at various levels of addition are shown in Fig. 6.24 to 6.27. At the 0.50 pphls level of addition, the latex compound containing polymer MAA/EHA(80:20)D was found to be gelled. Therefore the effects of this polymer were investigated at levels of addition between 0.10 pphls and 0.40 pphls. The viscosities of the latex compounds containing various levels of polymer MAA/EHA(80:20)D and those containing polymer MAA/EHA(70:30)D were found to be much higher than that of the control compound before the maturation. So, it appeared that plots of variation of η/η_0 with time, where η_0 is the viscosity of latex compound before maturation, and η is the viscosity of latex compound after maturation, would be more suitable for comparison of the effects of polymers of high molecular weight upon the zinc-oxide thickening of NR latex. These plots are given in Figs. 6.28 to 6.31.

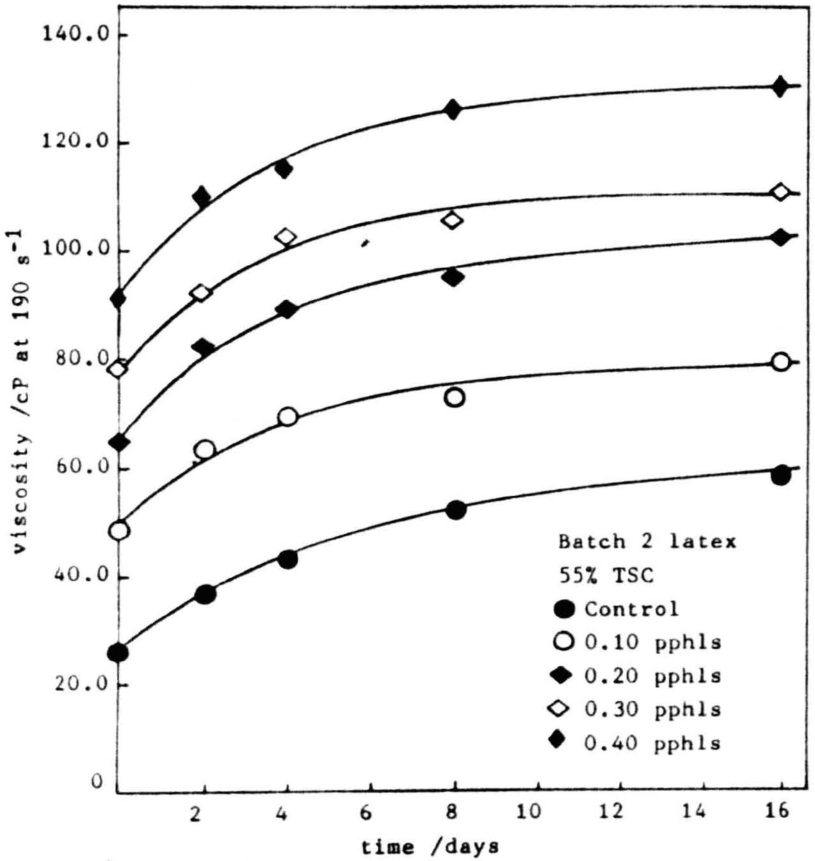


Fig. 6.24 : Effects of polymer MAA/EHA(80:20)D upon zinc-oxide thickening of NR latex at various levels of addition

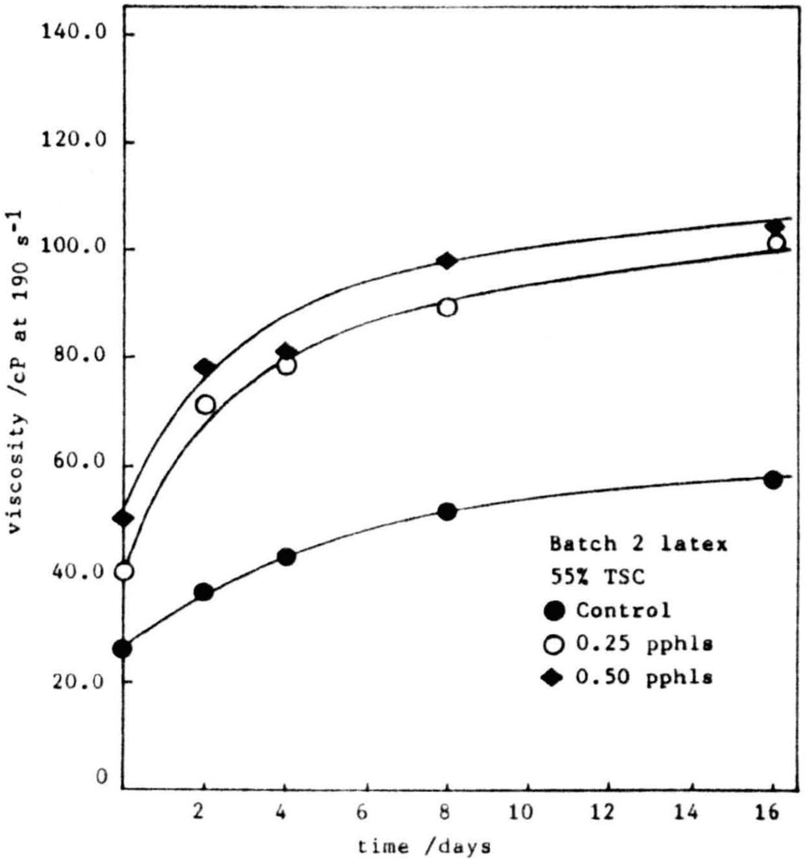
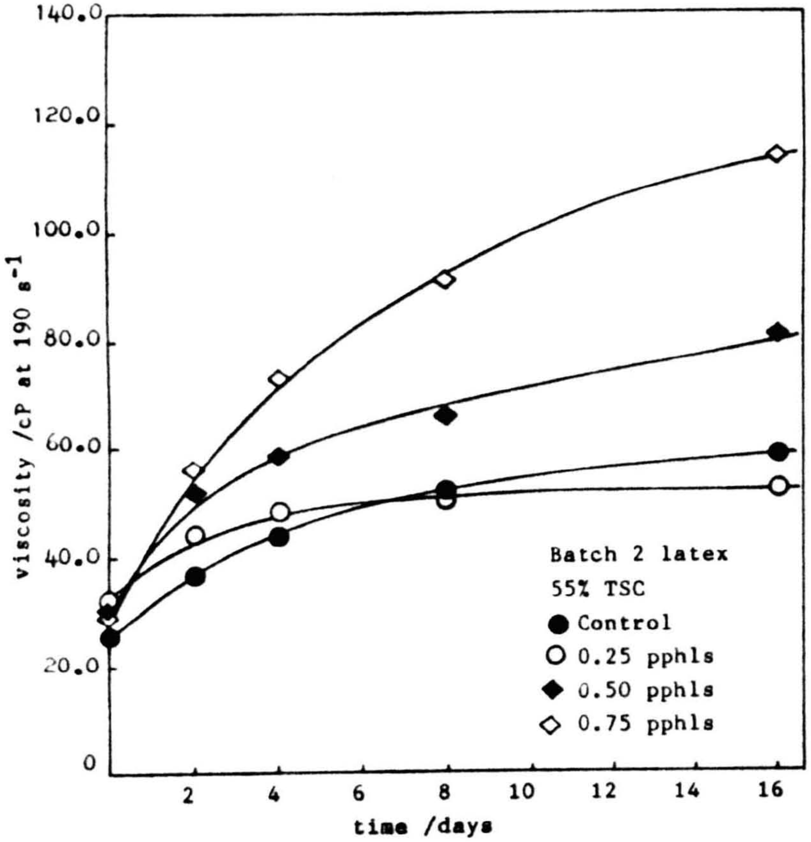


Fig. 6.25 : Effects of polymer MAA/EHA(70:30)D upon zinc-oxide thickening of NR latex at various levels of addition



. 6.26 : **Effects of polymer MAA/EHA(60:40)D upon zinc-oxide thickening of NR latex at various levels of addition**

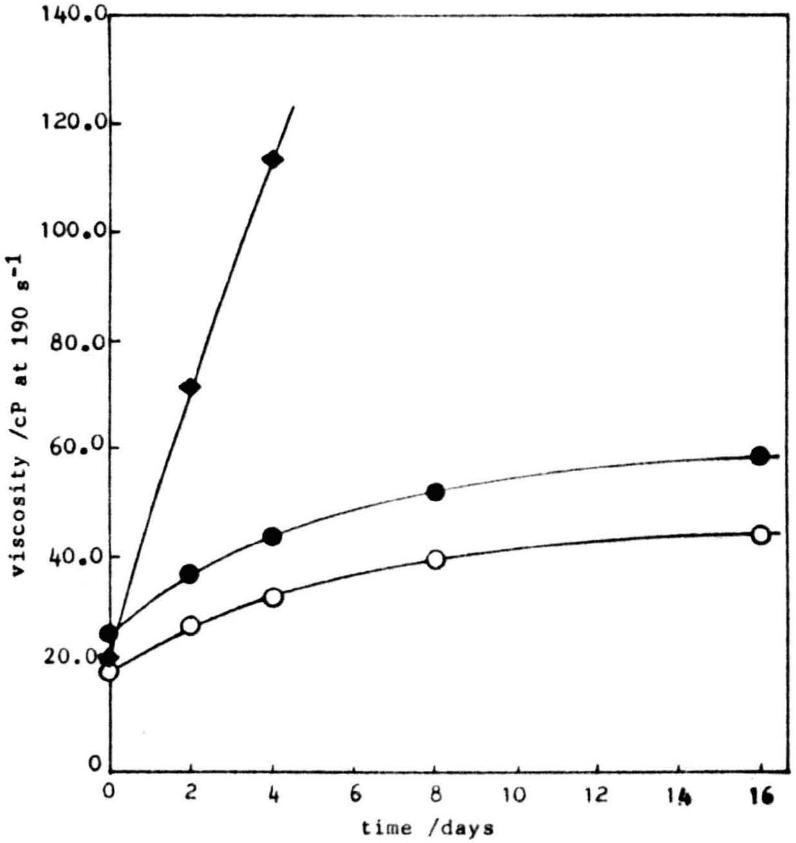


Fig. 6.27 : Effects of polymer MAA/EHA(50:50)B upon zinc-oxide thickening of NR latex at various levels of addition

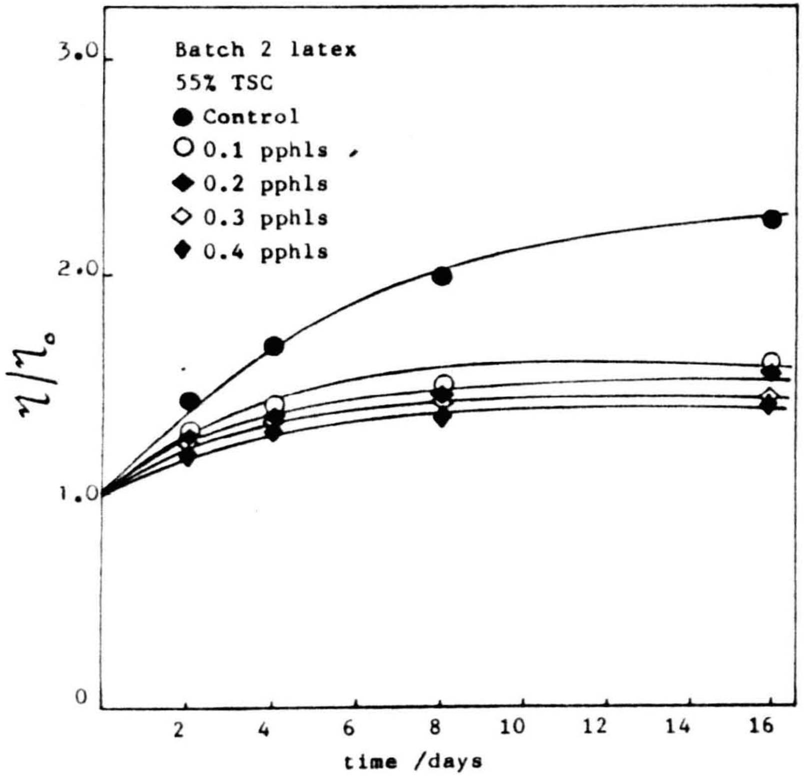


Fig. 6.28 : Variation of η/η_o with time for NR latex containing polymer MAA/EHA(80:20)D

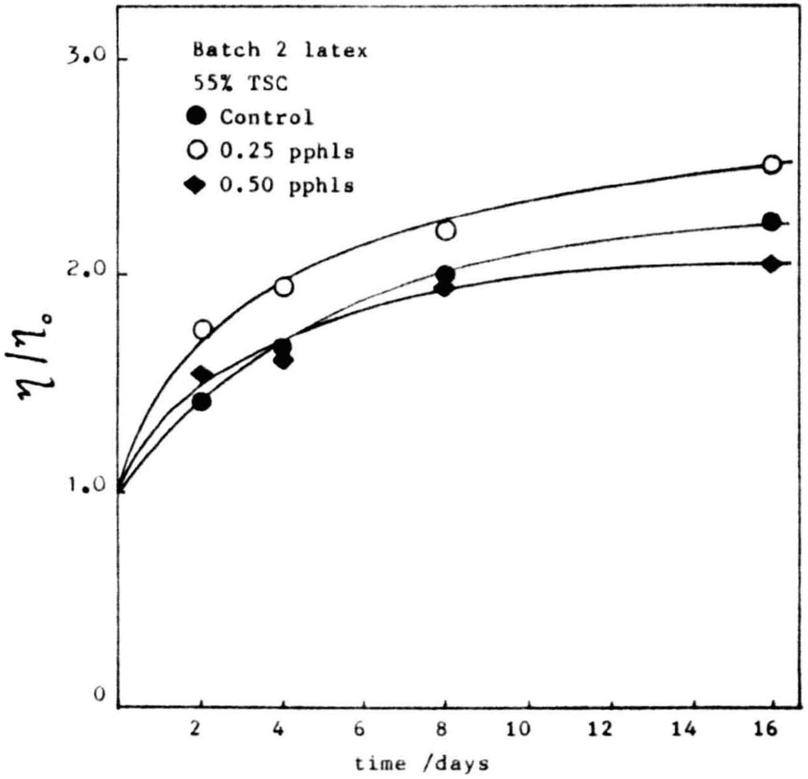


Fig. 6.29 : Variation of η/η_o with time for NR latex containing polymer MAA/EHA(70:30)D

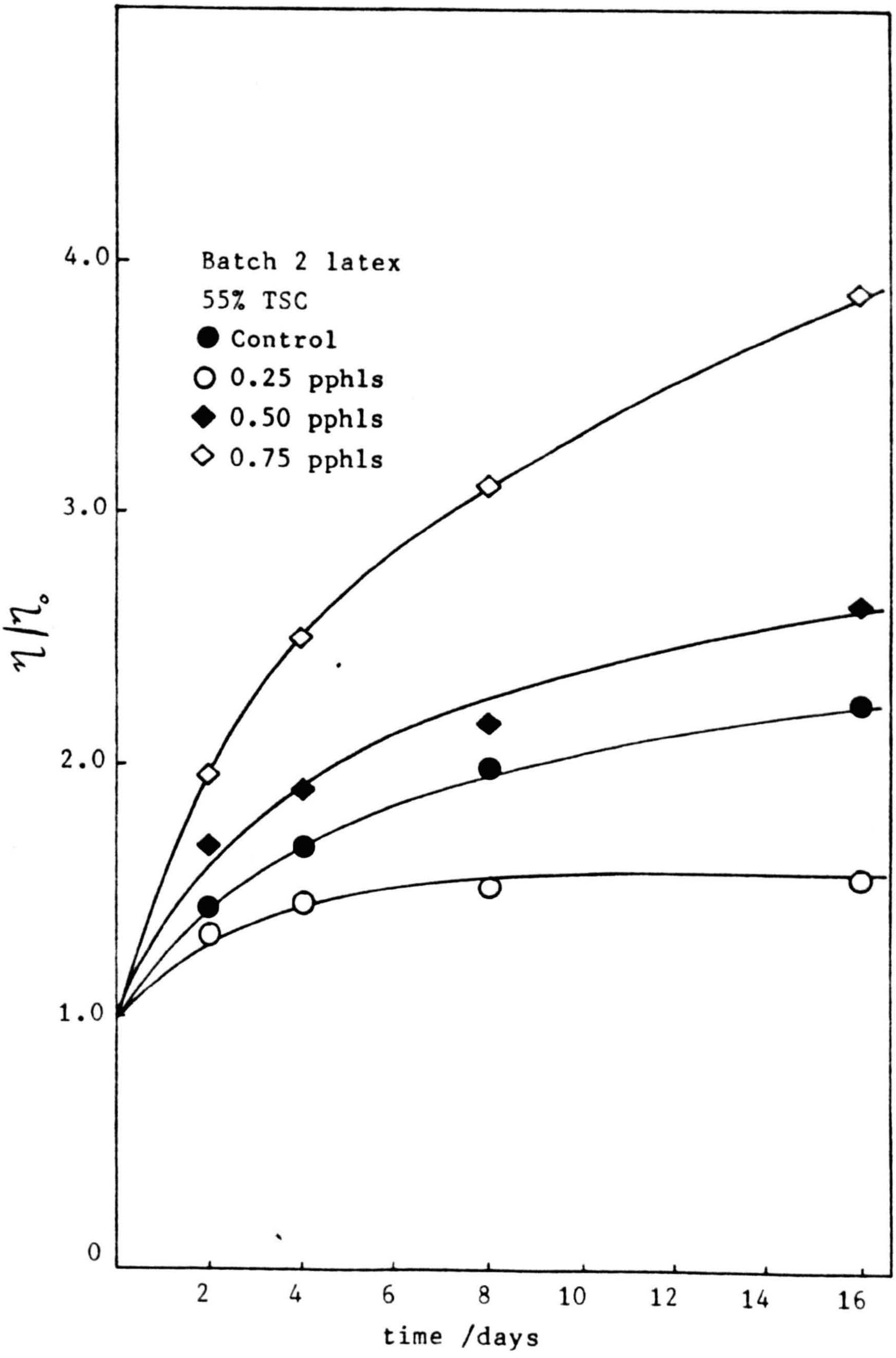


Fig. 6.30 : Variation of η/η_o with time for NR latex containing polymer MAA/EHA(60:40)D

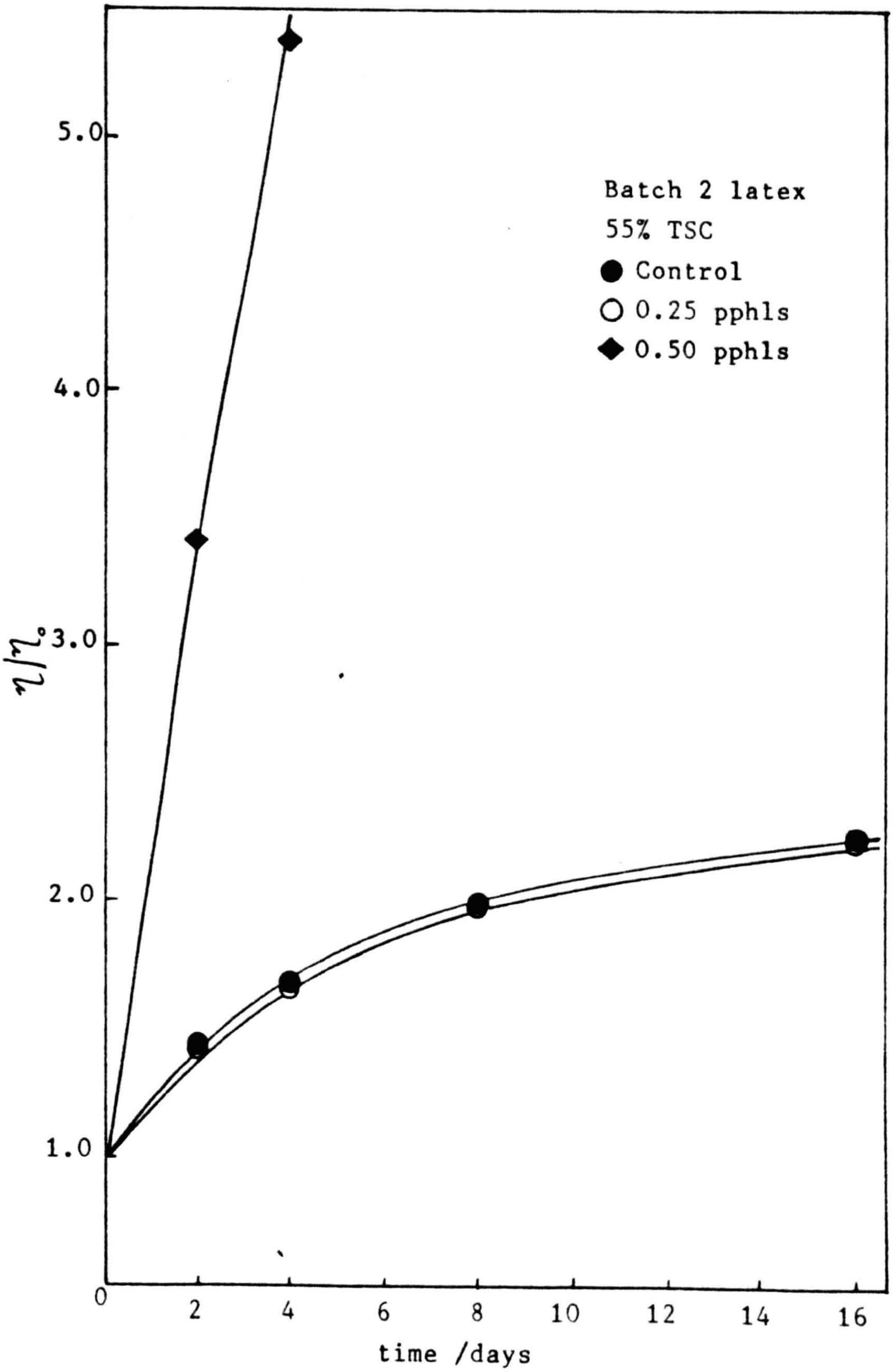


Fig. 6.31 : Variation of η/η_o with time for NR latex containing polymer MAA/EHA(50:50)B

At all the levels investigated, the polymer MAA/EHA(80:20)D retarded zinc-oxide thickening, and extent of retardation was found to decrease as the level of addition was increased although the effect was small. The polymer MAA/EHA(70:30)D accelerated zinc-oxide thickening at the 0.25 pphls level of addition. But the zinc-oxide thickening of the latex compound containing polymer MAA/EHA(70:30)D at the 0.50 pphls level of addition was found to be slightly less than that of the control compound. The polymers MAA/EHA(60:40)D and MAA/EHA(50:50)B retarded zinc-oxide thickening at the 0.50 pphls levels of addition, although the retardation caused by polymer MAA/EHA(50:50)B was insignificant. The latex compound which contained polymer MAA/EHA(50:50)B at the 0.50 pphls of addition was found to gel after 4 days. The rate of zinc-oxide thickening of the latex compound which contained polymer MAA/EHA(60:40)D at the 0.50 pphls level of addition was found to be higher than that of the control compound, and the rate of zinc-oxide thickening further increased as the level of addition was increased from 0.50 pphls to 0.75 pphls.

6.5.3 Effects of branched polymers

The effects of branched polymers of groups MAA/EHA(80:20) and MAA/EHA(60:40) upon the zinc-oxide thickening at two levels of addition, namely, 0.20 pphls and 0.40 pphls, are shown in Figs. 6.32 and 6.33

respectively. The corresponding variations of η/η_0 with time are shown in Figs. 6.34 and 6.35 respectively.

At the 0.20 pphls levels of addition, all the branched polymers investigated retarded zinc-oxide thickening. At the 0.40 pphls level of addition the branched polymers of group MAA/EHA(60:40) accelerated zinc-oxide thickening, whilst those of the group MAA/EHA(80:20) retarded thickening. At the 0.20 pphls of addition the polymer MAA/EHA(60:40)Ca was the most effective of the branched polymers investigated in retarding thickening, whereas at the 0.40 pphls level of addition this polymer was the most effective in accelerating thickening. This illustrates the complexity of the phenomena which can be observed when water-soluble polymers are added to NR latex.

6.6 Discussion of the effects of polymers of Type 1 upon zinc-oxide thickening of NR latex

6.6.1 Effects of polymers of low molecular weight

It is apparent from the results for the effects of polymers of low molecular weight of Type 1 upon the zinc-oxide thickening of NR latex that the hydrophobicity of the added polymer greatly affects its influence the rate of zinc-oxide thickening. Similar results have been reported by Blackley and Emengo(131) for the effects of

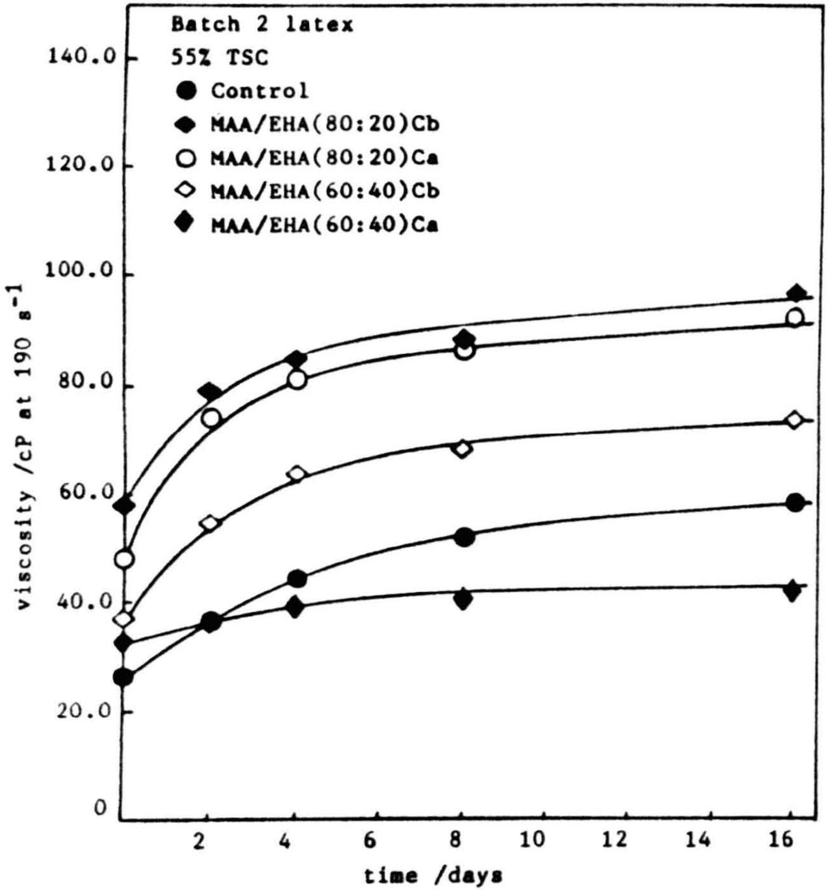


Fig. 6.32 : Effects of branched polymers upon zinc-oxide thickening of NR latex at 0.20 pphls level of addition

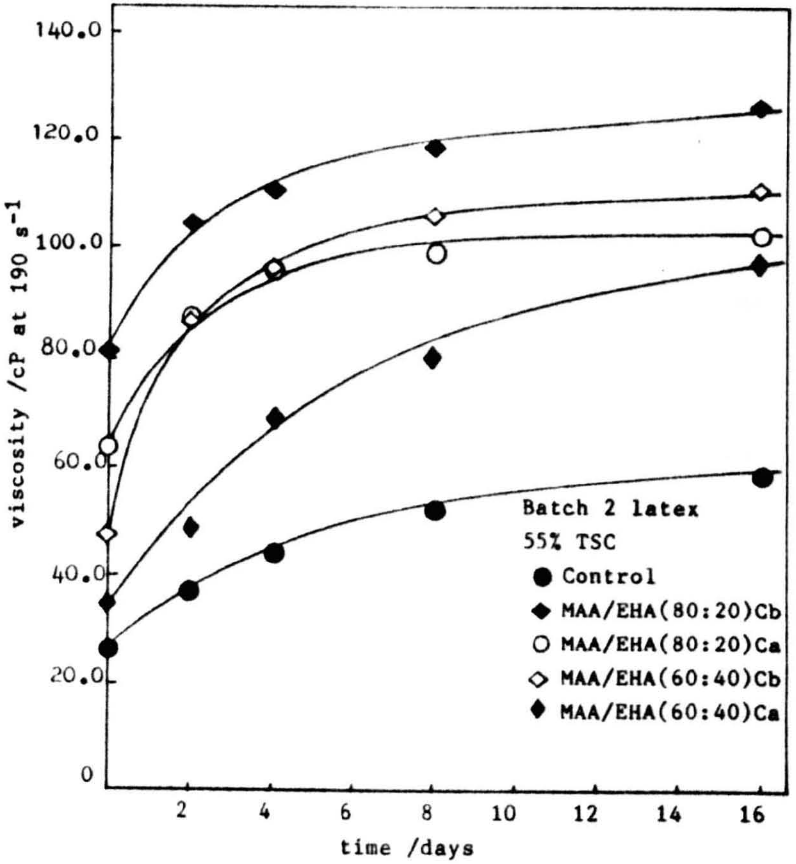


Fig. 6.33 : Effects of branched polymers upon zinc-oxide thickening of NR latex at 0.40 pphls level of addition

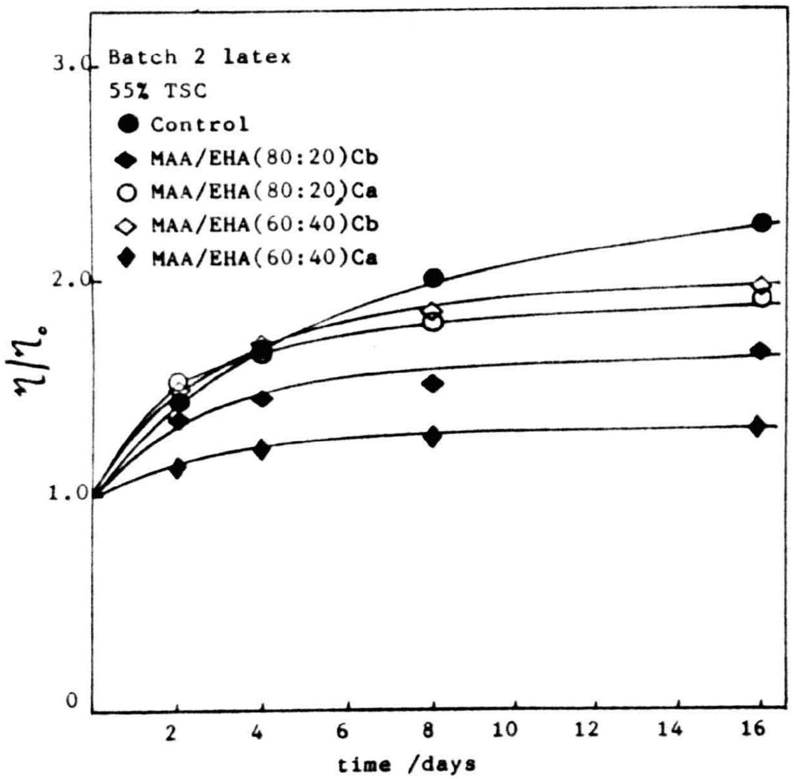


Fig. 6.34 : Variation of / with me for NR latex containing branched p t 0.20 pphls level of addition

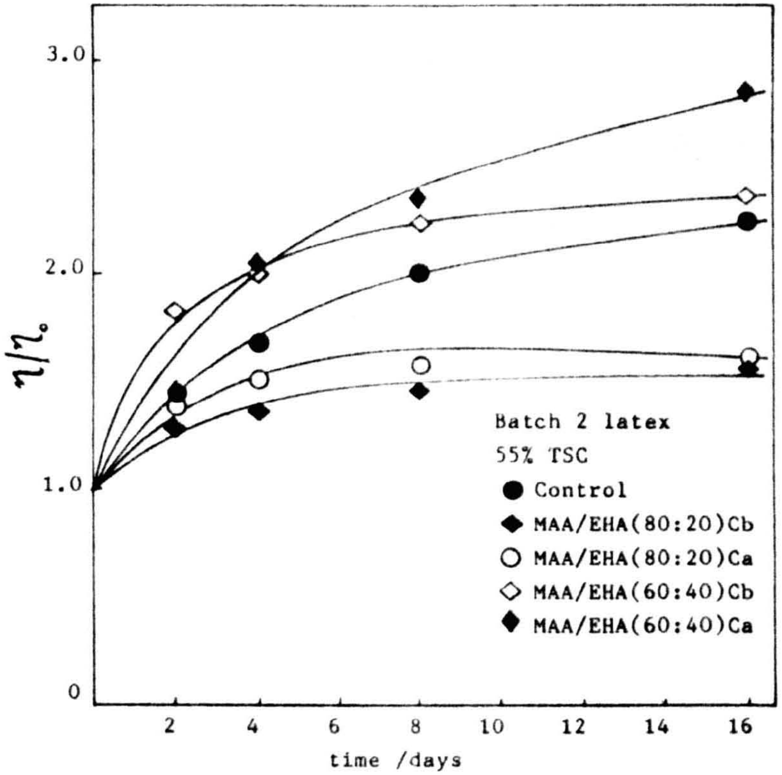


Fig. 6.35 : Variation of η/η_o with time for NR latex containing branched polymers at 0.40 pphls level of addition

various sulphate and sulphonate surfactants upon the rate of zinc-oxide thickening of NR latex. They have found that the ability of the surfactant to influence zinc-oxide thickening is dependent upon its alkyl chain length. On the basis of this finding, they have proposed that the added surfactants interact with the proteinaceous substances at the rubber/water interface to form complexes whose zinc derivatives are less hydrated than are the zinc derivatives of corresponding uncomplexed proteinaceous substances, and therefore less able to function as steric stabilisers. By means of this hypothesis, it is not difficult to understand in a general way the results of the present investigation, that the ability of the added polymer to enhance the rate of zinc-oxide thickening increased as the hydrophobicity of the polymer increased. This is because it is reasonable to suppose that the tendency of the added polymer to be adsorbed at the rubber/water interface and to form complexes with the proteinaceous substances, possibly by hydrophobic association, increases as the hydrophobicity of the polymer increases.

The results for the effects of various levels of added polymers upon the rate of zinc-oxide thickening indicate that the level of added polymer also affects its ability to influence zinc-oxide thickening. Figs. 6.36(a) to 6.36(d) demonstrate how the process of zinc-oxide thickening varies with the level of addition, for each of the polymers of low molecular weight. The results shown in Figs. 6.36(A) to 6.36(D) indicate that the observed zinc-oxide thickening of NR latex compound containing an added polymer may be the result of a balance between two opposing tendencies:

1. the tendency of the polymer to impart colloidal stability to the latex ; and
2. the tendency of the polymer to interact with proteinaceous substances at the rubber/water interface to give complexes which form zinc derivatives of low hydration tendency

It appears that, at low levels of addition, the ability of the added polymer to enhance colloid stability outweighs its ability to increase the rate of zinc-oxide thickening. For most of the polymers investigated, the rate of zinc-oxide thickening was found to increase with increasing level of addition. This can be interpreted as implying that at higher levels of addition the tendency of the added polymer to interact with proteinaceous substances at the rubber/water interface to give complexes which form zinc derivatives of low hydration tendency dominates its ability to impart colloid stability.

It is interesting to note that the polymer MAA/EHA(70:30)B did not cause much acceleration of zinc-oxide thickening when the level of addition was increased

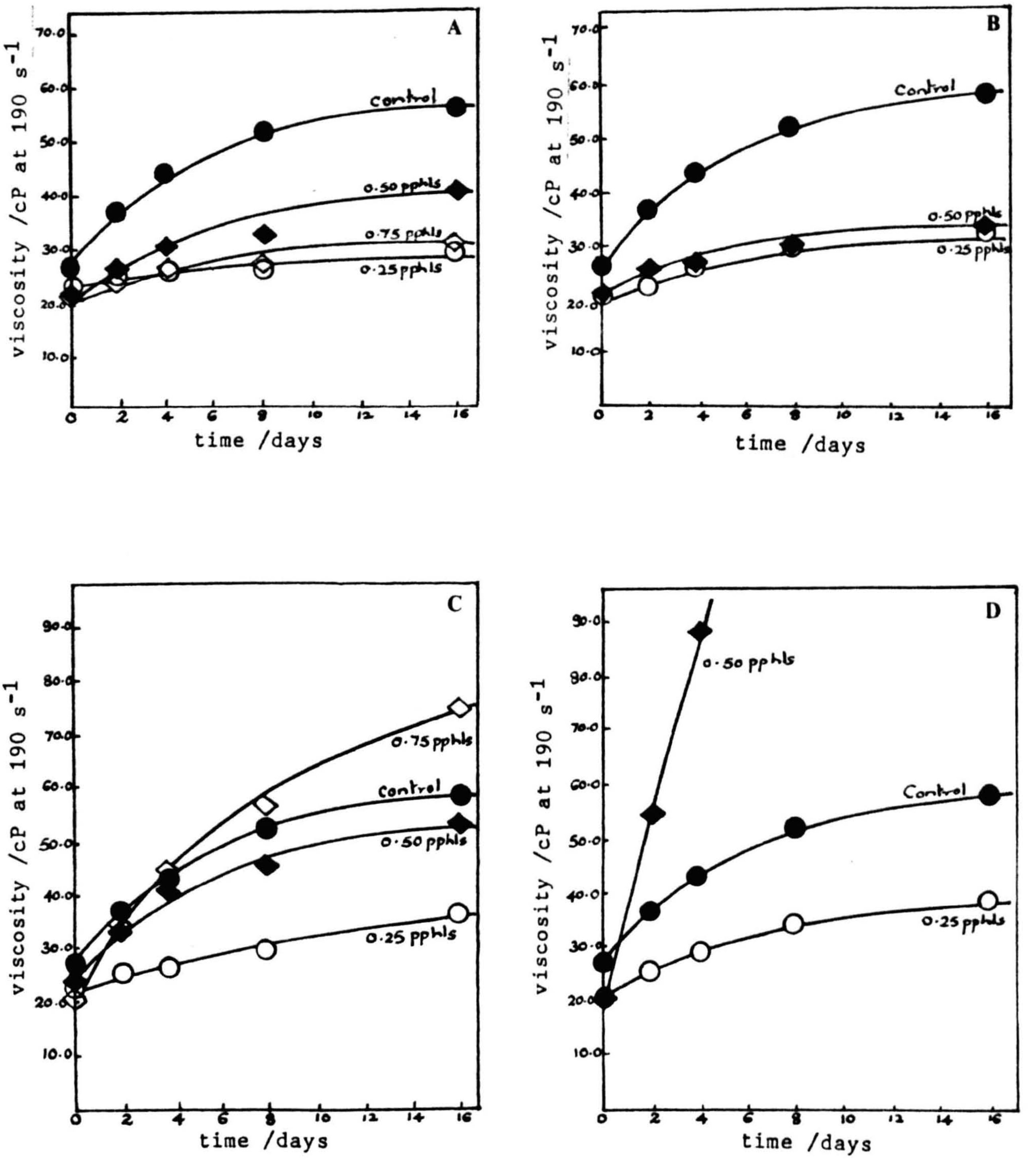


Fig. 6.36 : Effects of polymers of low molecular weight and various compositions upon zinc-oxide thickening of NR latex at various levels of addition

A - effects of polymer MAA/EHA(80:20)B

B - effects of polymer MAA/EHA(70:30)B

C - effects of polymer MAA/EHA(60:40)B

D - effects of polymer MAA/EHA(50:50)A

from 0.25 pphls to 0.50 pphls, and that at both levels of addition the rate of zinc-oxide thickening was well below that of the control compound. Furthermore, it should be recalled that, amongst the polymers of low molecular weight investigated, this was the polymer which brought about the greatest enhancement of MST.

The polymer MAA/EHA(50:50)A was very effective in accelerating the zinc-oxide thickening. As the level of addition was increased from 0.25 pphls to 0.50 pphls the extent of acceleration was found to increase progressively. Furthermore, this was the polymer which gave the greatest acceleration of zinc-oxide thickening. This might be a consequence of its great tendency to adsorb at the rubber/water interface and form complexes with proteinaceous substances whose zinc derivatives are relatively unhydrated.

6.6.2 Effects of polymers of high molecular weight

It is apparent from the results presented in the Section 6.5.2 that most of the polymers of high molecular weight are more effective in accelerating the zinc-oxide thickening of NR latex than are the corresponding polymers of low molecular weight. This might be a consequence of the fact that the adsorption tendencies of polymers of high molecular weight are higher than those of the polymers of low molecular weight. The ability of some of the polymers of high molecular weight, namely polymers MAA/EHA(70:30)D and MAA/EHA(80:20)D, to accelerate the thickening might not be solely dependent upon whether or not they form complexes with proteinaceous substances at the rubber/water interface, because these two polymers were also found to enhance the viscosity of uncompounded latex to considerable extents. On the other hand, the ability of the polymer MAA/EHA(50:50)B, which at the 0.50 pphls level of addition was found to gel the latex compound after 4 days, to enhance the viscosity of uncompounded latex was found to be very small. Furthermore this polymer had the lowest intrinsic viscosity amongst the polymers of high molecular weight investigated. Even though it is not legitimate to compare the intrinsic viscosities of the polymers directly, since they were of different compositions, it is reasonable to assume that the polymer MAA/EHA(50:50)B had the lowest molecular weight amongst the polymers of high molecular weight investigated, because the concentration of the initiator used in the preparation of this polymer was much higher than that used in the preparation of all the other polymers. Therefore it can be suggested that the ability of the polymer MAA/EHA(50:50)B to accelerate the rate of zinc-oxide thickening would have been even higher if its molecular weight was as high as others in the series. A similar explanation is proposed for the acceleration of the rate of zinc-oxide thickening by the polymer MAA/EHA(50:50)B to that has been proposed for the similar effects of the polymer MAA/EHA(50:50)A.

6.6.3 Effects of branched polymers

It is apparent from the results presented in Section 6.6.3 that the effects of branched polymers upon the zinc-oxide thickening of NR latex are broadly similar to those of the linear polymers of high molecular weight. These results together with the results for the effects of polymers of low molecular weight suggest that even though the polymers of high molecular weight are, in general, more effective in accelerating the rate of zinc-oxide thickening than are the polymers of low molecular weight, the role of the composition of the added polymer in modifying the rate of zinc-oxide thickening is far more important than that of the molecular weight of the added polymer.

6.7 Results of effects of some polymers of Type 1 upon heat-sensitisation of NR latex in the presence of zinc-ammine ions

These experiments were carried out in order to ascertain if the effects of added polymers upon zinc-oxide thickening are paralleled by similar effects upon the zinc-ammine heat sensitisation of NR latex by zinc-ammine ions. Some of the polymers of groups MAA/EHA(80:20) and MAA/EHA(60:40) were used in this investigation. The results are given in Table 6.3. The effects of the polymers of high molecular weight of group MAA/EHA(80:20) were investigated at the 0.25 pphls level of addition, because at the 0.50 pphls level of addition the latex compounds containing these polymers became too viscous, and were unsuitable for dipping experiments.

The polymers of low molecular weight were found to reduce the zinc-ammine heat sensitivity of NR latex, and the ability of polymers of low molecular weight of group MAA/EHA(80:20) to reduce zinc-ammine heat sensitivity was found to be slightly higher than that of the polymer of low molecular weight of group MAA/EHA(60:40). This is similar to that observed for the effects of these polymers upon the zinc-oxide thickening of NR latex. The linear polymers

polymer	level of addition /pphls	deposit thickness/mm		
		t=30	t=45	t=60
MAA/EHA(80:20)A	0.50	0.41	0.51	0.63
MAA/EHA(80:20)B	0.50	0.50	0.73	0.92
MAA/EHA(80:20)Cb	0.50	1.95	2.41	2.72
MAA/EHA(60:40)B	0.50	0.58	0.79	0.99
MAA/EHA(60:40)Ca	0.50	1.21	1.55	1.75
MAA/EHA(60:40)Cb	0.50	1.31	1.79	2.16
MAA/EHA(60:40)D	0.50	1.05	1.25	1.45
MAA/EHA(80:20)D	0.25	0.77	1.11	-
MAA/EHA(80:20)E	0.25	1.19	1.62	-
Control	-	0.91	1.12	1.31

Table 6.3 : Effects of some polymers of groups MAA/EHA(80:20) and MAA/EHA(60:40) upon heat-sensitisation of NR latex by zinc-ammine ions (t = dwell time in seconds)

of high molecular weight and the branched polymers of both groups were found to enhance the zinc-ammine heat-sensitivity of NR latex. This might be due to the ability of these polymers to enhance the initial viscosity of the latex to considerably greater extents. So it is not possible to state with certainty that the effects of branched polymers upon zinc-ammine heat sensitivity of NR latex are not paralleled by similar effects upon the zinc-oxide thickening of NR latex.

6.8 Effects of some polymers of Type 1 as replacements for polyvinylmethyl ether(PVME) as heat-sensitisers for NR latex

These experiments were carried out in order to to ascertain if the water-soluble polymers of the type used in this investigation might be used as replacements for PVME as heat-sensitisers for NR latex. The polymers MAA/EHA(80:20)B, MAA/EHA(80:20)D, MAA/EHA(60:40)B, MAA/EHA(60:40)D and two other polymers, namely, MAA/HEMA(2:98)B and MAA/HEMA/EHA(80:10:10)B, were used in this investigation. The latter two polymers were prepared according to the procedure used for the preparation of all the other polymers of Type 1. The nomenclature used for the identification of the polymers was also the same. The heat-sensitivities of the latex compounds containing these polymers were assessed at two different pH values, namely, pH=8.0 and pH=8.5, and were compared with that of a latex compound which contained PVME.

At pH=8.5, the deposits obtained from all the latex compounds were found to be extremely thin. At pH=8.0, the latex compound containing PVME and the latex compound containing polymer MAA/HEMA(2:98)B were found to give films of reasonable thicknessess, but the thickness of the deposit obtained from the latter was relatively thin. The thicknesses of the deposits obtained from these two latex compounds were as follows:

thickness of the deposit obtained from latex compound containing PVME = 3.00mm

thickness of the deposit obtained from latex compound containing polymer MAA/HEMA(2:98)B = 0.62mm

From these results, it appears that, under the conditions investigated, these polymers are not of interest as replacements for PVME as heat-sensitisers for NR latex.

6.9 Effects of polymers of Type 1 upon creaming of NR latex

The results for the effects of various polymers of Type 1 upon the creaming of NR latex at the 0.50 pphls of addition are given in Table 6.4. The results for the effects of sodium alginate upon the creaming of NR latex at the same level of addition are also given in Table 6.4. It was observed that most of polymers investigated induced the creaming of NR latex, and the rate of creaming increased as the molecular weight and the hydrophilicity of

polymer	serum layer (% by weight)	nature of the serum layer
MAA(100)B	10.0	very clear
MAA(100)D	10.9	very clear
MAA/MA(80:20)B	8.3	very clear
MAA/MA(80:20)D	10.0	very clear
MAA/MA(60:40)B	8.3	very clear
MAA/MA(60:40)D	9.8	very clear
MAA/EHA(80:20)B	0	-
MAA/EHA(80:20)Ca	0	-
MAA/EHA(80:20)Cb	0	-
MAA/EHA(80:20)D	7.2	milky
MAA/EHA(60:40)B	0	-
MAA/EHA(60:40)Ca	0	-
MAA/EHA(60:40)Cb	0	-
MAA/EHA(60:40)D	2.4	milky
MAA/EHA/HEMA(80:10:10)B	8.6	milky
sodium alginate	11.0	very clear

Table 6.4 : Effects of polymers of Type 1 upon creaming of NR latex at the 0.50 pphls level of addition (Batch 2 latex)

It was observed that most of the polymers investigated induced the creaming of NR latex, and the rate of creaming increased as the molecular weight and the hydrophilicity of the added polymer were increased. The linear polymer of high molecular weight of group MAA, <u>i.e.</u>, MAA-D, was as effective as sodium alginate in inducing creaming of NR latex.

6.10 <u>Discussion of effects of polymers of Type 1 upon creaming of NR latex</u>

The creaming of NR latex by the addition of water-soluble polymers such as gums, pectins and gelatin has long been known. As shown in the literature review, several theories have been put forward to explain the creaming of NR latex by added water-soluble polymers. The results of the present work indicate that both the solubility of the added polymer in the dispersion medium and the tendency of the added polymer to adsorb on to the particle surface determine the extent of creaming. This inference has been drawn because if it is only the solubility of the added polymer that determines the extent of creaming, decreased creaming should result with increasing molecular weight as a result of increased adsorption. On the other hand, if it is only the adsorption of the added polymer that determines the extent of creaming, increased creaming should result with increasing hydrophobicity as a result of increased adsorption. In practice, the opposite effects were observed. This observation implies that the efficiency of an added polymer in enhancing the creaming of NR latex is dependent upon both its solubility in the dispersion medium and its tendency to adsorb on to the particle surfaces.

CHAPTER SEVEN

EFFECTS OF POLYMERS OF TYPE 2 UPON SOME PROPERTIES OF NR LATEX

7.1 Introduction

The results of the investigation of the effects of polymers of Type 1 upon some properties of NR latex indicated that such properties of NR latex as MST, viscosity and zinc-oxide thickening can be modified by the addition of water-soluble polymers, and that the extent to which each of these properties is modified depends upon the characteristics of the added polymer. It appears that the inferences which have been drawn hitherto could have been drawn with greater certainty if the polymers employed had been better defined. In particular, it was difficult hitherto to distinguish effects arising from the change in overall copolymer composition from those arising from compositional heterogeneity. For this reason, it was desirable to repeat some of the investigation using polymers having better-defined characteristics. This chapter gives the results and discussion of such an investigation which was carried out using polymers of Type 2. These polymers were prepared under conditions which control compositional heterogeneity.

A high-ammonia natural rubber latex

concentrate (Batch 4) was used throughout this investigation. A preliminary investigation of the effects of polymer MAA/EHA(80:20)0.068 upon the MST, viscosity and zinc-oxide thickening of two types of NR latex, namely, Batch 3 and Batch 4, was also carried out in order to ascertain if the pattern of behaviour of the added polymers in NR latex is dependent upon the type of latex. The results of this investigation are shown in Figs. 7.1(a) to 7.1(c). The corresponding variations of the ratios of mechanical stability, viscosity and zinc-oxide thickening are shown in Figs. 7.2(a) to 7.2(c) respectively. It is apparent from these figures that the pattern of behaviour of an added polymer in NR latex does not vary significantly with the type of latex.

7.2 Results of effects of various groups of polymers of Type 2 upon mechanical stability and viscosity of NR latex

7.2.1 Effects of polymers of group MAA/EHA(90:10)

The effects of various levels of added polymers of group MAA/EHA(90:10) upon the MST and viscosity of NR latex (Batch 4) are shown in Figs. 7.3 and 7.4 respectively. In each case, the added polymer enhanced the MST of latex at all the levels of addition, and the extent of the enhancement depended upon the molecular weight of the polymer. As the the molecular weight of the polymer was increased, the extent of the enhancement of MST increased

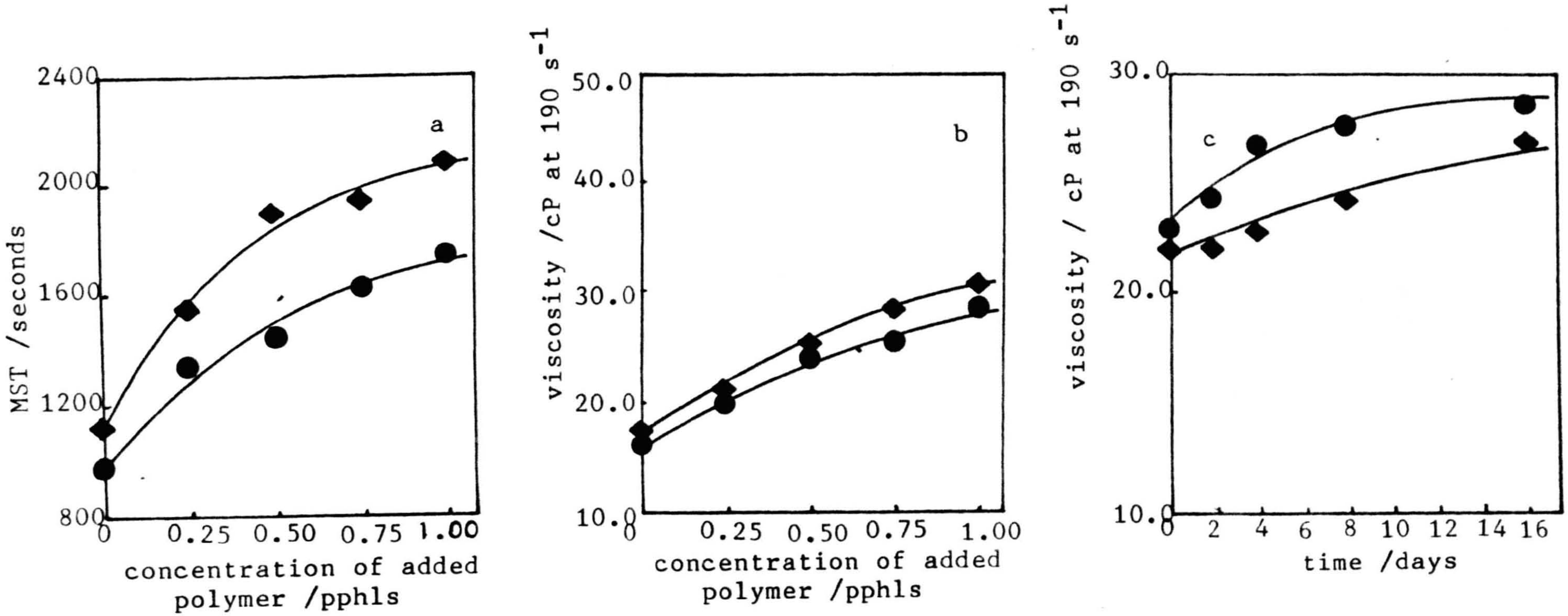


Fig. 7.1 : Effects of polymer MAA/EHA(80:20)0.068 upon (a) MST (b) viscosity and (c) zinc-oxide thickening of Batch 3 (●) and Batch 4 (◆) latex

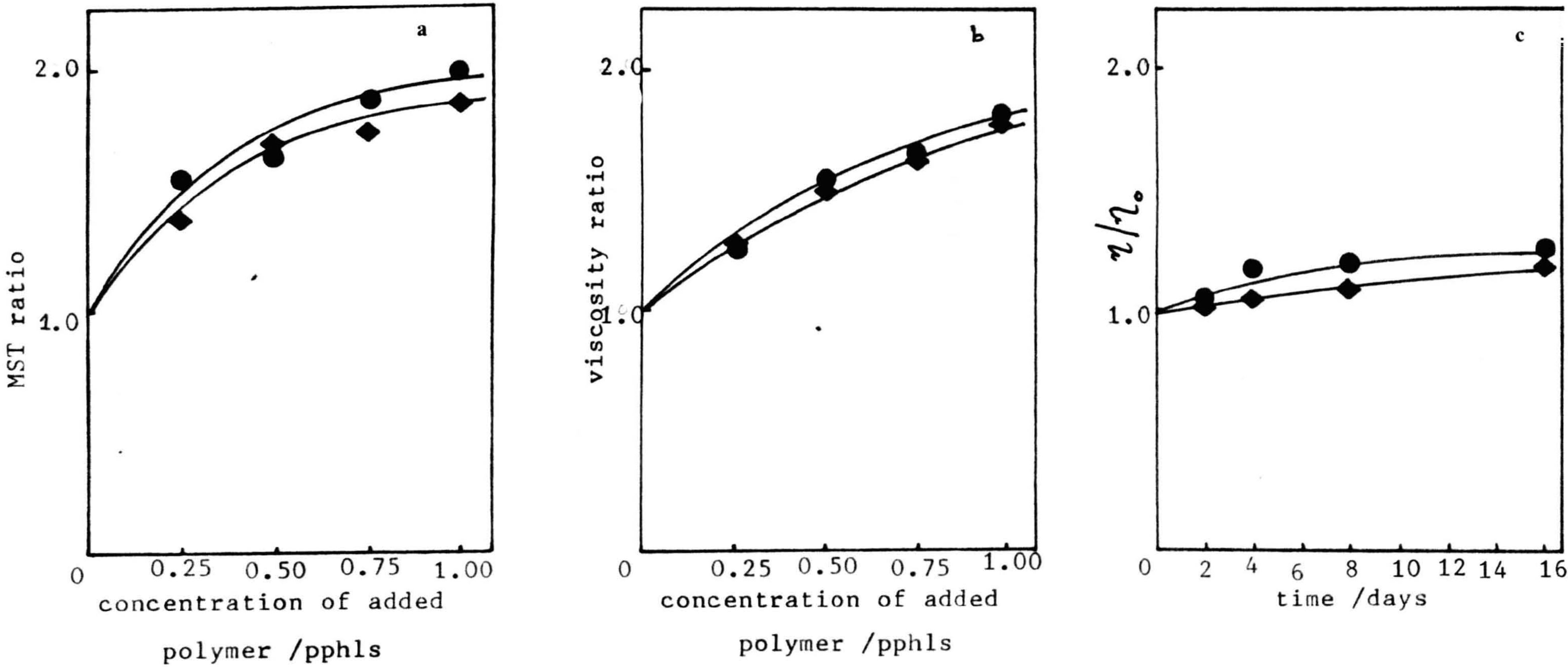
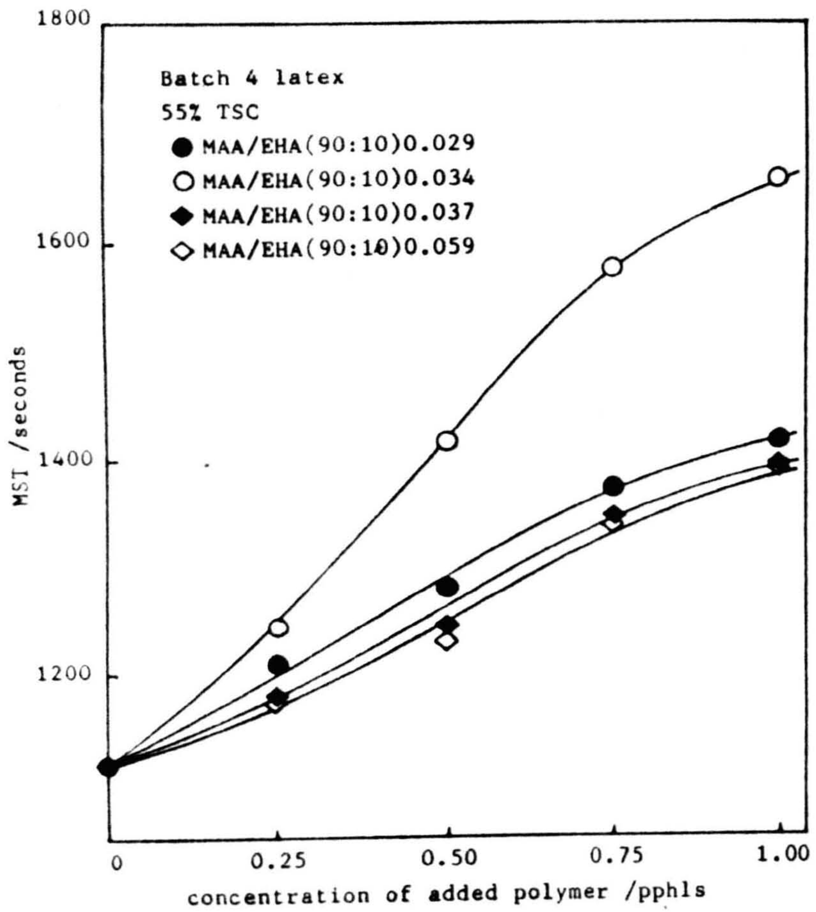


Fig. 7.2 : Effects of polymer MAA/EHA(80:20)0.068 upon ratios of (a) MST, (b) viscosity and (c) zinc-oxide thickening of Batch 3 (●) and Batch 4 (◆) latex



ig. 7.3 : Effects of polymers of Type 2 group MAA/EHA(90:10) upon MST of NR latex

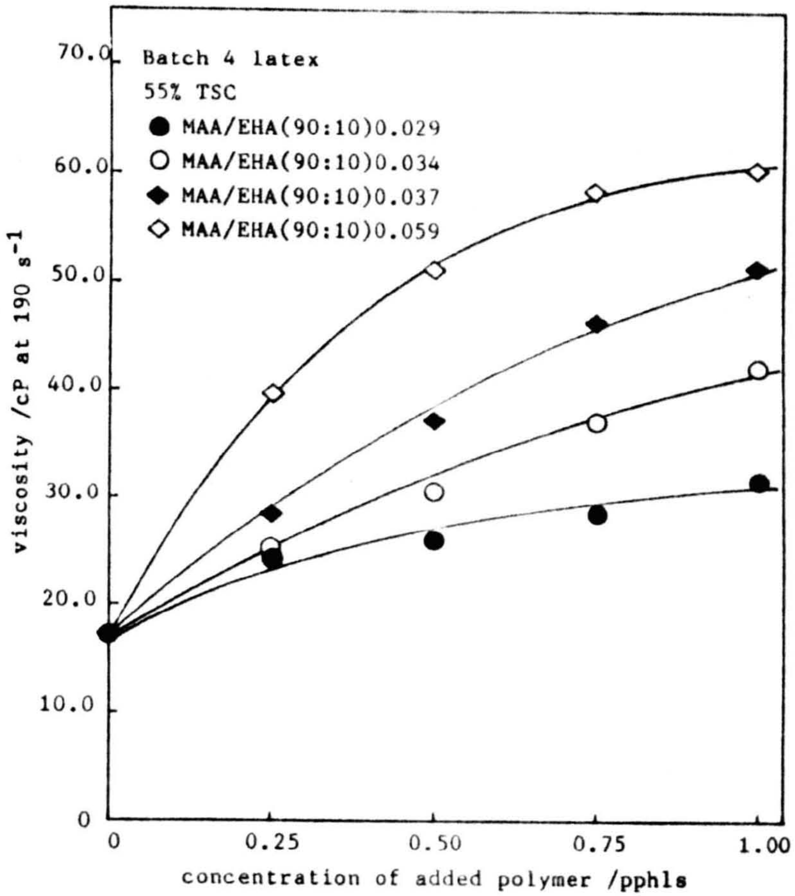


Fig. 7.4 : Effects of polymers of Type 2 group MAA/EHA(90:10) upon viscosity of NR latex

passed through a maximum and then decreased. This is slightly different from what was observed for the effects of the molecular weight of the polymers of Type 1 upon the extent of the enhancement of MST, where in most cases the extent of the enhancement of MST was found to increase progressively with increasing molecular weight of the polymer.

As regards the effects upon viscosity, all the polymers enhanced the viscosity of latex, the extent of the enhancement of viscosity depended upon the molecular weight of the polymer, being apparently greatest for the polymer of highest molecular weight.

7.2.2 Effects of polymers of group MAA/EHA(80:20)

The effects of various levels of added polymers of group MAA/EHA(80:20) upon the MST and viscosity of NR latex (Batch 4) are shown in Figs. 7.5 and 7.6 respectively. The effects of polymers of this group upon the MST and viscosity of NR latex were found to be similar to those of the polymers of group MAA/EHA(90:10). However, the polymers of this group are slightly more effective in enhancing the MST and slightly less effective in enhancing the viscosity than the are corresponding polymers of group MAA/EHA(90:10).

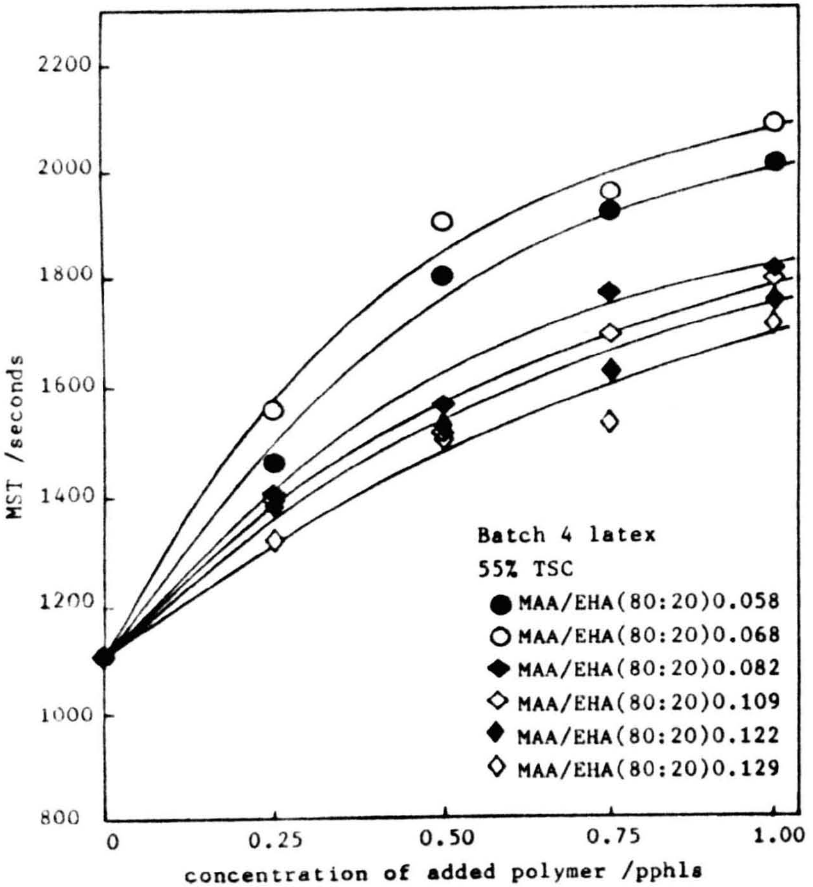


Fig. 7.5 : Effects of polymers of Type 2 group MAA/EHA(80:20) upon MST of NR latex

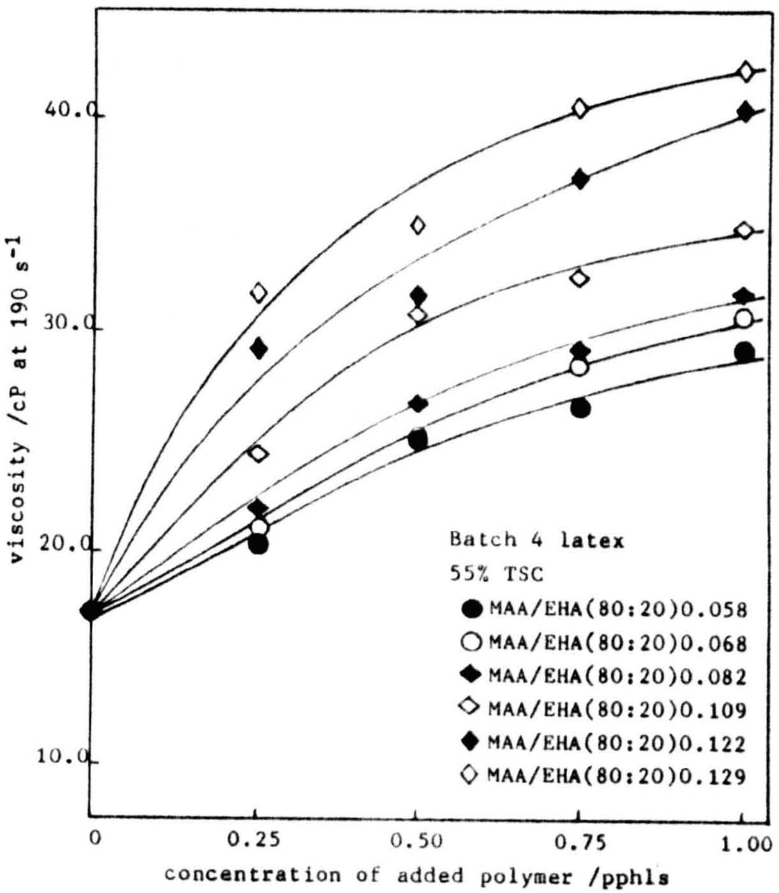


Fig. 7.6 : Effects of polymers of Type 2 group MAA/EHA(80:20 upon viscosity of NR latex

7.2.3 Effects of polymers of group MAA/EHA(70:30)

The effects of various levels of added polymers of group MAA/EHA(70:30) upon the MST and viscosity of NR latex (Batch 4) are shown in Figs. 7.7 and 7.8 respectively. All the polymers of this group enhanced the MST of latex, and the extent of the enhancement depended upon the molecular weight of the polymer, being apparently greatest for the polymer of lowest molecular weight. This is somewhat different from what was observed for the effects of molecular weight of the polymers of groups MAA/EHA(90:10) and the MAA/EHA(80:20) upon the extent of the enhancement of MST, but it is reasonable to expect that a similar variation of MST with the molecular weight of the polymer would have been observed if the polymers of even lower molecular weights had been used. In general the polymers of this group were found to be more effective in enhancing MST than the polymers of group MAA/EHA(80:20).

The effects of polymers of this group upon the viscosity of NR latex were found to be similar to those of the polymers of groups MAA/EHA(90:10) and MAA/EHA(80:20), but the efficiency of these polymers in enhancing the viscosity was found to be slightly less.

7.2.4 Effects of polymers of group MAA/EHA(60:40)

The effects of various levels of added polymers

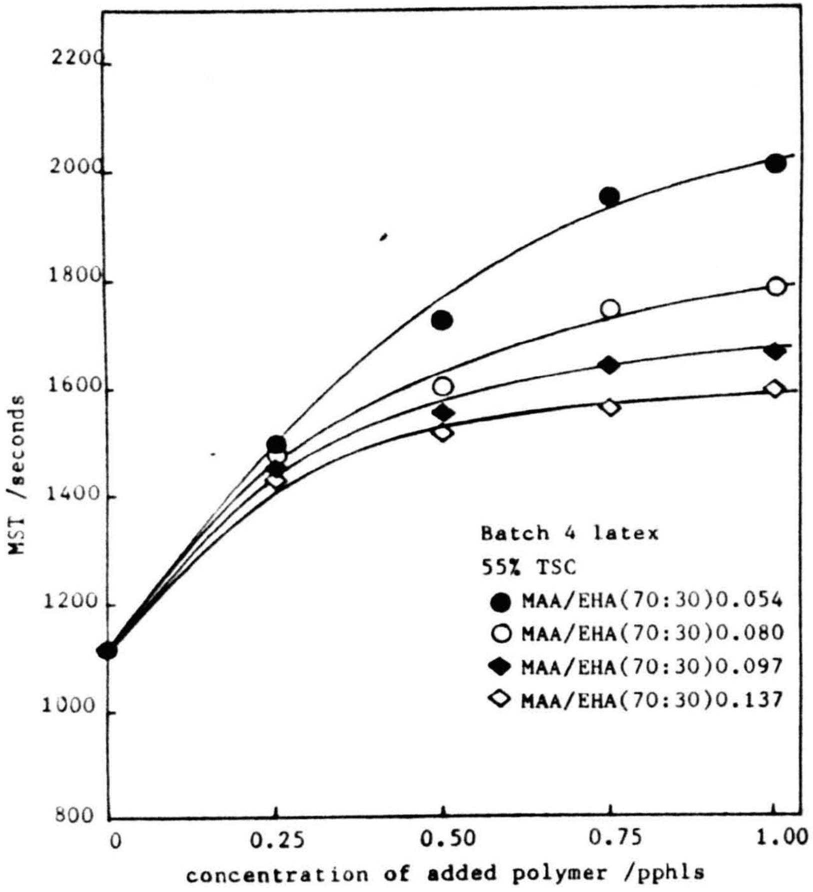


Fig. 7.7 : **Effects of polymers of Type 2 group MAA/EHA(70:30) upon MST of NR latex**

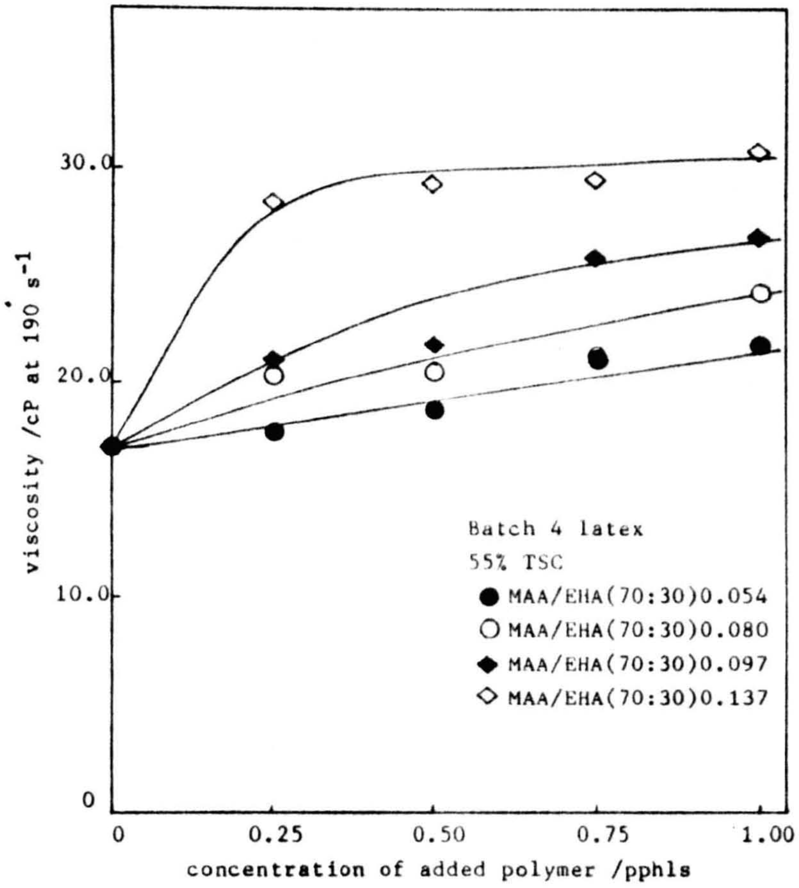


Fig. 7.8 : **Effects of polymers of Type 2 group MAA/EHA(70:30) upon viscosity of NR latex**

of group MAA/EHA(60:40) upon the MST and viscosity of NR latex (Batch 4) are shown in Figs. 7.9 and 7.10 respectively. All the polymers investigated enhanced the MST of latex, and, again the extent of the enhancement depended upon the molecular weight of the polymer. The variation of the extent of the enhancement of MST with molecular weight of the polymer was found to be similar to that observed for the polymers of groups MAA/EHA(90:10) and MAA/EHA(80:20).

As regards the effects upon viscosity of latex, all the polymers of this group enhanced the viscosity of latex, but the variation of the extent of the enhancement of viscosity with the level of addition was found to be different from that observed for the polymers of groups MAA/EHA(90:10), MAA/EHA(80:20) and group MAA/EHA(70:30). As shown in Fig. 7.10, the viscosity of latex first increased, passed through a maximum, then decreased passed through a minimum, and then again increased as the concentration of the polymer in latex was increased.

7.2.5 Effects of polymers of group MAA/EHA(50:50)

The effects of various levels of added polymers of group MAA/EHA(50:50) upon the MST and viscosity of NR latex (Batch 4) are shown in Figs. 7.11 and 7.12 respectively. All the polymers of this group enhanced the MST of latex but the the extent of the enhancement of MST depended upon the molecular weight of the polymer as well as upon

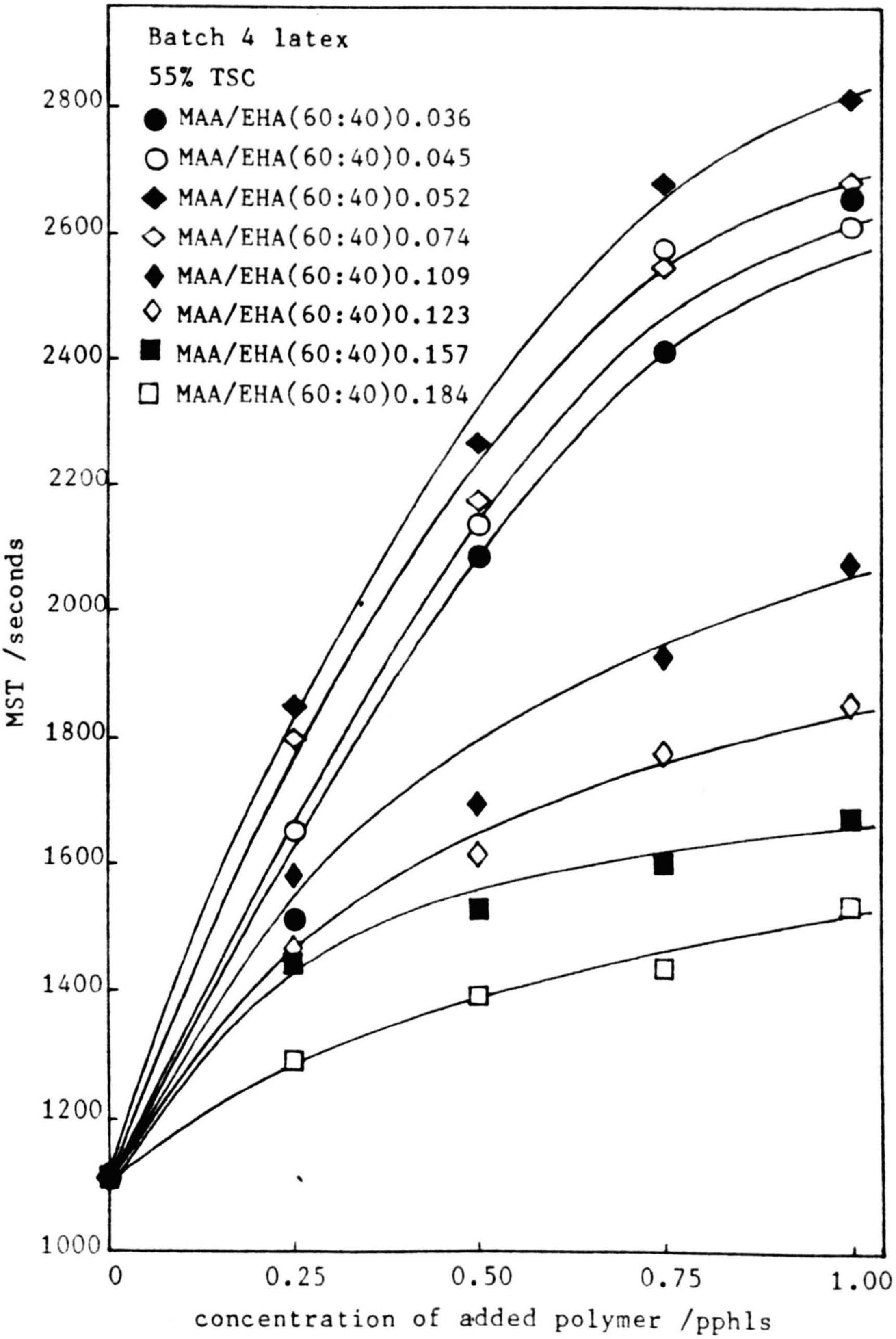


Fig. 7.9 : Effects of polymers of Type 2 group MAA/EHA(60:40) upon MST of NR latex

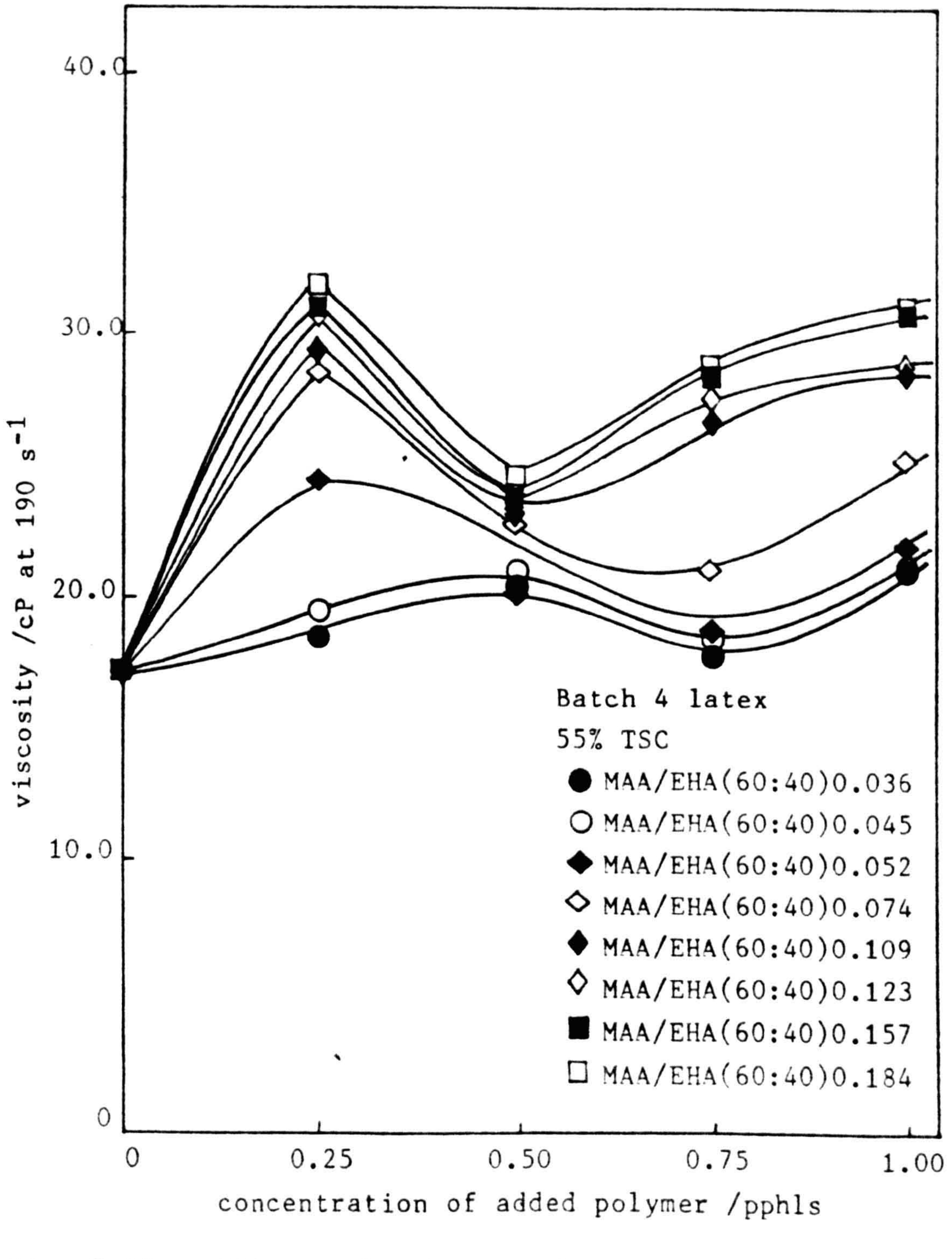


Fig. 7.10 : Effects of polymers of Type 2 group MAA/EHA(60:40) upon viscosity of NR latex

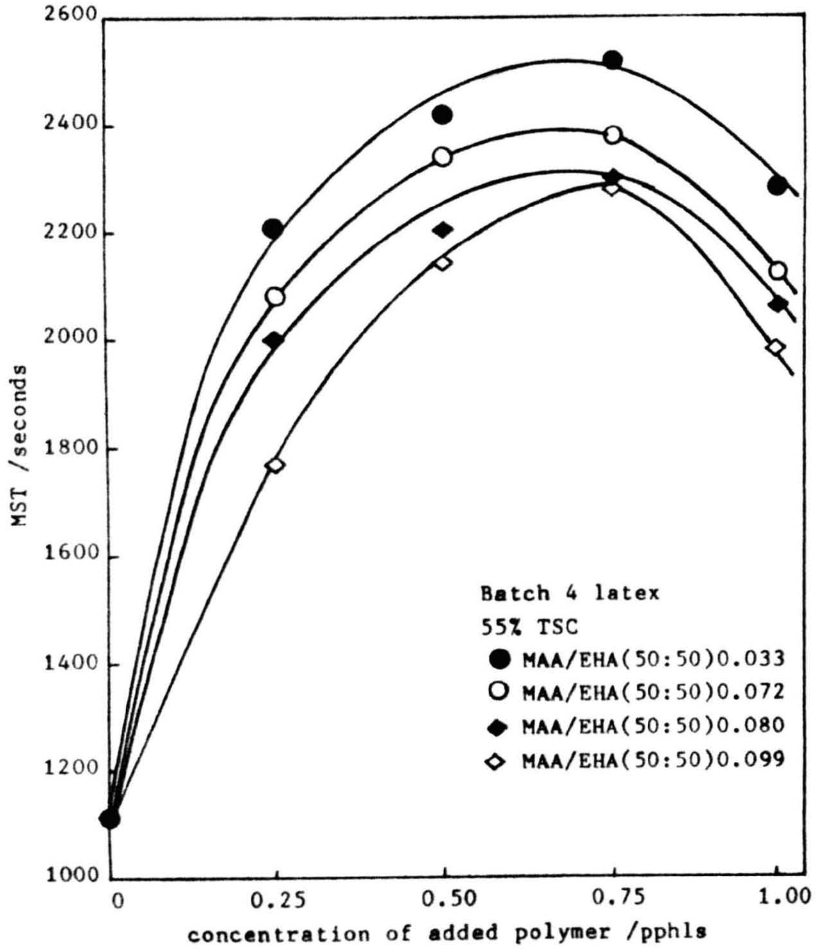


Fig. 7.11 : Effects of polymers of Type 2 group MAA/EHA(50:50) upon MST of NR latex

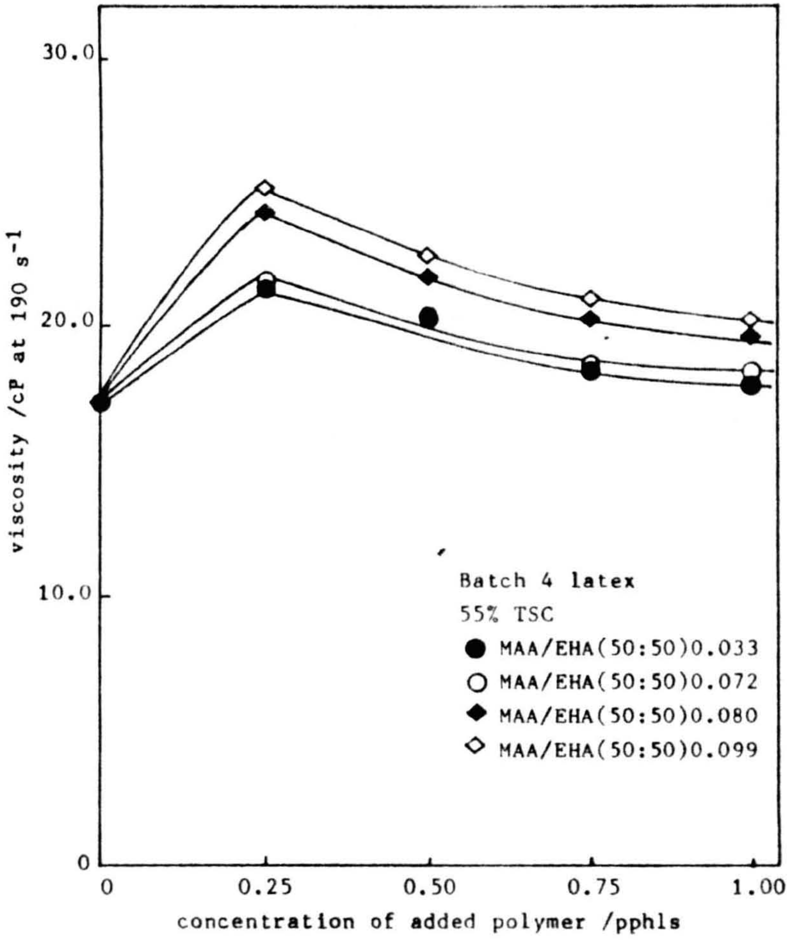


Fig. 7.12 : Effects of polymers of Type 2 group MAA/EHA(50:50) upon viscosity of NR latex

the level of addition. As the molecular weight of the polymer was increased the extent of the enhancement of MST decreased. Furthermore, unlike in all the other cases, as the level of addition of polymer increased, the extent of the enhancement of MST of latex first increased, passed through a maximum and then decreased with further increase in the level of addition of the polymer.

As regards the effects upon viscosity, these polymers were generally less effective in enhancing viscosity than all the other polymers investigated. The extent of enhancement of viscosity was found to depend upon the level of addition in such a way, that as the level of addition was increased the extent of the enhancement of viscosity first increased, passed through a maximum and then decreased. Unlike in the case of polymers of group MAA/EHA(60:40), the minima in the curves of variation of viscosity with the level of added polymer were not observed, at least over the range of concentrations investigated.

7.2.6 Effects of polymers of group AA/EHA(80:20)

The effects of various levels of added polymers of group AA/EHA(80:20) upon the MST and viscosity of NR latex (Batch 4) are shown in Figs. 7.13 and 7.14 respectively. All the polymers of this group enhanced the MST of NR latex, and, again the extent of the enhancement depended

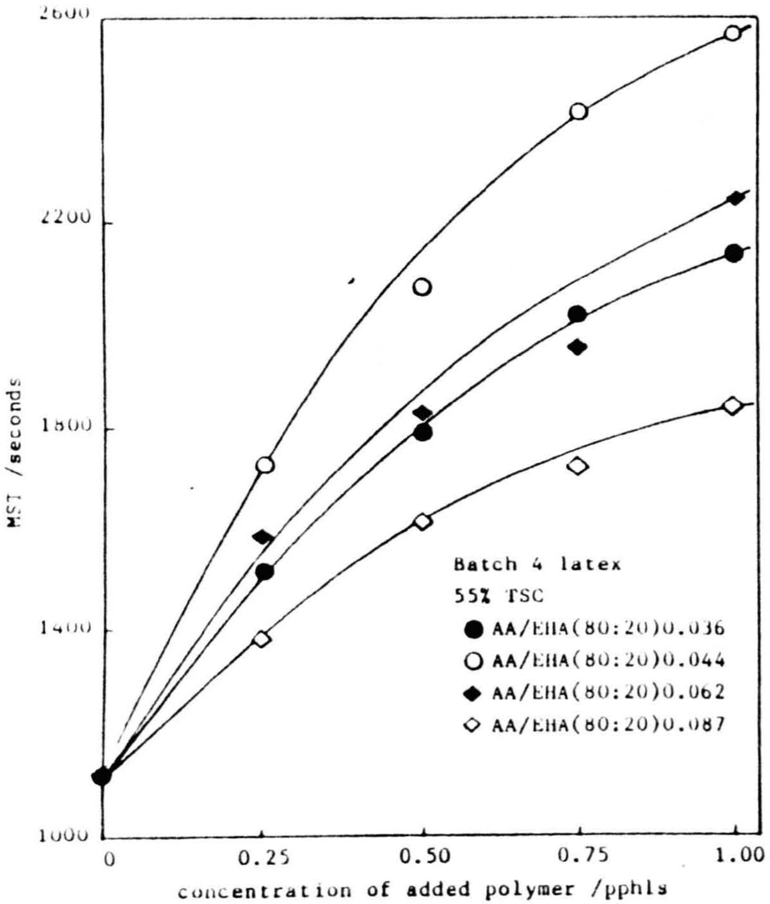


Fig. 7.13 : Effects of polymers of Type 2 group AA/EHA(80:20) upon MST of NR latex

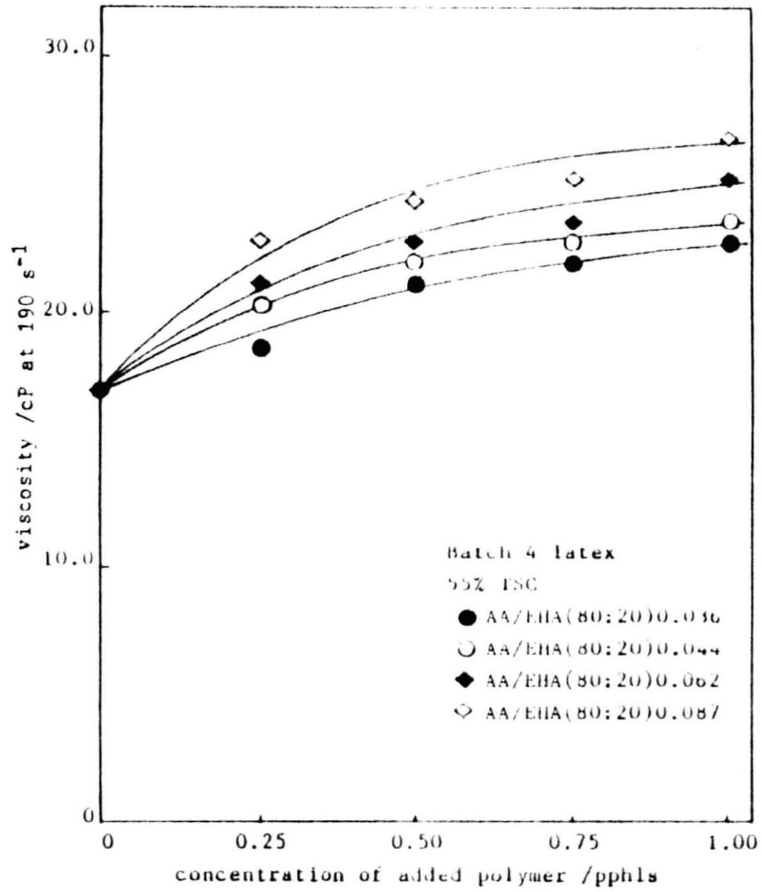


Fig. 7.14 : Effects of polymers of Type 2 group AA/EHA(80 upon viscosity of NR latex

upon the molecular weight of the polymer. Similar to what was observed in most other cases, as the molecular weight of the polymer was increased the extent of the enhancement of MST first increased, passed through a maximum and then decreased with further increase in molecular weight. The efficiency of the polymers of this group in enhancing the MST was found to be slightly higher than that of the polymers of group MAA/EHA(80:20).

As regards effects upon the viscosity, these polymers enhanced the viscosity of NR latex at all the levels of addition, and, again the extent of the enhancement of viscosity depended upon the molecular weight of the polymer, being apparently greatest for the polymer of highest molecular weight. The polymers of this group were found to be slightly more efficient in enhancing the viscosity than the polymers of group MAA/EHA(80:20).

7.2.7 Effects of polymers of group AA/EHA(60:40)

The effects of various levels of added polymers of group AA/EHA(60:40) upon the MST and viscosity of NR latex (Batch 4) are shown in Figs. 7.15 and 7.16 respectively. The effects of polymers of this group upon the MST of NR latex were found to be similar to those of the polymers of group AA/EHA(80:20). But their efficiencies in enhancing the MST were found to be higher than those of the polymers of groups AA/EHA(80:20) and MAA/EHA(60:40).

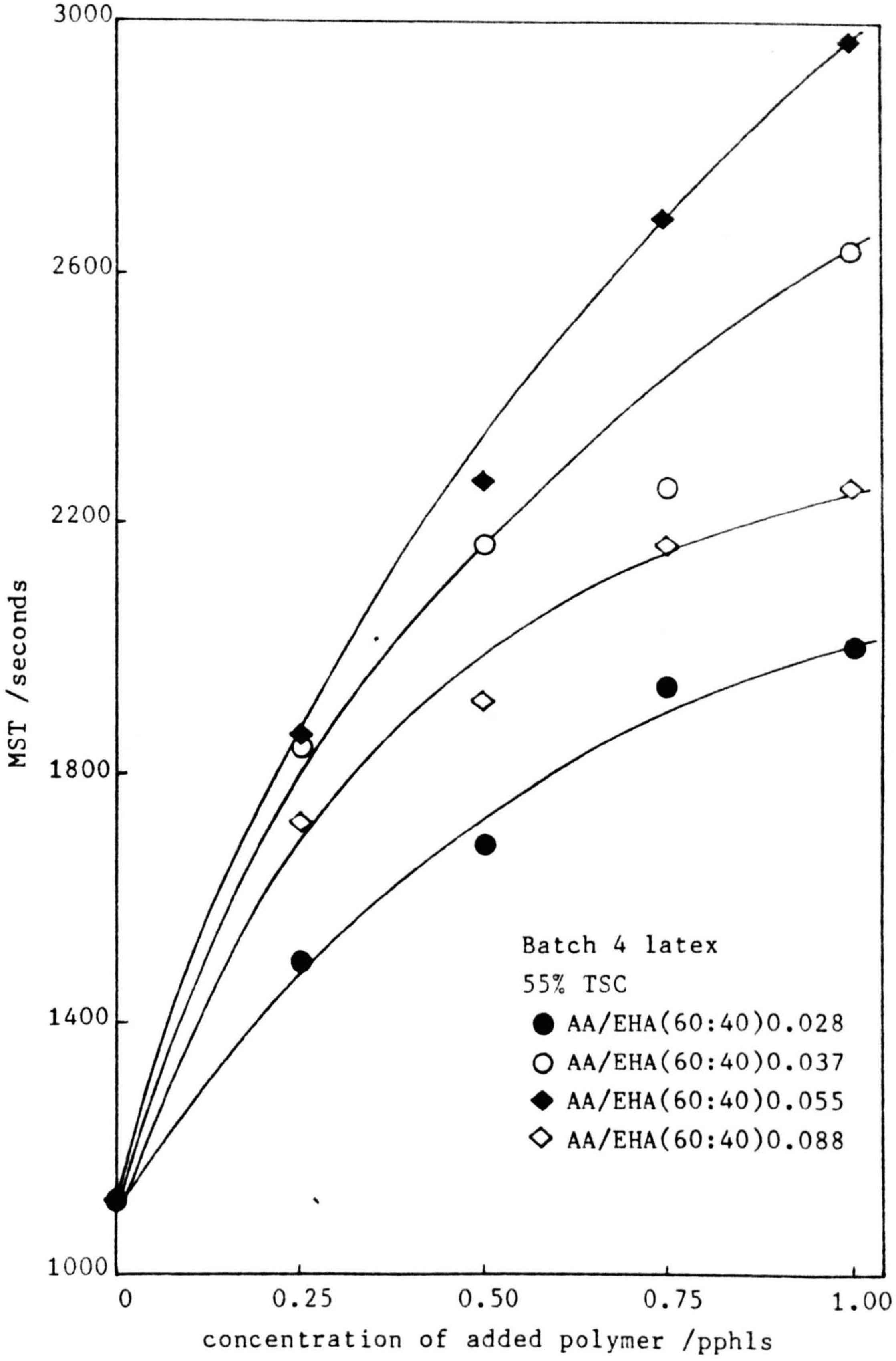


Fig. 7.15 : Effects of polymers of Type 2 group AA/EHA(60:40) upon MST of NR latex

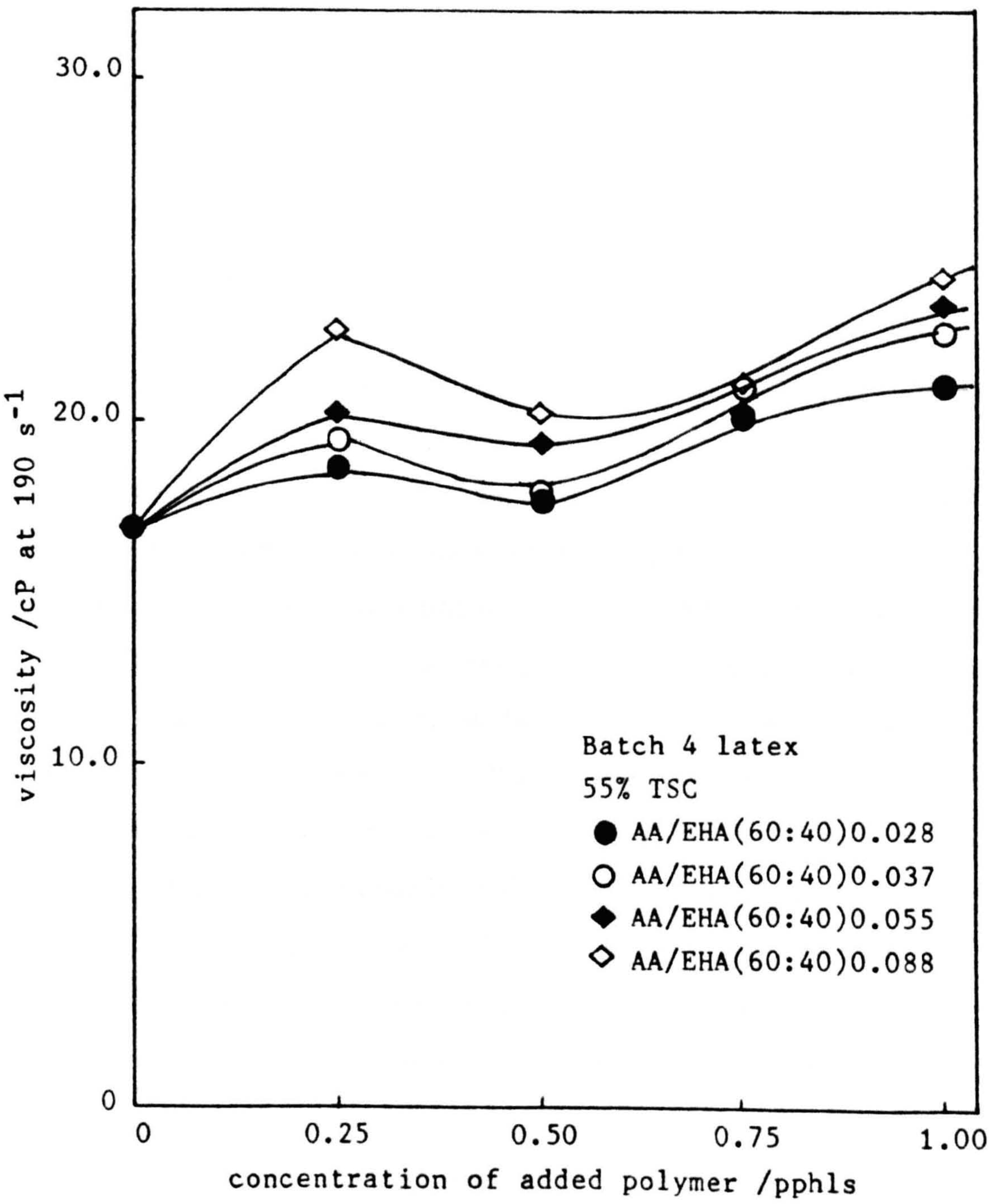


Fig. 7.16 : Effects of polymers of Type 2 group AA/EHA(60:40) upon viscosity of NR latex

The effects of polymers of this group upon viscosity of latex were found to be similar to those of the polymers of group MAA/EHA(60:40), i.e., as the concentration of the added polymer was increased the viscosity of NR latex first increased, passed through a maximum, then decreased, passed through minimum and then again increased.

7.3 Discussion of the effects of polymers of Type 2 upon mechanical stability and viscosity of NR latex

7.3.1 Effects of molecular weight

It is apparent from the results presented in Section 7.2 that as in the case of polymers of Type 1 the ability of polymers of Type 2 to enhance MST of NR latex is dependent upon their molecular weight. However, in most cases the correlation between the extent of the enhancement of MST and the molecular weight of the added polymers of Type 2 was found to be different from that observed with the polymers of Type 1. Therefore it is appropriate to re-plot the results for the polymers of Type 2 in a way which shows more clearly how the extent of the enhancement of MST vary with the polymer molecular weight. Figs. 7.17 to 7.23 shows the variation of MST with the intrinsic viscosity of the polymer at various levels of addition to NR latex. The intrinsic viscosities of the polymers were used as the independent variable, as the molecular weights of the polymers were not available. From the Figs 7.17 to

7.23, it is apparent that, in most cases, the variation of the enhancement of MST with intrinsic viscosity of the polymer follows a common but unexpected trend. As the intrinsic viscosity of the polymer is increased, the extent of enhancement of MST first increases, passes through a maximum and then decreases. The initial increase in the efficiency of the added polymer in enhancing the MST with increasing molecular weight may be in part due to the increased tendency for adsorption at the rubber/water interface, as suggested for the polymers of Type 1. The subsequent decrease in the efficiency of the added polymer in enhancing MST with further increase in molecular weight may be a consequence of one or more of the following reasons:

1. Polymers of high molecular weight are more capable of inducing interparticle bridging than are corresponding polymers of low molecular weight. Interparticle bridging would be expected to reduce mechanical stability by increasing effective size of latex particles.

2. It is reasonable to expect that, at any given level of addition, the number of loops of the adsorbed polymer increases at the expense of number of tails with increasing the molecular weight. This is illustrated in an extreme way in Fig. 2.24.

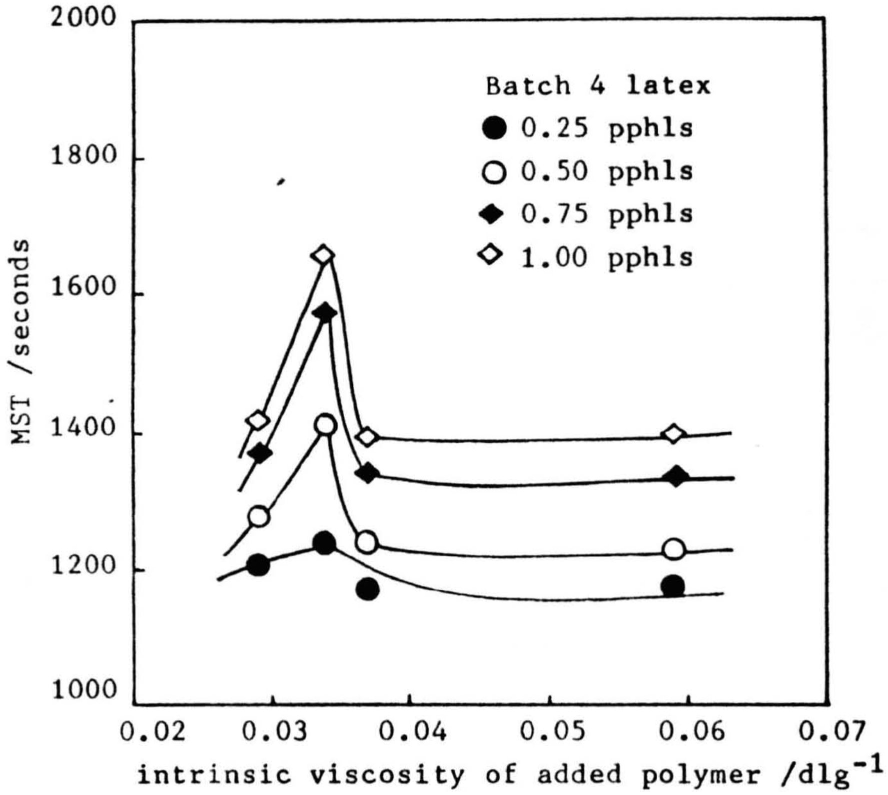


Fig. 7.17 : Effects of intrinsic viscosity of polymers of Type 2 group MAA/EHA(90:10) upon extent of enhancement of MST of NR latex at various levels of addition

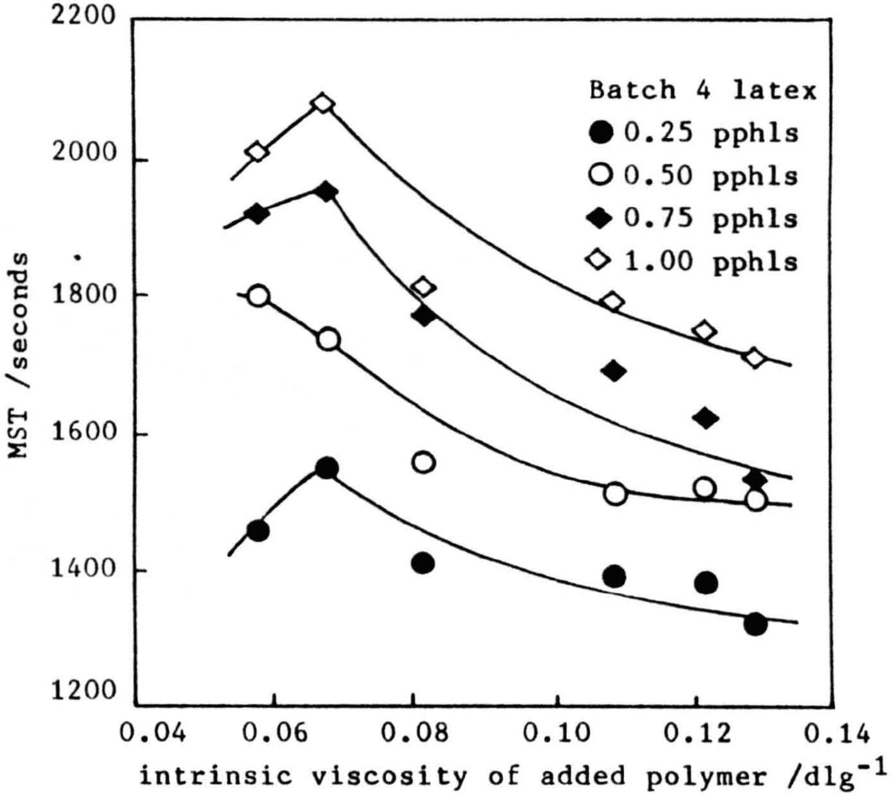


Fig. 7.18 : Effects of intrinsic viscosity of polymers of Type 2 of group MAA/EHA(80:20) upon extent of enhancement of MST of NR latex at various levels of addition

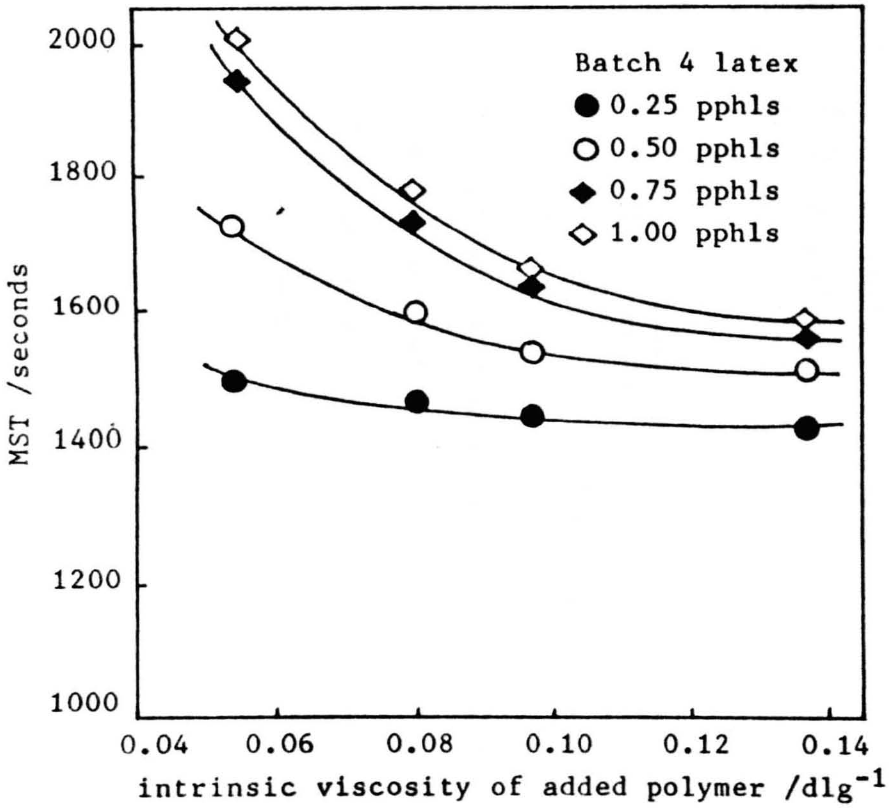


Fig. 7.19 : Effects of intrinsic viscosity of polymers of Type 2 group MAA/EHA(70:30) upon extent of enhancement of MST of NR latex at various levels of addition

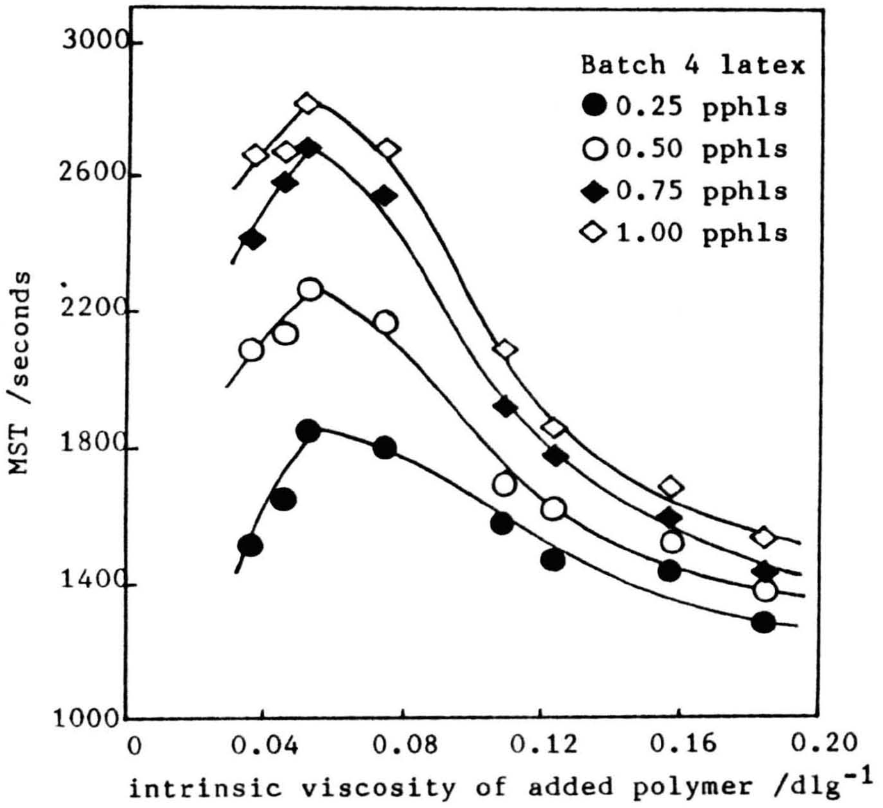


Fig. 7.20 : Effects of intrinsic viscosity of polymers of Type 2 of group MAA/EHA(60:40) upon extent of enhancement of MST of NR latex at various levels of addition

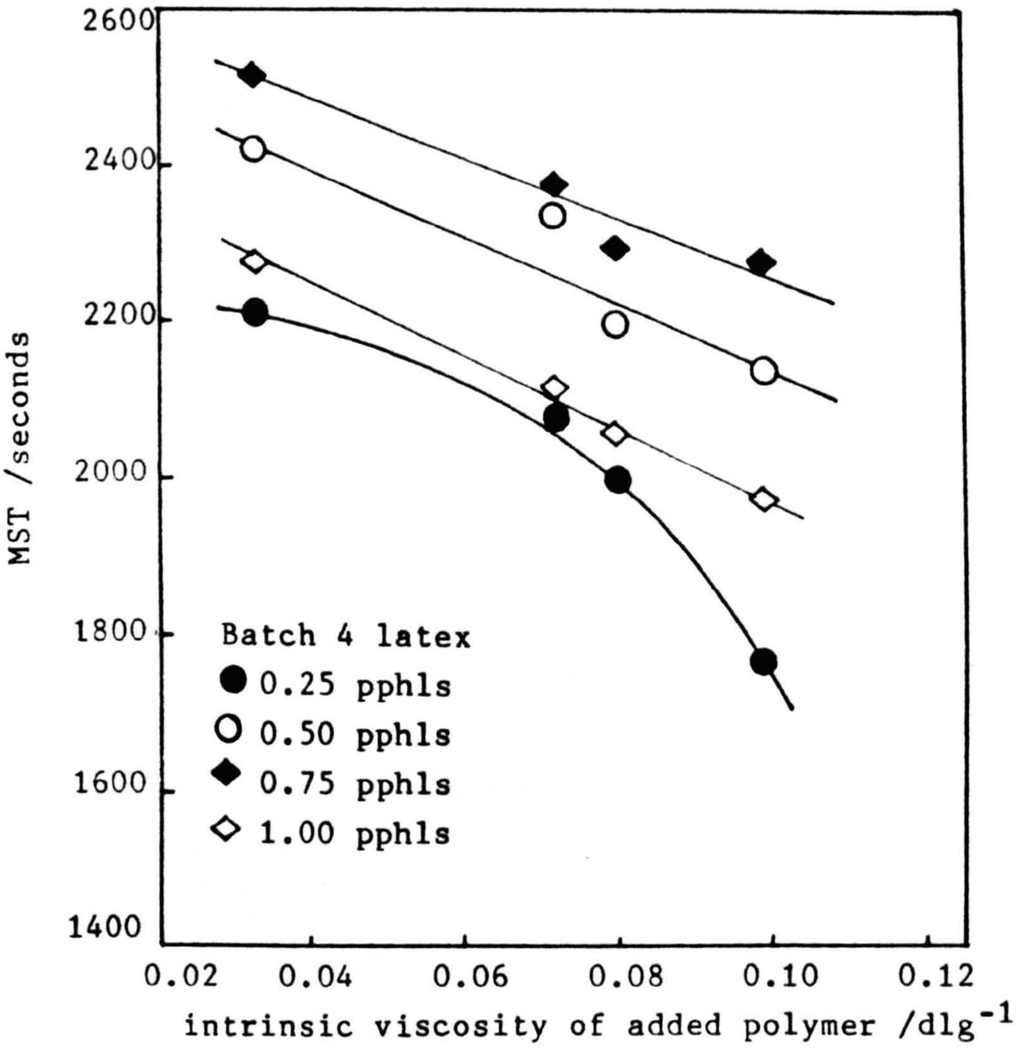


Fig. 7.21 : Effects of intrinsic viscosity of polymers of Type 2 group MAA/EHA(50:50) upon extent of enhancement of MST of NR latex at various levels of addition

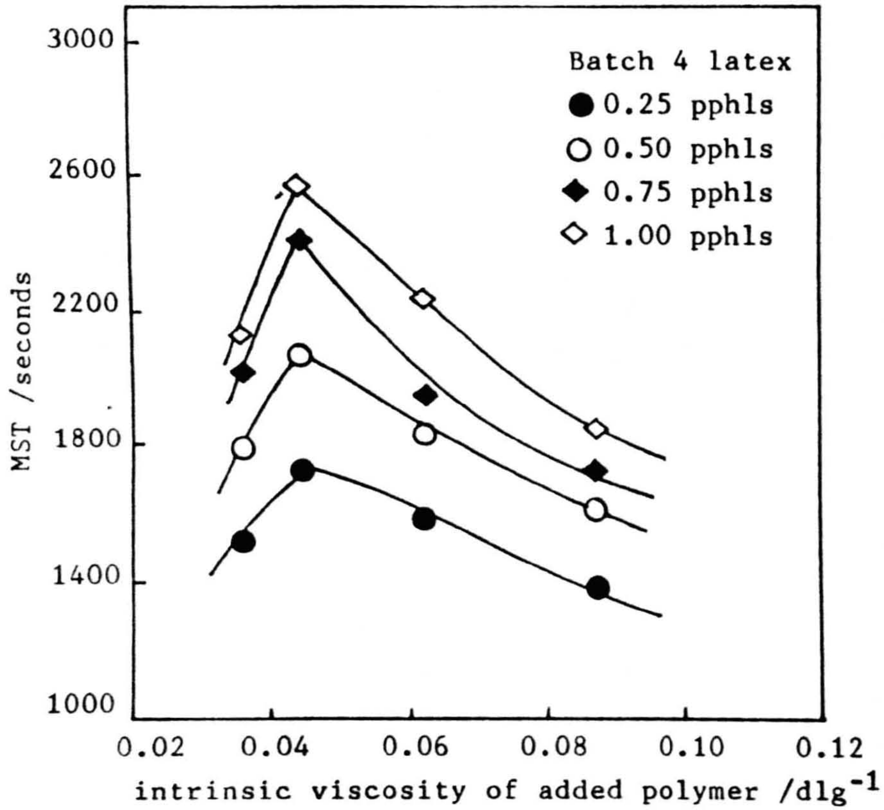


Fig. 7.22 : Effects of intrinsic viscosity of polymers of Type 2 group AA/EHA(80:20) upon extent of enhancement of MST of NR latex at various levels of addition

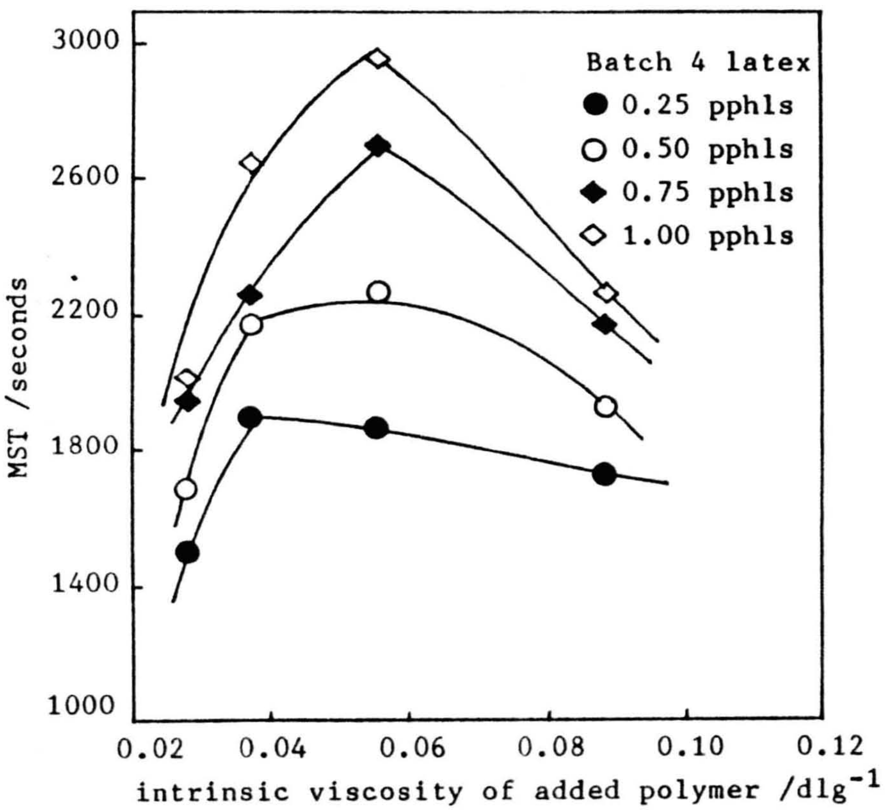


Fig. 7.23 : Effects of intrinsic viscosity of polymers of Type 2 of group AA/EHA(60:40) upon extent of enhancement of MST of NR latex at various levels of addition

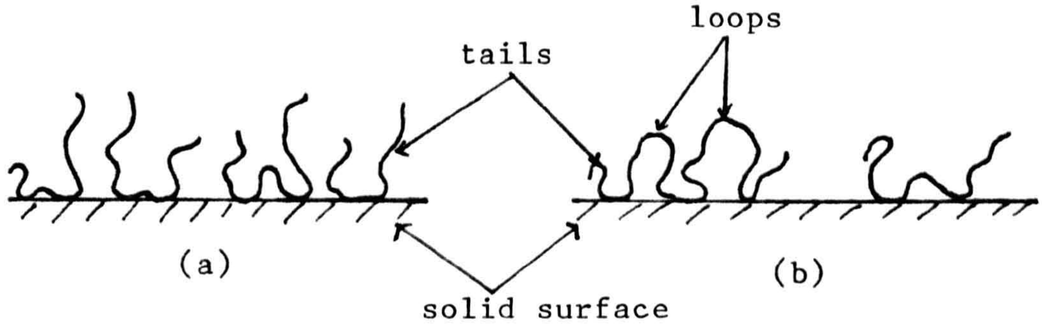


Fig. 7.24 : Schematic representation of conformation of a polymer molecule of (a) low molecular weight, and (b) high molecular weight, at the solid/liquid interface

There are then at least two possible ways why the extent of enhancement of MST decreases at high molecular weight:

a. Tails are more effective than loops in conferring MST, possibly because, on average, they extend twice as far into the dispersion medium;

b. Loops encourage structuring of indigenous adsorbed soap anions, thereby causing them to be less effective as colloid stabilisers

Of these two possibilities the first appears to be the more likely cause for the decrease in the efficiency of the added polymer in enhancing MST with increasing molecular weight.

3. As the extent of adsorption increases with increasing molecular weight, it is reasonable to expect that at any given level of addition, increase in molecular weight will eventually create a situation in which the particle surfaces are overcrowded by the added polymer. One of the consequences of this effect would be the extension of some of the hydrophobic parts of the polymer in to the dispersion medium, which would otherwise have functioned as anchor groups. Such hydrophobic parts would force the neighbouring hydrophilic moieties towards the surface of the particle as shown in Fig. 7.25, thus reducing their ability to stabilise the latex particles.

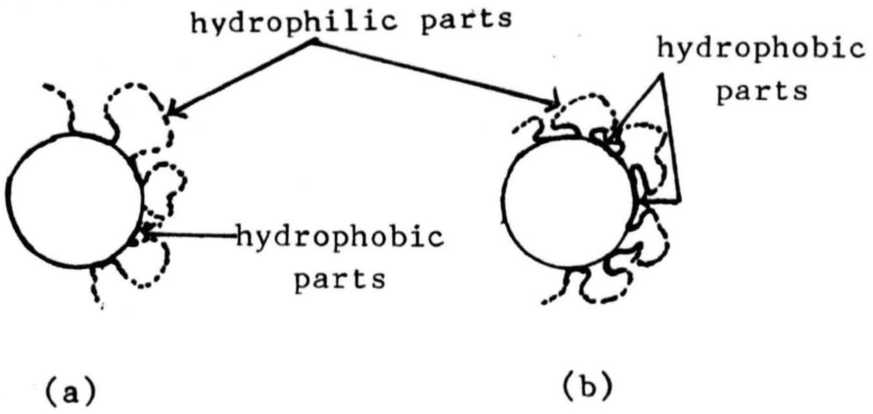


Fig. 7.25 : Schematic representation of the conformation of a polymer of (a) low molecular weight, and (b) high molecular weight, at the rubber/water interface

Explanation 1 seems to be unlikely for the following reasons:

a. It was observed that the difference between the efficiency of polymers of high molecular weight and polymers of low molecular weight in enhancing the MST is higher at high levels of addition. If it is interparticle bridging which reduces the extent of the enhancement of MST, the opposite effect would have been observed, because it is known that interparticle bridging is higher at low levels of addition.

b. If it is interparticle bridging which reduces the ability of the added polymer to enhance the MST, the trends which have been observed for the correlation between the enhancement of MST and molecular weight of the polymer, should have been the same for polymers of both Type 1 and Type 2, because it is reasonable to suppose that the polymers of high molecular weight of Type 1 are more capable of inducing interparticle bridging than the polymers of Type 2 because they are of higher molecular weight than the polymers of Type 2. However, the ability of the polymers of Type 1 to enhance MST has been found to increase progressively with increasing molecular weight of the polymer, at least over the range of molecular weights investigated.

c. The insensitivity of the MST enhancement to increasing molecular weight at high molecular weight indicates that interparticle bridging is not the cause of the reduction in MST as molecular weight is increased at lower molecular weight.

Therefore it is suggested that the reduction of the extent of the enhancement of MST with increasing molecular weight of the polymer may be a consequence of one or both of factors 2 and 3. However, on this basis it is not possible to explain why the ability of the polymers of Type 1 to enhance the MST increased progressively with increasing molecular weight. On the other hand, it is not possible to make a proper comparison of the effects of polymers of Type 1 with those of polymers of Type 2 because the polymers of Type 1 were all of considerably higher molecular weight than those of Type 2. Furthermore, in the case of polymers of Type 1 the effects arising from variation of molecular weight have been masked to some extent by the effects due to compositional heterogeneity.

As regards the effects of molecular weight upon the extent of the enhancement of viscosity, in all cases extent of the enhancement of viscosity increased with increasing molecular weight of the polymer. This effect is shown in Figs. 7.26 to 7.32. These figures show the effects of intrinsic viscosity of the added polymer upon the enhancement of viscosity of NR latex for polymers of various groups at various levels of addition. In

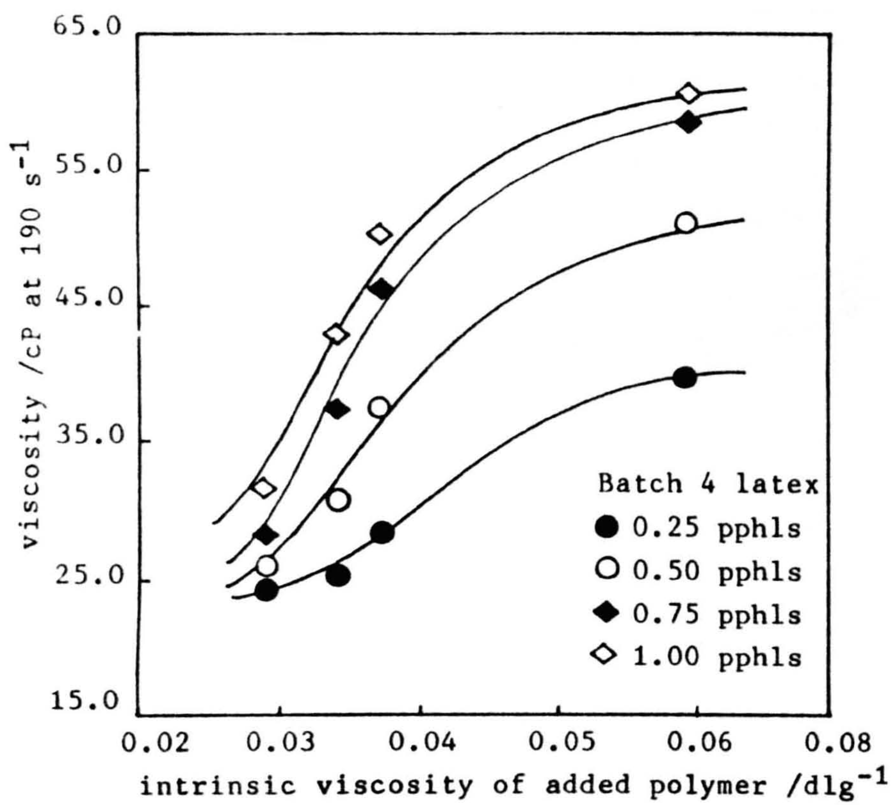


Fig. 7.26 : Effects of intrinsic viscosity of polymers of Type 2 group MAA/EHA(90:10) upon extent of enhancement of viscosity of NR latex at various levels of addition

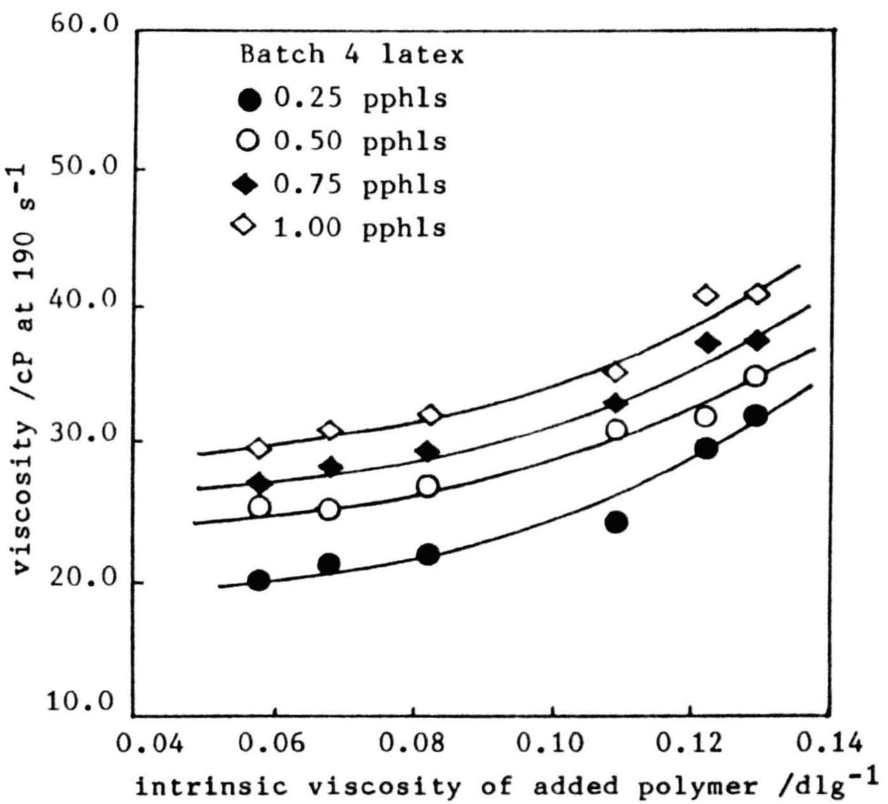


Fig. 7.27 : Effects of intrinsic viscosity of polymers of Type 2 of group MAA/EHA(80:20) upon extent of enhancement of viscosity of NR latex at various levels of addition

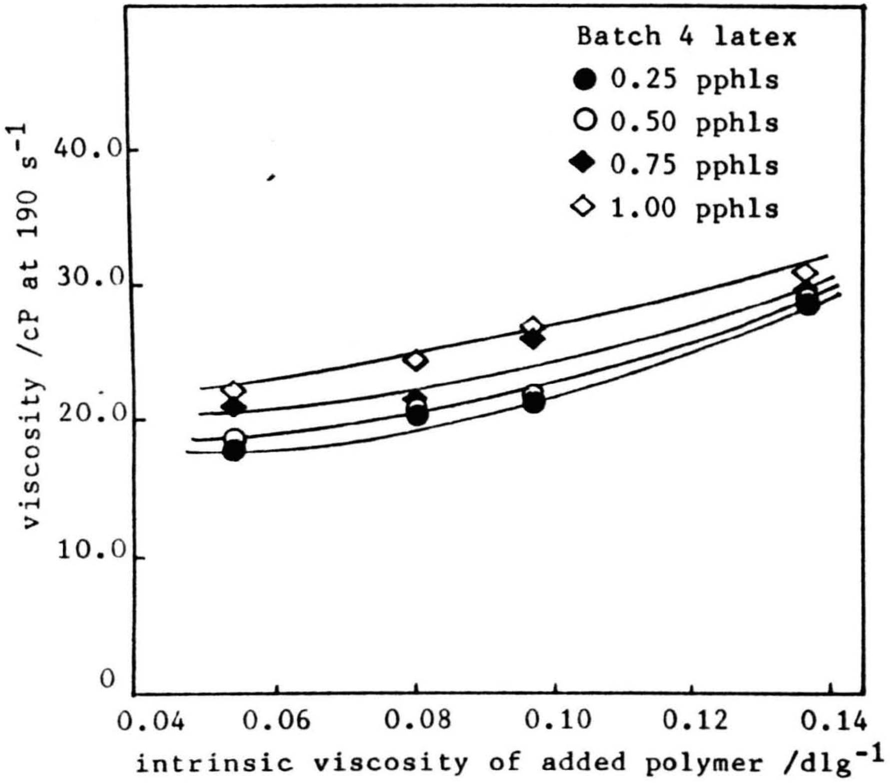


Fig. 7.28 : Effects of intrinsic viscosity of polymers of Type 2 group MAA/EHA(70:30) upon extent of enhancement of viscosity of NR latex at various levels of addition

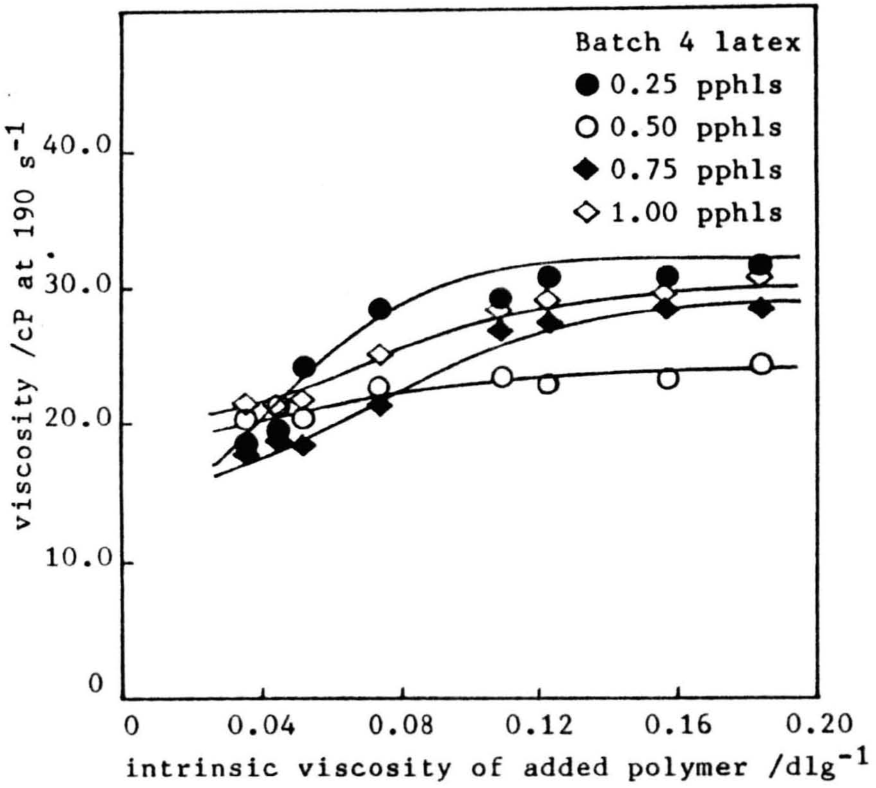


Fig. 7.29 : Effects of intrinsic viscosity of polymers of Type 2 of group MAA/EHA(60:40) upon extent of enhancement of viscosity of NR latex at various levels of addition

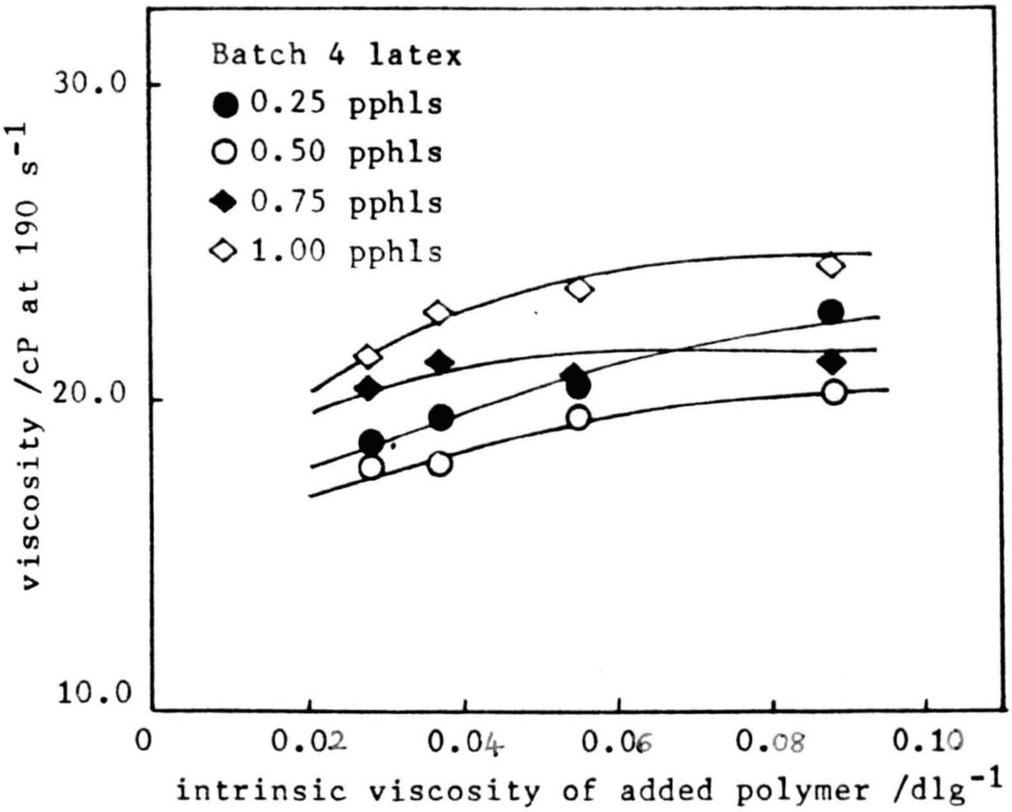


Fig. 7.30 : Effects of intrinsic viscosity of polymers of Type 2 group AA/EHA(60:40) upon extent of enhancement of viscosity of NR latex at various levels of addition

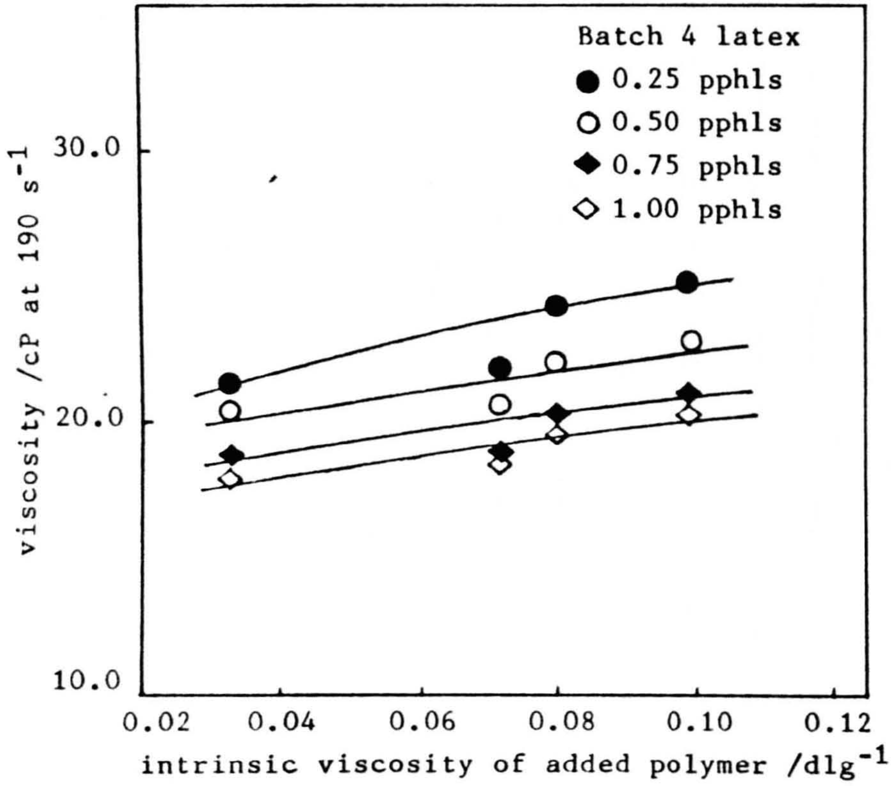


Fig. 7.31 : Effects of intrinsic viscosity of polymers of Type 2 groupMAA/EHA(50:50) upon extent of enhancement of viscosity of NR latex at various levels of addition

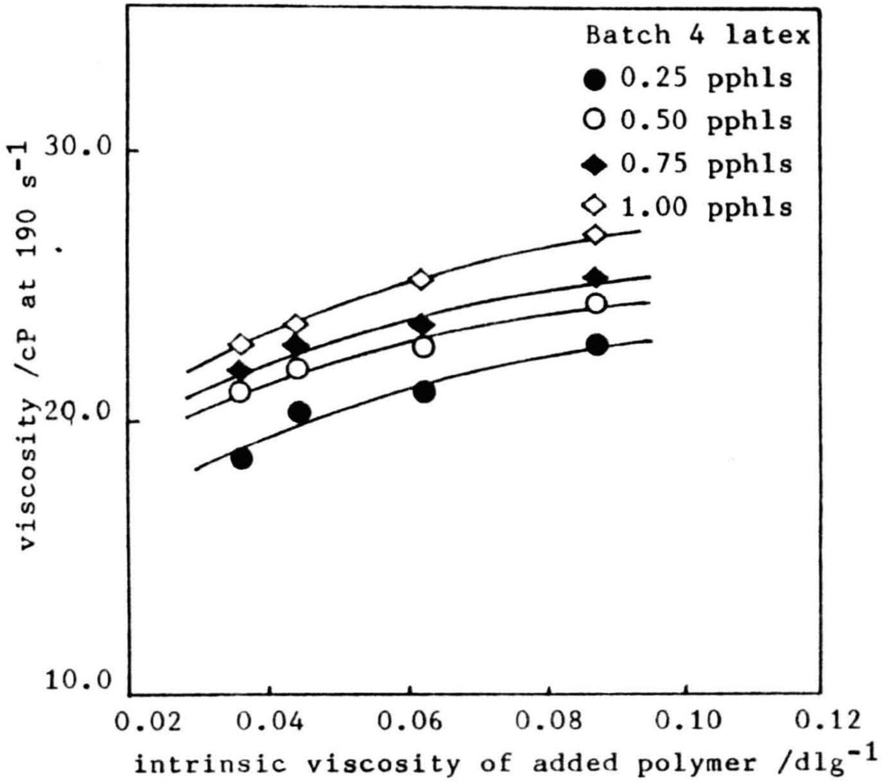


Fig. 7.32 : Effects of intrinsic viscosity of polymers of Type 2 of group AA/EHA(80:20) upon extent of enhancement of viscosity of NR latex at various levels of addition

considering the effects of molecular weight of added polymers of Type 1 upon the enhancement of viscosity of NR latex, three possible ways by which an added polymer might enhance the viscosity of NR latex were discussed (see Section 6.3.1). Similar explanations are proposed for the effects of molecular weight of the added polymers of Type 2 upon the extent of the enhancement of viscosity. However, it is also necessary to discuss the interesting and unexpected trends which have been observed for polymers of some groups, namely, groups MAA/EHA(60:40) and AA/EHA(60:40), for the variation of viscosity with the level of added polymers of Type 2. It has been observed for the polymers of these groups, as the level of added polymer is increased, the extent of the enhancement of viscosity first increased, passed through a maximum, then decreased, passed through a minimum, and then again increased. For the polymers of group MAA/EHA(50:50), the curves for the variation of viscosity with level of added polymer show only a maximum over the range of additions investigated. These observations indicate that the polymers of groups MAA/EHA(60:40), MAA/EHA(50:50) and AA/EHA(50:50) induce interparticle bridging at low levels of addition. If this is so, the inability of the polymers of all the other of groups of Type 2 to induce interparticle bridging at low levels of addition has to be explained. A possible explanation for this observation will be given in the following section, where the effects of composition upon the enhancement of MST viscosity of NR latex are discussed.

7.3.2 Effects of composition

The effects of composition of the polymers of Type 2 upon their ability to enhance the MST of NR latex were found to be basically similar to those for the polymers of Type 1. It appears that the most appropriate way to compare the effects of composition of the added polymers of Type 2 upon the enhancement of MST of NR latex is to choose the polymer which brought about the maximum enhancement of MST in each group, and compare their effects upon the MST of NR latex at each level of addition. The results of this comparison are given in Fig.7.33. Unfortunately, two compositions, namely, MAA/EHA(70:30) and MAA/EHA(50:50) had to be excluded from this comparison, because, in these two groups, polymers which would have given the maximum enhancement of MST appeared to be outside the range of molecular weights investigated.

It is apparent from Fig.7.33 that the efficiency of the polymers of Type 2 in enhancing MST increases as the hydrophobicity of the polymer is increased. However, it is not possible to state with certainty that the composition MAA/EHA(60:40) is the optimum composition for maximum enhancement of MST, because of the unavailability of the corresponding results for the composition MAA/EHA(70:30). There is little doubt that the composition MAA/EHA(50:50)

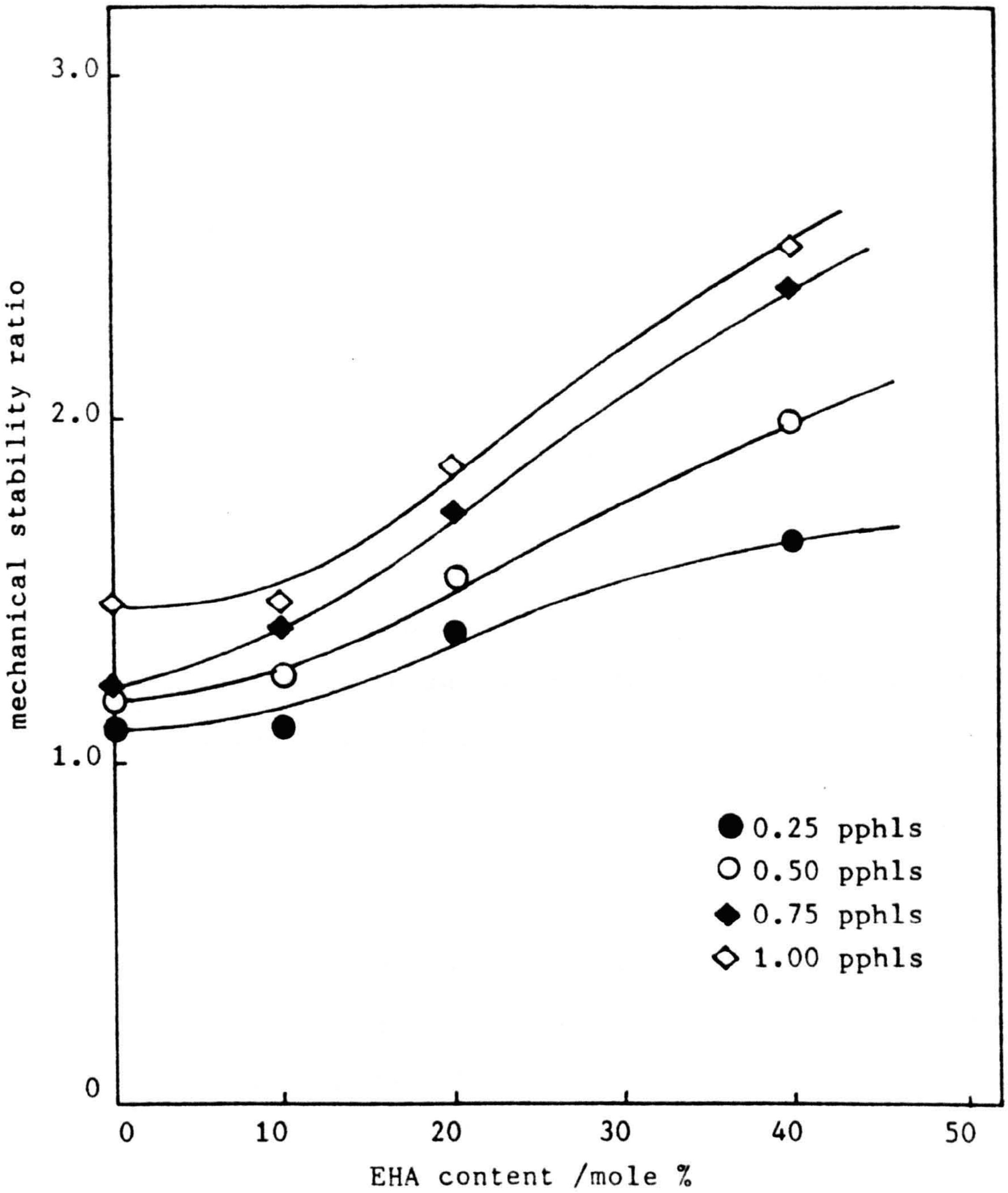


Fig. 7.33 : Effect of EHA content of added MAA/EHA copolymers of Type 2 upon enhancement of MST of NR latex at various levels of addition

would not give greater enhancement of MST than MAA/EHA(60:40), because, if it did it would be expected that the ability of the polymers of group MAA/EHA(50:50) to enhance MST should have increased with increasing level of addition. The observed opposite trend suggests that the efficiency of these polymers in enhancing MST is less than that of indigenous stabilisers, and that the decrease in the enhancement of MST with increasing level of addition is a consequence of the displacement of indigenous stabilisers by the added polymers. At this point, it should be recalled that the ability of polymers of group MAA/EHA(50:50) of Type 1 to enhance MST increased with the level of addition. It may be that the differences in the behaviour of polymers of group MAA/EHA(50:50) of Type 1 and Type 2 is a consequence of the differences in their compositional distribution which determines the extent of the adsorption of added polymer at the rubber/water interface.

The effects of composition of the polymers of Type 2 upon the enhancement of viscosity of NR latex were found to be basically similar to those of the polymers of Type 1. However, for some groups of polymers, namely, groups MAA/EHA(60:40), MAA/EHA(50:50) and AA/EHA(60:40), an indication for the occurrence of interparticle bridging at low levels of additions can be obtained from the curves of the variation of viscosity of latex with the level of addition. This observation is somewhat surprising because all the polymers of Type 2, which have been used in this investigation, are of relatively low molecular weight and hence the probability of these polymers covering more than one particle is low. However, if the unexpected trends which have been observed for the variation of viscosity of latex with the level of addition for polymers of groups MAA/EHA(60:40), MAA/EHA(50:50), and AA/EHA(60:40) are a consequence of interparticle bridging, the inability of the polymers of all the other groups of Type 2 at low levels of addition has to be explained. It is suggested that these polymers may also induce interparticle bridging perhaps to an even greater extent than the polymers of groups MAA/EHA(60:40), MAA/EHA(50:50), and AA/EHA(60:40). It is not possible to infer ability to induce interparticle bridging from curves of viscosity vs level of addition for these polymers. This may be because their high hydrophilicities reduce the adsorption at the rubber/water interface. It appears that the polymers of groups MAA/EHA(90:10), MAA/EHA(80:20), MAA/EHA(70:30) and AA/EHA(80:20) of Type 2 enhance the viscosity of NR latex mainly by dissolving in the dispersion medium. Therefore it might be expected that evidence of the ability of these polymers to induce interparticle bridging would have been obtained if their effects upon viscosity had been investigated at higher levels of addition. That is, of course, if these polymers do induce interparticle bridging of NR latex at all.

7.3.3 Effects of nature of the stabilising moieties

The ability of the added polymer to enhance the MST and viscosity of NR latex is not appreciably affected by replacing the MAA stabilising moieties by AA. This observation suggests that MAA and AA units have comparable stabilising capacities.

7.4 Results for effects of polymers of Type 2 upon zinc-oxide thickening of NR latex

Some copolymers of MAA and EHA of Type 2 were chosen for this investigation. Two polymers, namely, the polymer which brought about the highest enhancement of MST, and the polymer which brought about the lowest enhancement of MST, were selected from each group. Their effects upon the zinc-oxide thickening of NR latex were investigated at various levels of addition. The effects of similar polymers of group MAA were also investigated at the same levels of addition. In each case the progress of zinc-oxide thickening was observed over a period from 0 to 16 days.

7.4.1 Effects of polymers of low molecular weight

The effects of polymers of low molecular weight and various compositions upon the rate of zinc-oxide thickening of NR latex (Batch 4) at the 0.25 pphls level of addition is shown in Fig. 7.34(a). The corresponding variation of η/η_0 with time is shown in Fig.7.34(b). At the 0.25 pphls level of addition, some of the polymers, namely, MAA-B, MAA/EHA(90:10)0.034, MAA/EHA(60:40)0.052, and MAA/EHA(50:50)0.033 accelerated zinc-oxidethickening, whereas the others, namely, MAA/EHA(80:20)0.068 and MAA/EHA(70:30)0.054 retarded zinc-oxide thickening. The latex compound containing polymer MAA/EHA(50:50)0.033 was found to be gelled after 4 days. From these results, it appears, that as the hydrophilicity of the added polymer is increased, the rate of zinc-oxide thickening first decreases, passes through a minimum and then again increases with further increase in the hydrophobicity.

The effects of the same polymers upon the zinc-oxide thickening of NR latex (Batch 4) at the 0.50 pphls level of addition are shown in Fig. 7.35(a). The corresponding variation of η/η_0 with time is shown in Fig.7.35(b). At the 0.50 pphls level of addition the latex compound which contained polymer MAA/EHA(50:50)0.033 was found to be gelled a few minutes after compounding with zinc oxide and ammonium acetate. Some of the polymers, namely, MAA-D, MAA/EHA(90:10)0.034, and MAA/EHA(80:20)0.068 retarded zinc-oxide thickening. Their ability to retard the thickening was found to decrease with increasing hydrophilicity. The other two polymers, namely, MAA/EHA(60:40)0.052 and the MAA/EHA(70:30)0.054 accelerated zinc-oxide thickening, the effect of the former being

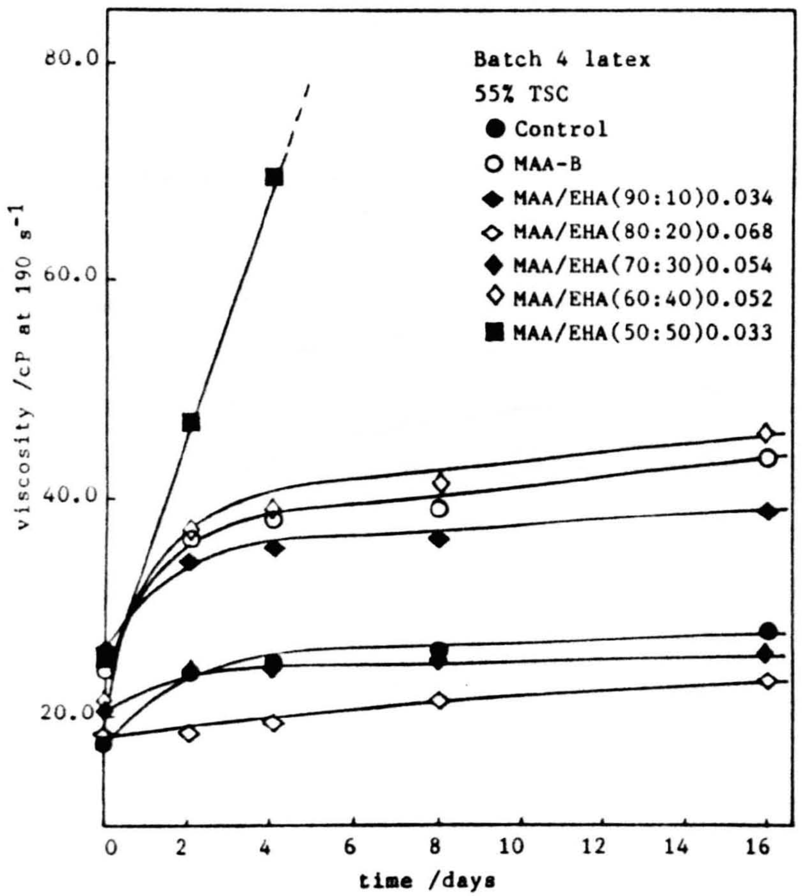


Fig. 7.34(a) : Effects of polymers of low molecular weight of Type 2 upon zinc-oxide thickening of NR latex at 0.25 pphls level of addition

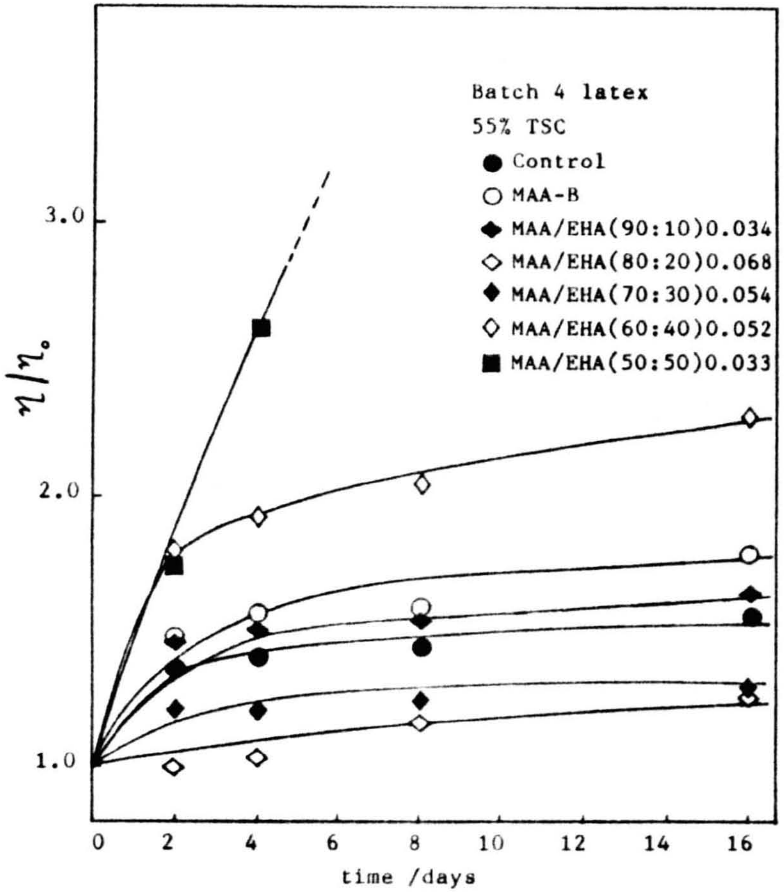


Fig. 7.34(b) : Variation of η/η_o with time for NR latex containing polymers of low molecular weight of Type 2 at 0.25 pphls level of addition

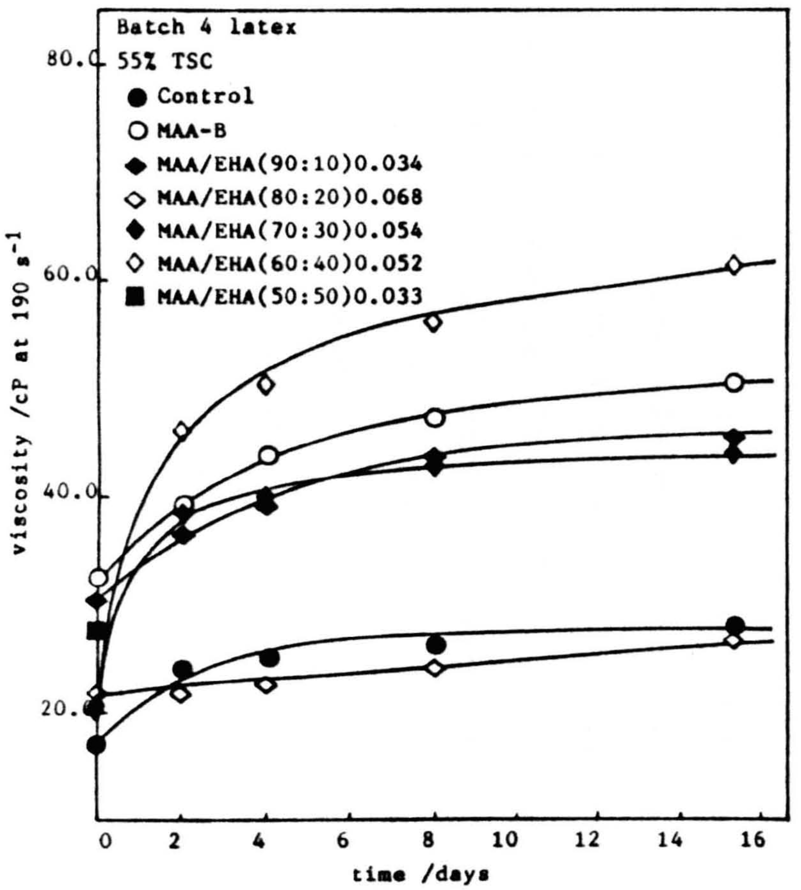


Fig. 7.35(a) : Effects of polymers of low molecular weight of Type 2 upon zinc-oxide thickening of NR latex at 0.50 pphls level of addition

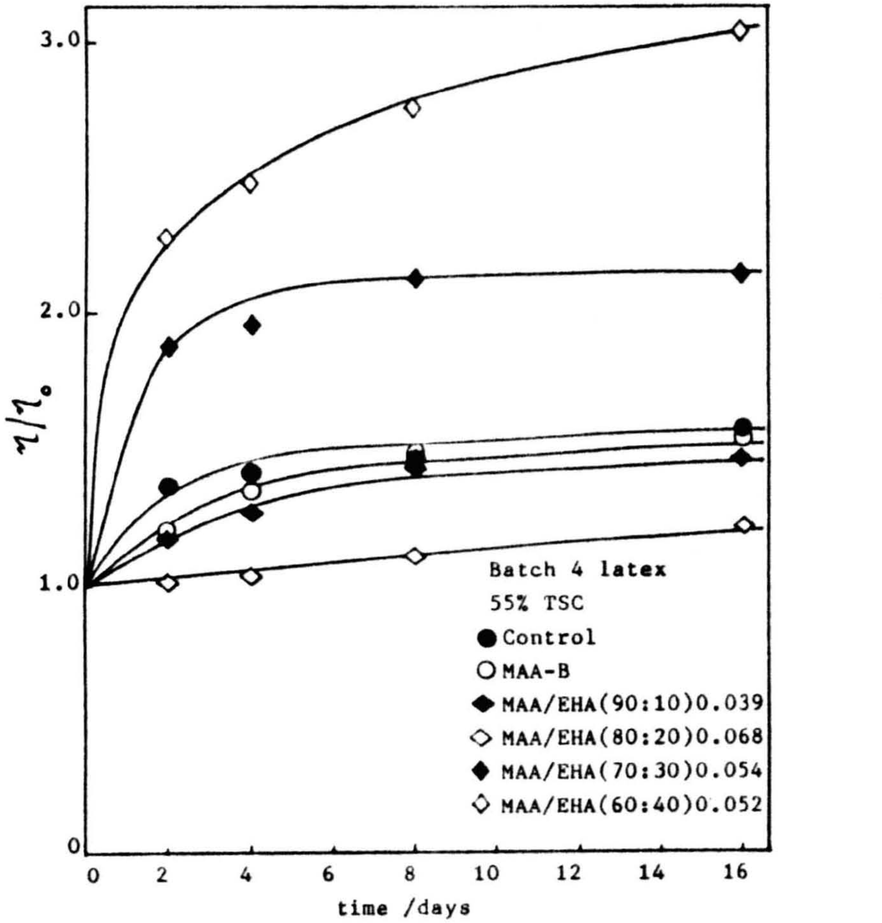


Fig. 7.35(b) : Variation of η/η_o with time for NR latex containing polymers of low molecular weight of Type 2 at 0.50 pphls level of addition

greater than that of the latter.

The effects of the same polymers upon the zinc-oxide thickening of NR latex (Batch 4) at the 0.75 pphls level of addition are shown in Fig. 7.36(a). The corresponding variation of η/η_0 with time is shown in Fig. 7.36(b). At the 0.75 pphls level of addition the latex sample which contained polymer MAA/EHA(50:50)0.033 gelled immediately after compounding with zinc-oxide and ammonium acetate, and the latex sample which contained polymer MAA/EHA(60:40)0.052 gelled a few minutes after compounding. The polymers MAA-D, MAA/EHA(90:10)0.034, MAA/EHA(80:20)0.068 greatly retarded zinc-oxide thickening, whereas the polymer MAA/EHA(70:30)0.054 accelerated zinc-oxide thickening.

7.4.2 Effects of polymers of high molecular weight

The effects of polymers of high molecular weight and various composition upon the rate of zinc-oxide thickening of NR latex (Batch 4) at the 0.25 pphls level of addition are shown in Fig. 7.37(a). The corresponding variation of η/η_0 with time is shown in Fig. 7.37(b). At the 0.25 pphls level of addition, the effects of polymers of high molecular weight upon zinc-oxide thickening were found to be generally similar to those of the corresponding polymers of low molecular weight, at the same level of addition. However, the efficiencies of the more

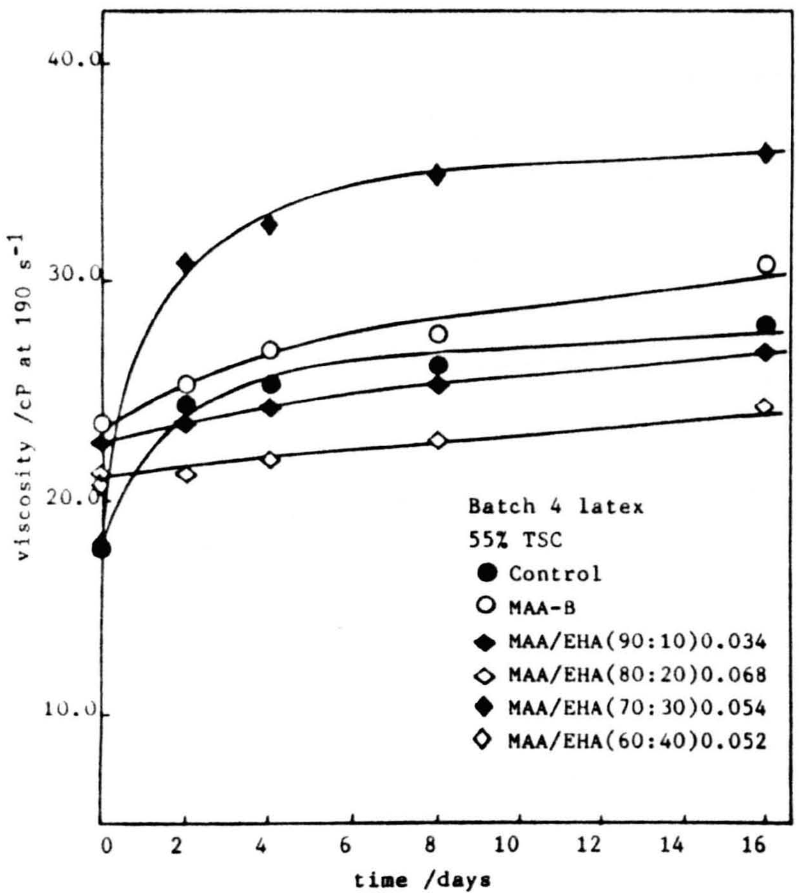


Fig. 7.36(a) : **Effects of polymers of low molecular weight of Type 2 upon zinc-oxide thickening of NR latex at 0.75 pphls level of addition**

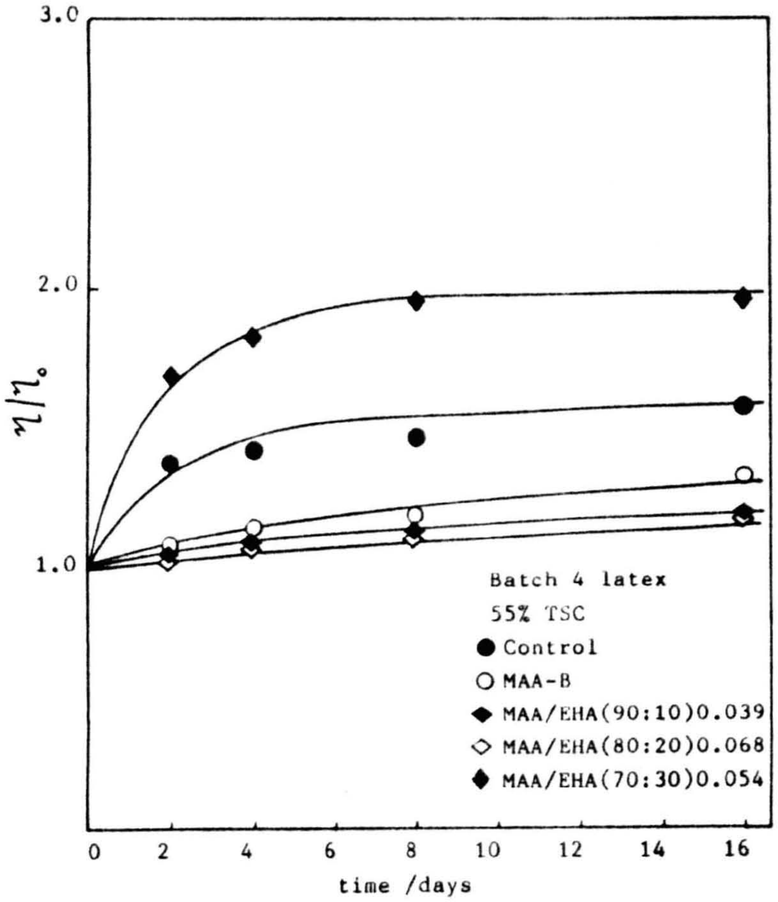


Fig. 7.36(b) : **Variation of η/η_0 with time for NR latex containing polymers of low molecular weight of Type 2 at 0.75 pphls level of addition**

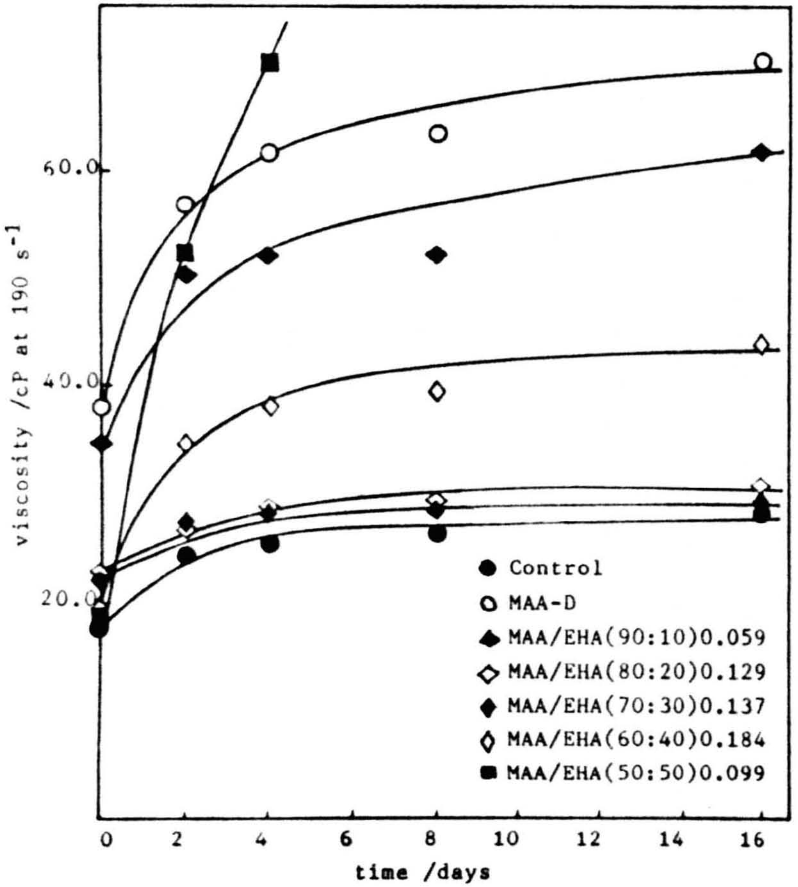


Fig. 7.37(a) : Effects of polymers of high molecular weight of Type 2 upon zinc-oxide thickening of NR latex at 0.25 pphls level of addition

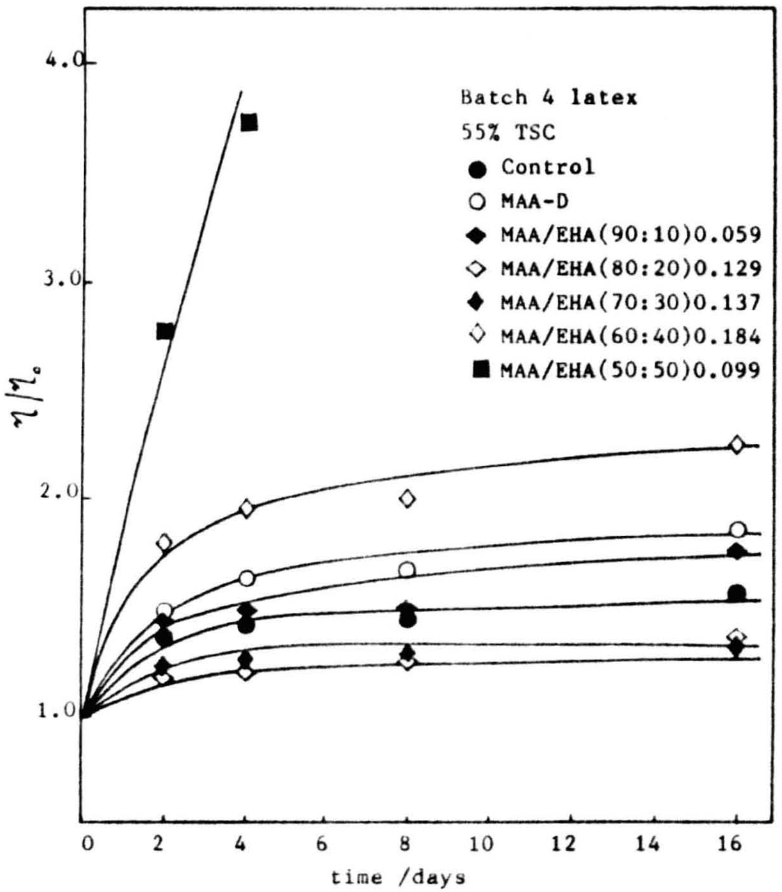


Fig. 7.37(b) : Variation of η/η_o with time for NR latex containing polymers of high molecular weight of Type 2 at 0.25 pphls level of addition

hydrophobic polymers in enhancing the thickening were found to be higher those of the corresponding polymers of low molecular weights. Thus latex compound which contained polymer MAA/EHA(50:50)0.099 gelled after 4 days.

The effects of the same polymers upon the zinc-oxide thickening of NR latex (Batch 4) at the 0.50 pphls of addition are shown in Fig. 7.38(a). The corresponding variation of η/η_0 with time is shown in Fig. 7.38(b). At the 0.50 pphls level of addition the effects of polymers of high molecular weight upon zinc-oxide thickening were found to be similar to those of the corresponding polymers of low molecular weight at the same level of addition. Again, the efficiencies of the more hydrophobic polymers in enhancing zinc-oxide thickening was found to be much higher than that of the corresponding polymers of low molecular weight. Thus the latex compound which contained polymer MAA/EHA(60:40)0.184 gelled after 8 days, and the latex compound which contained polymer MAA/EHA(50:50)0.099 gelled soon after compounding with zinc-oxide and ammonium acetate.

The effects of the same polymers upon the zinc-oxide thickening of NR latex (Batch 4) at the 0.75 pphls level of addition are shown in Fig. 7.39(a). The corresponding variations of η/η_0 with time is shown in Fig. 7.39(b). At the 0.75 pphls level of addition, the latex compound which contained polymer MAA/EHA(50:50)0.099

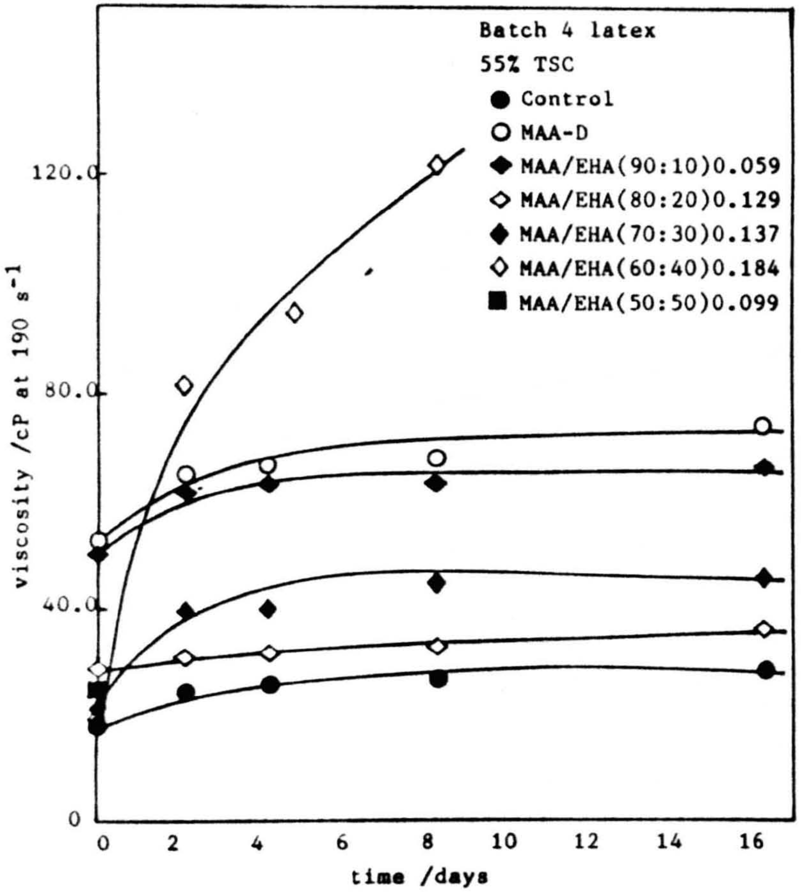


Fig. 7.38(a) : **Effects of polymers of high molecular weight of Type 2 upon zinc-oxide thickening of NR latex at 0.50 pphls level of addition**

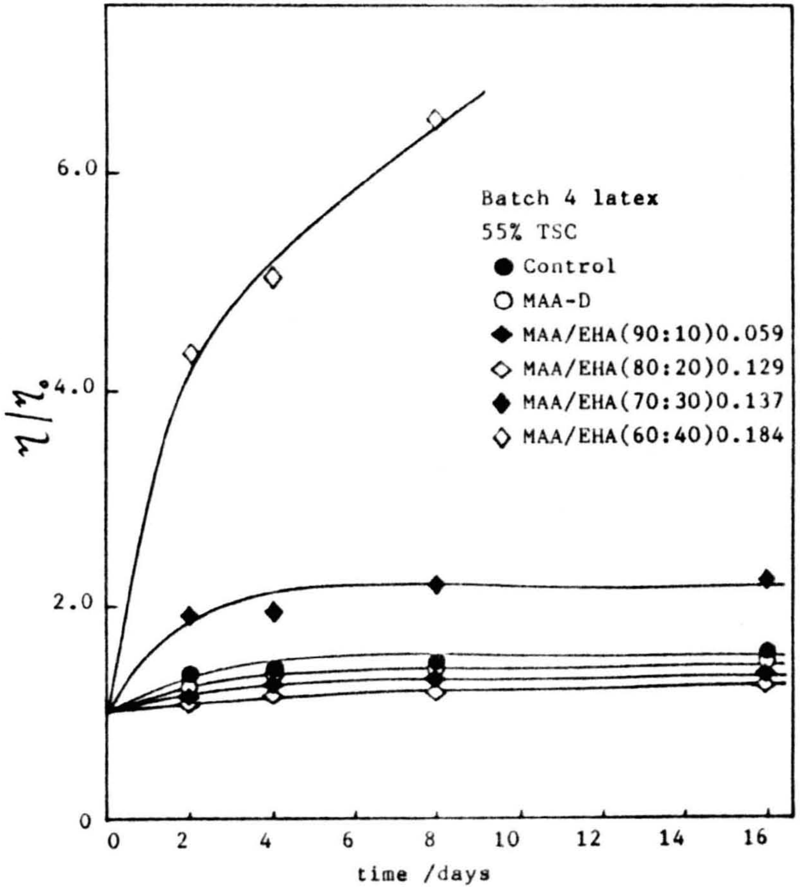


Fig. 7.38(b) : **Variation of η/η_0 with time for NR latex containing polymers of high molecular weight of Type 2 at 0.50 pphls level of addition**

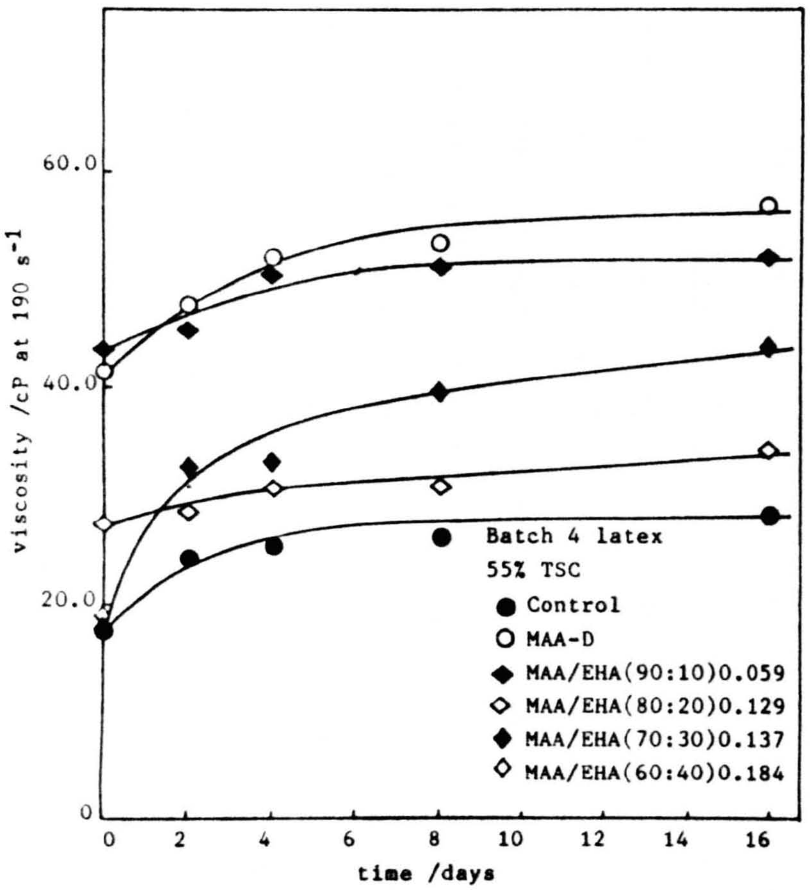


Fig. 7.39(a) : **Effects of polymers of high molecular weight of Type 2 upon zinc-oxide thickening of NR latex at 0.75 pphls level of addition**

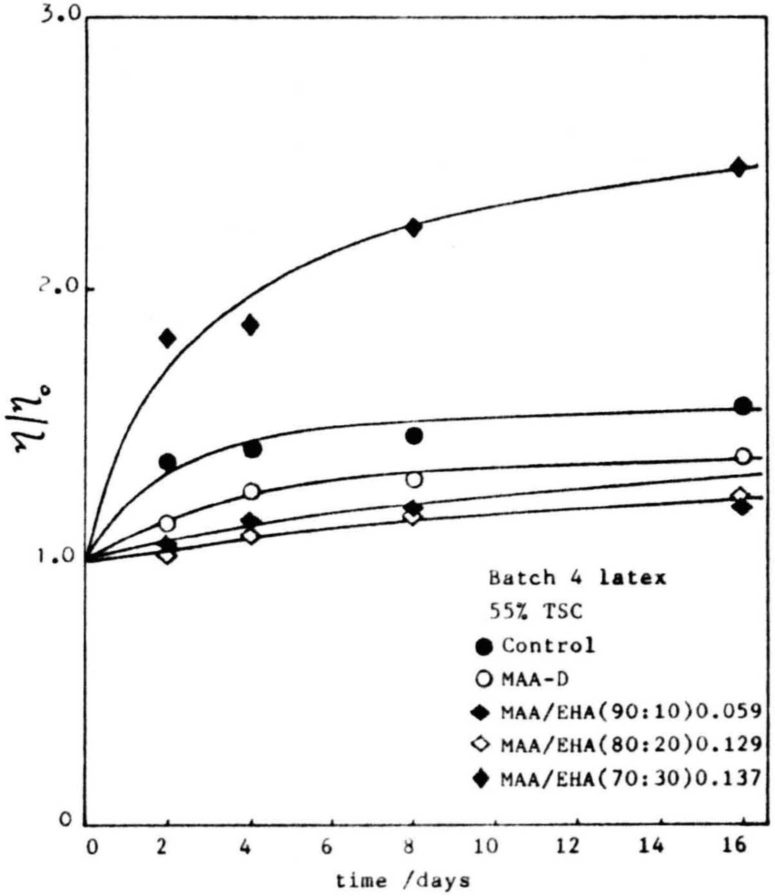


Fig. 7.39(b) : **Variation of η/η_0 with time for NR latex containing polymers of high molecular weight of Type 2 at 0.75 pphls level of addition**

gelled immediately after compounding with zinc oxide and ammonium acetate. The latex compound which contained polymer MAA/EHA(60:40)0.184 gelled a few minutes after compounding. The efficiency of polymer MAA/EHA(70:30)0.137 in accelerating zinc-oxide thickening was found to be higher than that of the polymer MAA/EHA(70:30)0.054.

7.5 Discussion of effects of polymers of Type 2 upon zinc-oxide thickening

7.5.1 Effects of molecular weight

It is apparent from the results presented in Sections 7.4.1 and 7.4.2 that the polymers of high molecular weight are in general more effective in accelerating the zinc-oxide thickening or NR latex than are the corresponding polymers of low molecular weight. Figs. 7.40 (a), (b) and (c) show the variation of the η/η_o after 16 days, i.e., η_{16}/η_o for polymers of various compositions of both high and low molecular weight at various levels of addition. It is apparent from Fig.7.40 (a) that the effects of polymers of both low and high molecular weights are the same at the 0.25 pphls level of addition. However, at the 0.50 pphls and 0.75 pphls levels of addition the ratio η_{16}/η_o was unmeasurable for polymers of high molecular weight of composition MAA/EHA(60:40) due to the rapid gelation of latex compounds. This relatively high efficiency of polymers of high molecular weight in

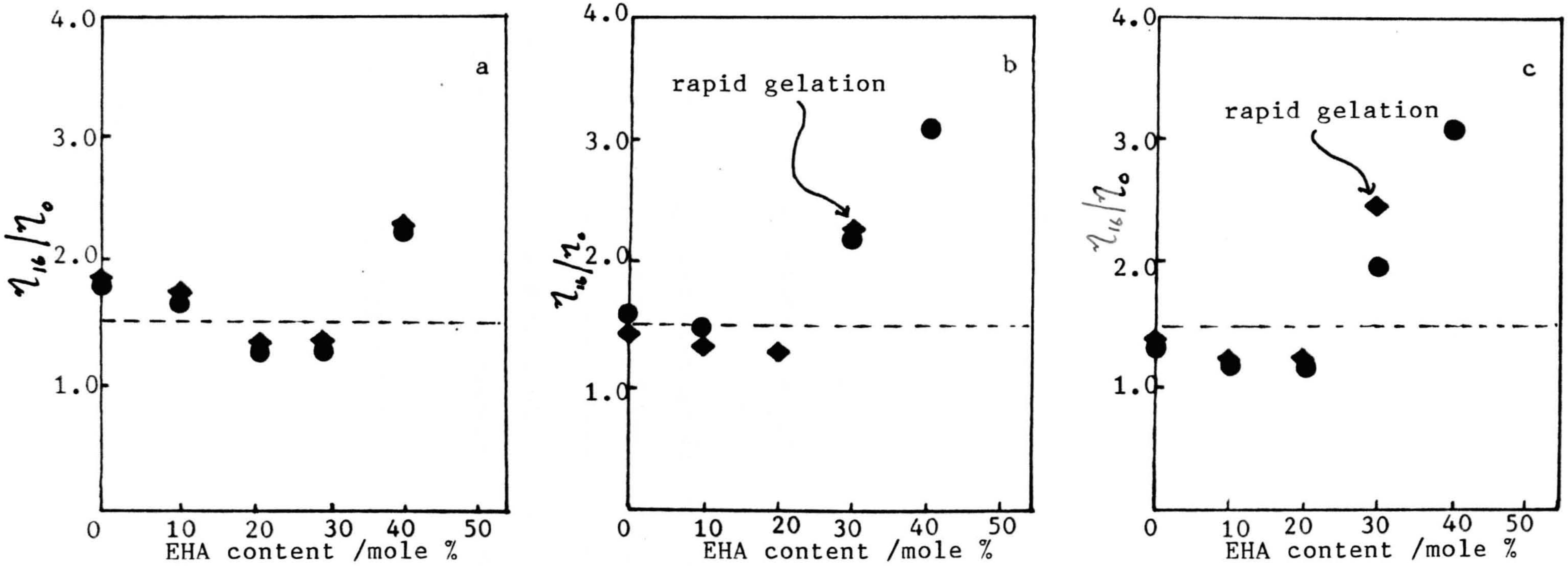


Fig. 7.40 : Comparison of the effects of polymers of low molecular weight (●) and high molecular weight (◆) of Type 2 upon zinc-oxide thickening of NR latex at various levels of addition

a - 0.25 pphls b - 0.50 pphls c - 0.75 pphls ----- control accelerating the zinc-oxide thickening of NR latex is not surprising for the following reasons:

1. The polymers of high molecular weight chosen for this investigation have been observed to be less effective in enhancing the MST of NR latex than the corresponding polymers of low molecular weight.

2. The polymers of high molecular weight are more capable of adsorbing at the rubber/water interface than the corresponding polymers of low molecular weight and hence of forming complexes with proteinaceous substances whose zinc derivatives are relatively unhydrated.

However, it appears that as in the case of polymers of Type 1 the molecular weight of the polymer has relatively little influence upon the zinc-oxide thickening of NR latex when compared with the effect of the composition of the polymer, at least for the two molecular weights investigated.

7.5.2 Effects of composition

The variations of η_{16}/η_0 with composition for polymers of high molecular weight are shown in Figs. 7.41(a) and 7.41(b) respectively. It is apparent from these figures that the effectiveness of the added polymer

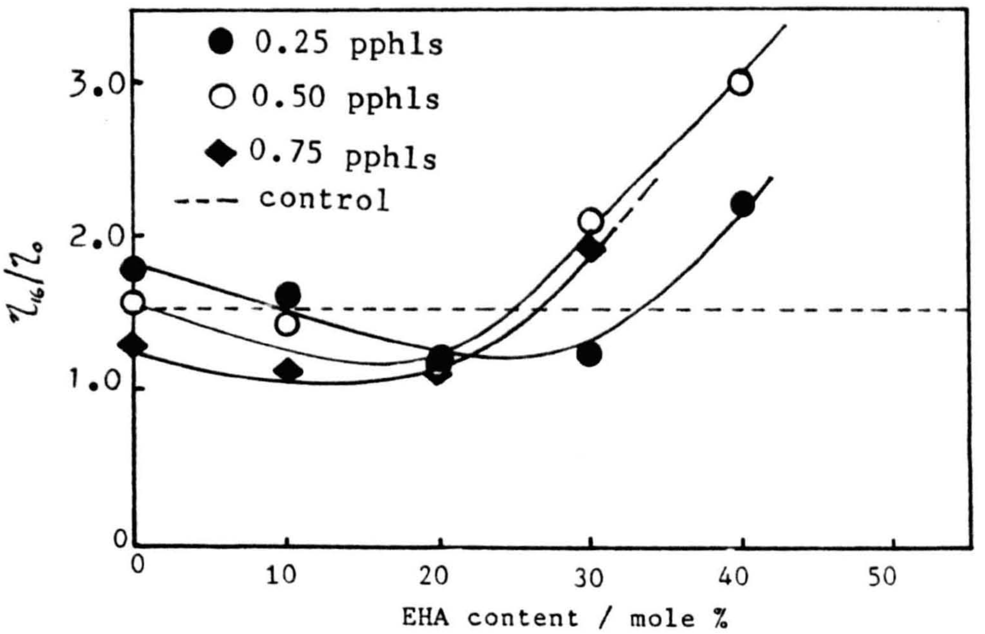


Fig. 7.41(a) : Variation of η_{16}/η_0 with composition for polymers of low molecular weight of Type 2 at various levels of addition

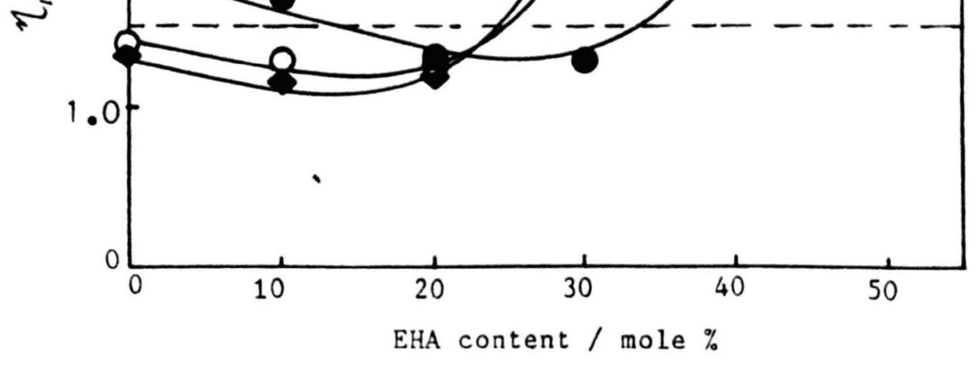
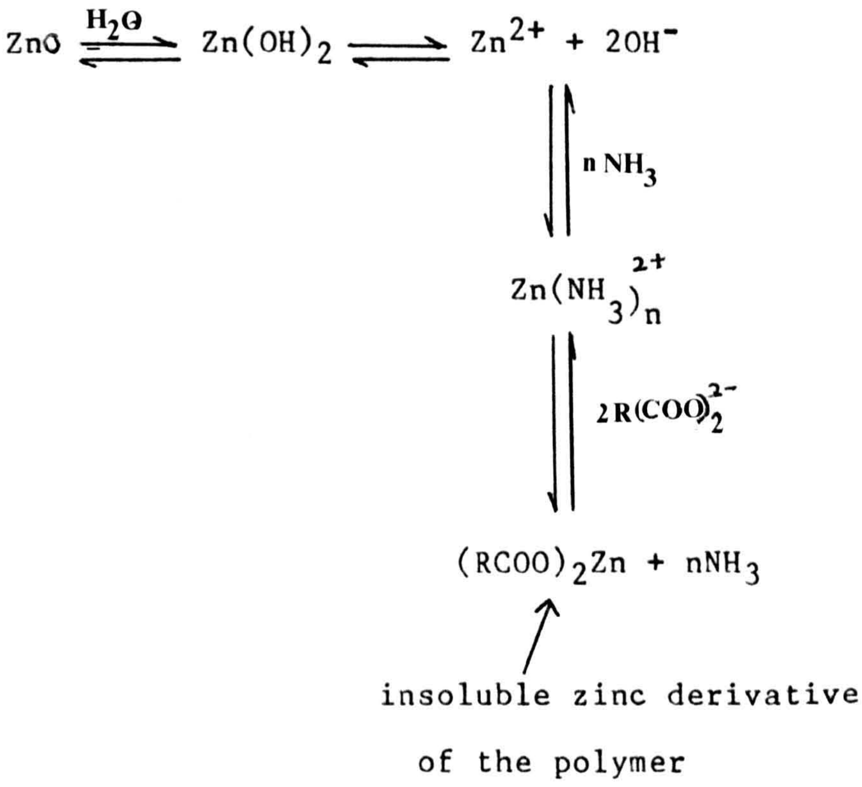


Fig. 7.41(b) : Variation of η_{16}/η_0 with composition for polymers of high molecular weight of Type 2 at various levels of addition

in accelerating zinc-oxide thickening of NR latex first decreases, passes through a minimum, and then increases as its hydrophobicity is increased. Similar results have been reported by Pok(132) for the effects of added MAA/DDA copolymers upon the zinc-oxide thickening of NR latex. The initial decrease in the rate of zinc-oxide thickening with increasing polymer hydrophobicity suggests that more hydrophilic polymers may accelerate zinc-oxide thickening by a mechanism which differs from that whereby more hydrophobic polymers accelerate zinc-oxide thickening. One possibility is that these more hydrophilic polymers accelerate the zinc-oxide thickening of NR latex by forming insoluble derivatives with zinc ions. The reactions which lead to the formation of insoluble zinc derivatives of the polymer can be outlined as follows:



This explanation seems to be plausible as all the polymers investigated have been shown to be capable of forming insoluble derivatives with zinc ions, (see Section 5.12). However, it appears that as the hydrophobicity of polymer increases, the ability of the polymer to enhance the colloid stability of latex outweighs its ability to sensitise latex towards zinc ions. The subsequent increase in the ability of the added polymer to accelerate zinc-oxide thickening with further increase in hydrophobicity can be attributed to the increase in its tendency to adsorb at the rubber/water interface, and thereby to form complexes with proteinaceous substances whose zinc derivatives are relatively unhydrated.

It is interesting to note that the effects of the level of addition upon the variation of η/η_0 with time for the more hydrophilic polymers is different from that observed for the more hydrophobic polymers. The effects of the level of addition upon the variation of η/η_0 with time are shown in Figs. 7.42 to 7.53 for each polymer separately. It is apparent from these figures that the ability of polymers of both high and low molecular weight of groups MAA, MAA/EHA(90:10), and MAA/EHA(80:20) to accelerate zinc-oxide thickening decreases as the level of addition is increased. On the other hand, the ability of polymers of both low and high molecular weight of groups MAA/EHA(70:30), MAA/EHA(60:40) and MAA/EHA(50:50) to accelerate zinc-oxide thickening increases as the level of

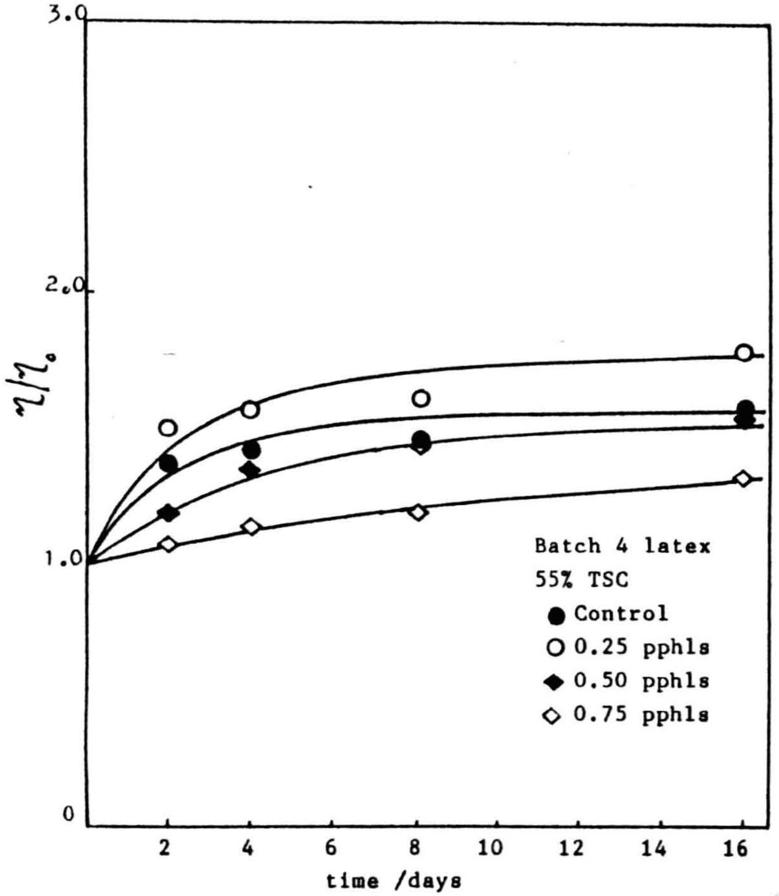


Fig. 7.42 : Variation of η/η_0 with time for NR latex containing polymer MAA-B at various levels of addition

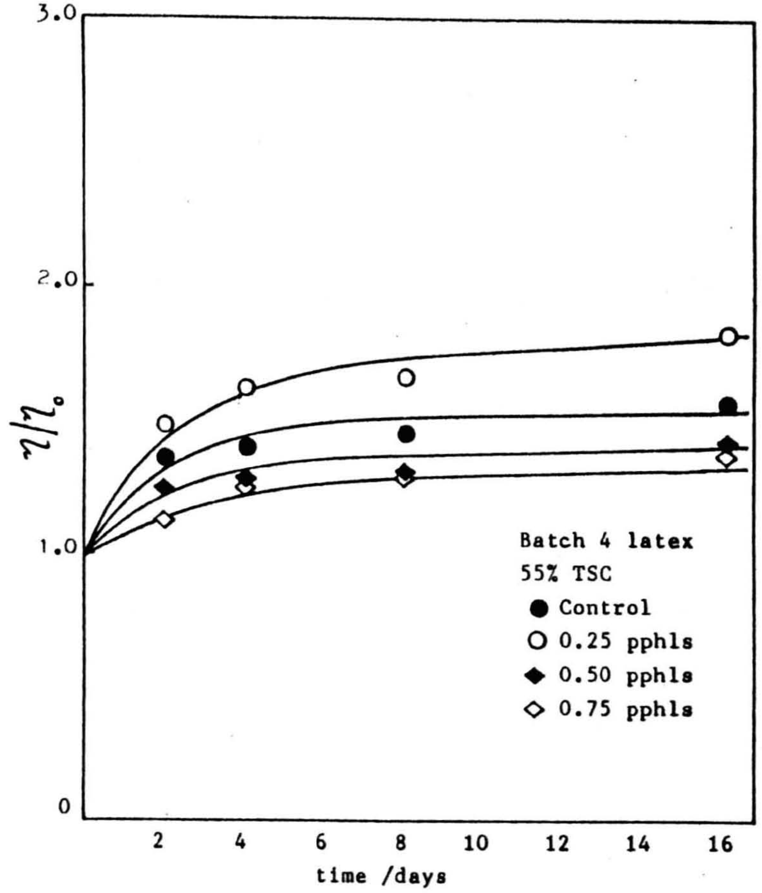


Fig. 7.43 : Variation of η/η_0 with time for NR latex containing polymer MAA-D at various levels of addition

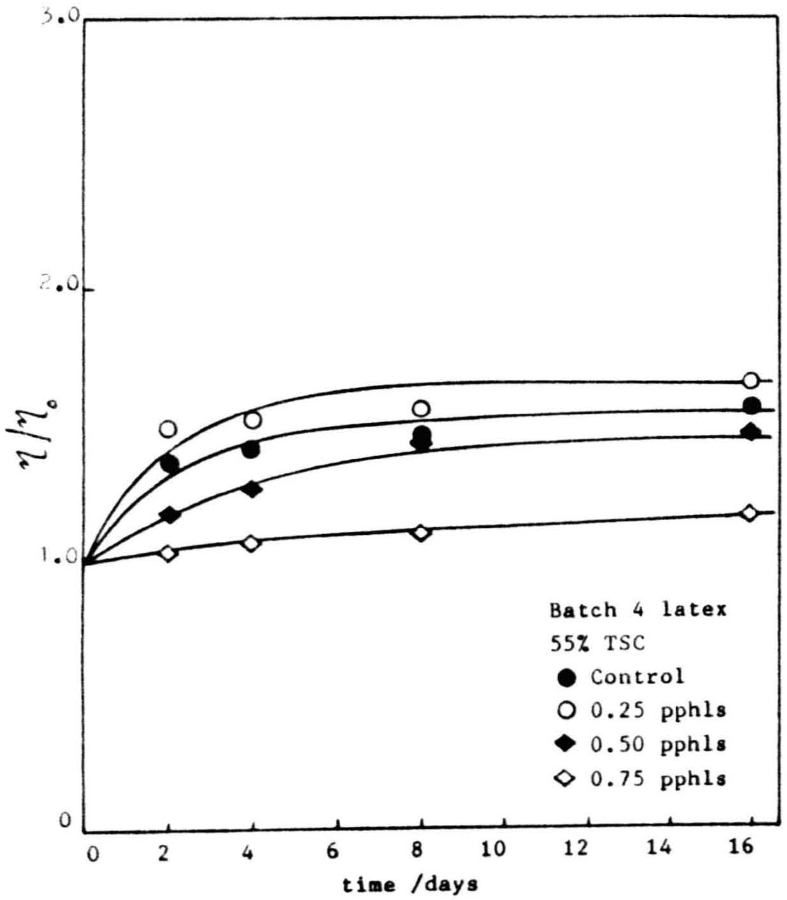


Fig. 7.44 : Variation of η/η_o with time for NR latex containing polymer MAA/EHA(90:10)0.034 at various levels of addition

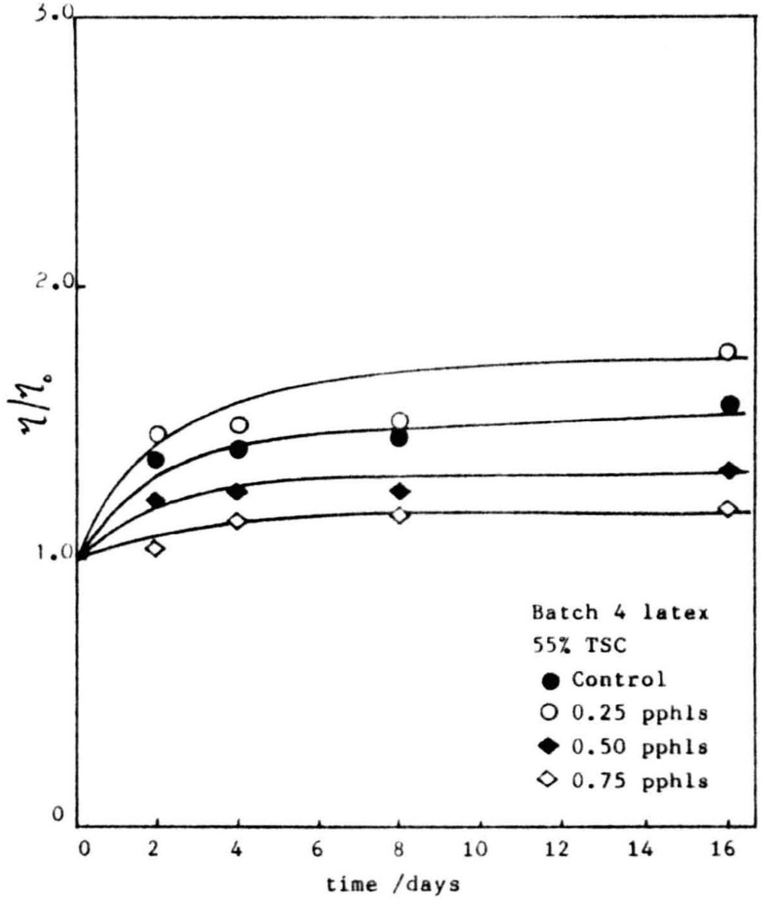


Fig. 7.45 : Variation of η/η_o with time for NR latex containing polymer MAA/EHA(90:10)0.059 at various levels of addition

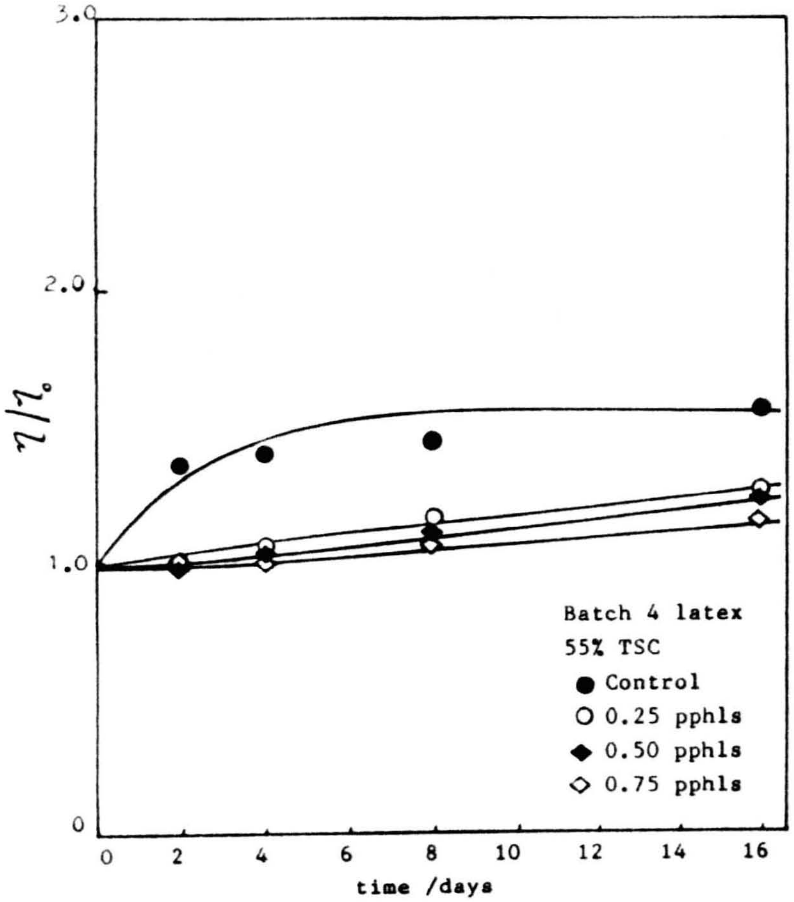


Fig. 7.46 : Variation of η/η_o with time for NR latex containing polymer MAA/EHA(80:20)0.068 at various levels of addition

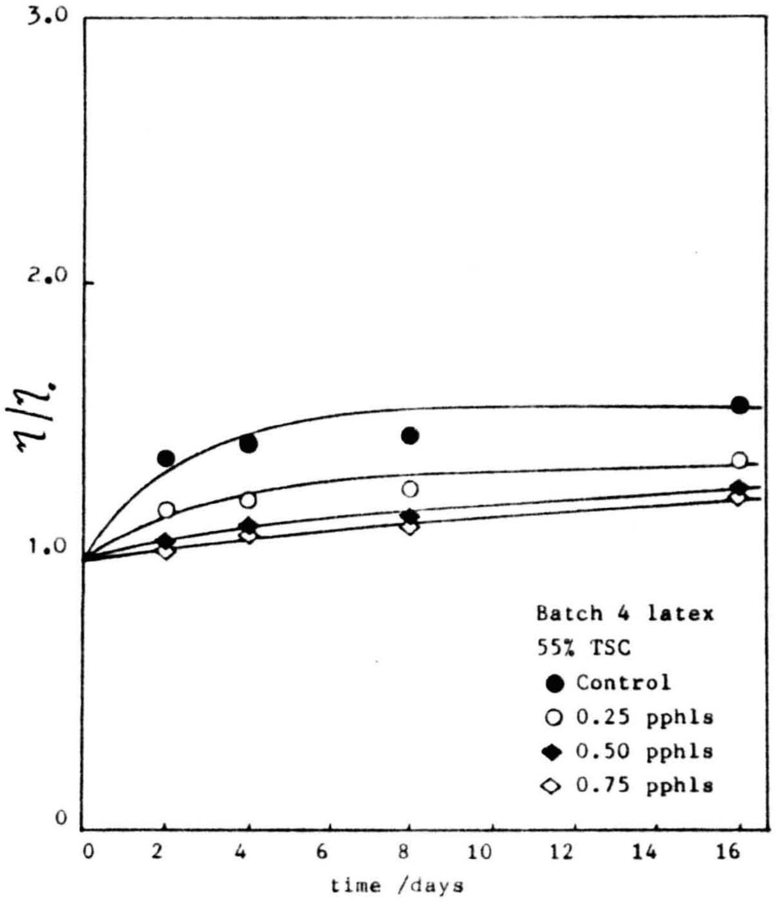
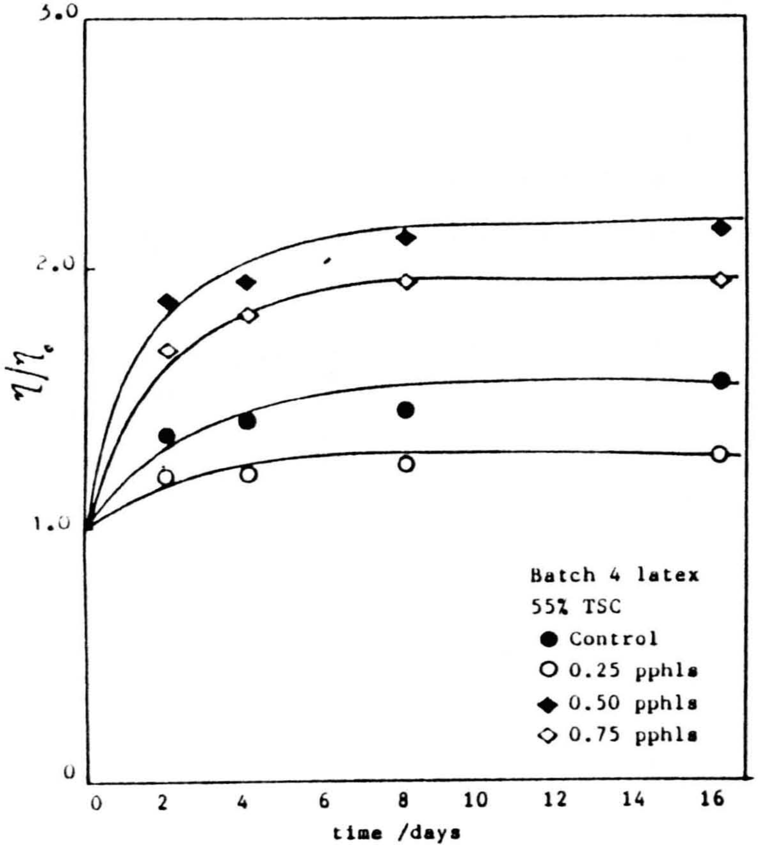


Fig. 7.47 : Variation of η/η_o with time for NR latex containing polymer MAA/EHA(80:20)0.129 at various levels of addition

293



Fi Fig. 7.48 : Variation of η/η_0 with time for NR latex containing polymer MAA/EHA(70:30)0.054 at various levels of addition

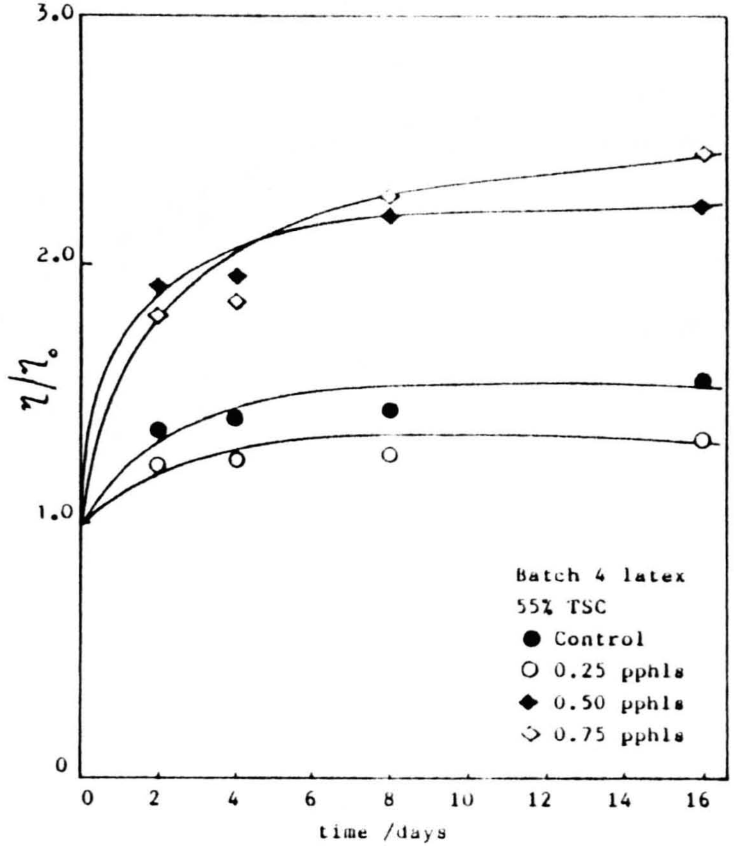


Fig. 7.49 : Variation of η/η_0 with time for NR latex containing polymer MAA/EHA(70:30)0.137 at various levels of addition

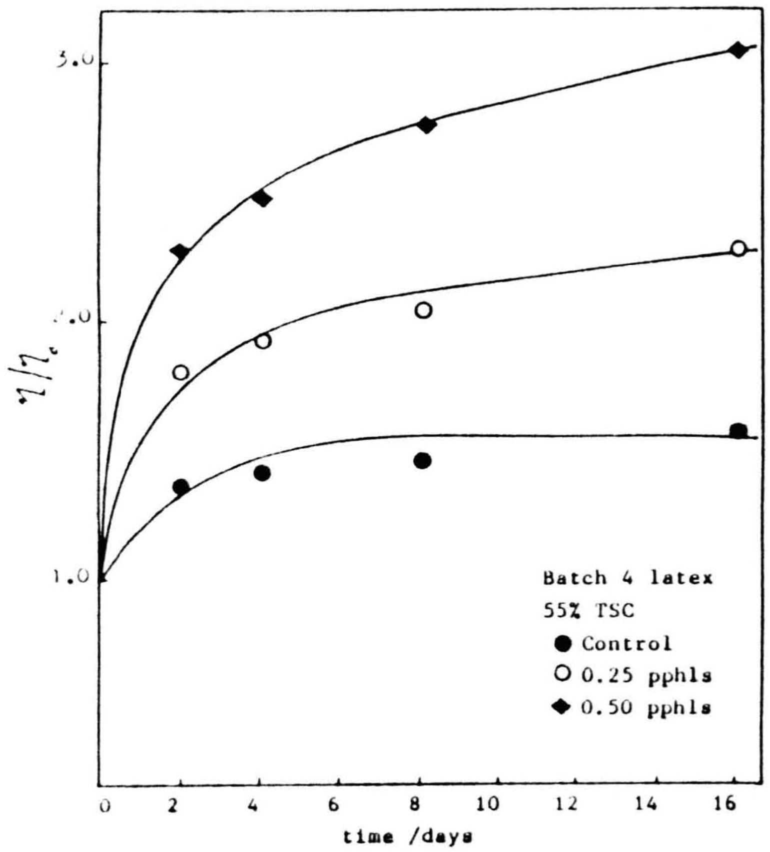


Fig. 7.50 : Variation of η/η_o with time for NR latex containing polymer MAA/EHA(60:40)0.052 at various levels of addition

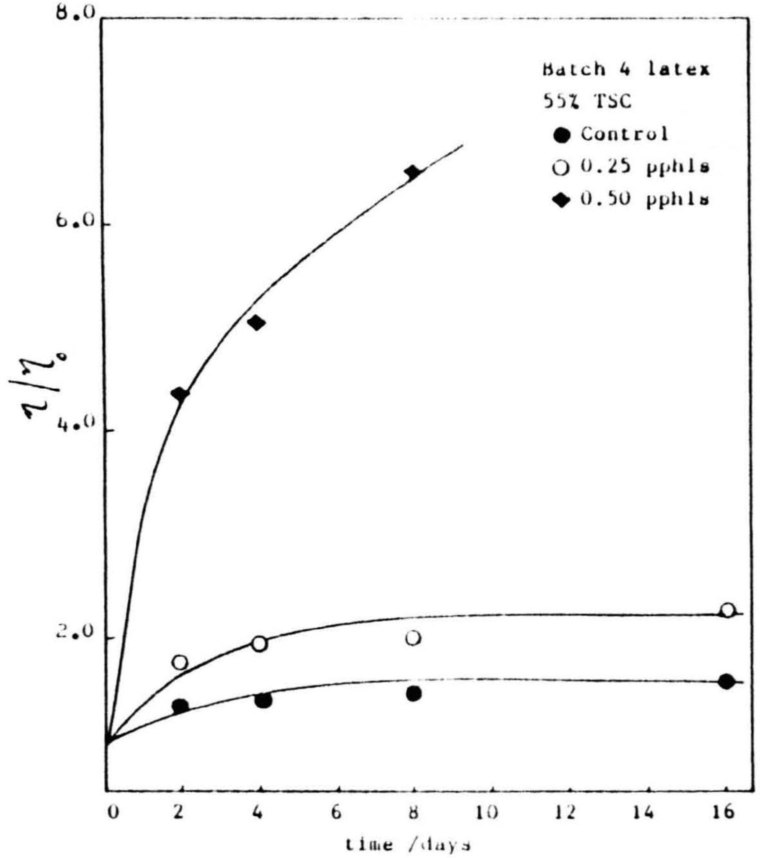
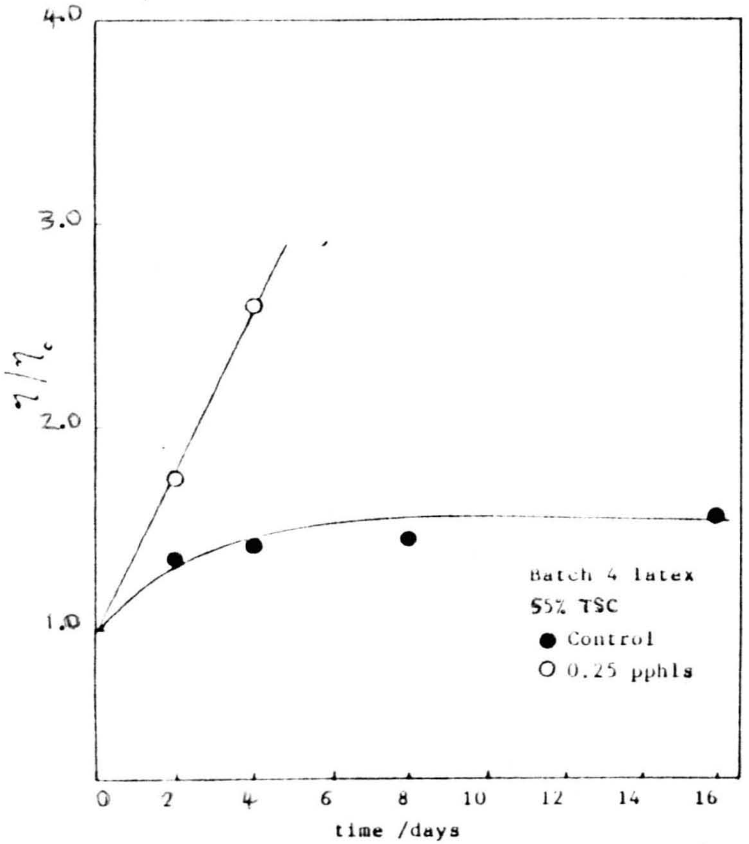


Fig. 7.51 : Variation of η/η_o with time for NR latex containing polymer MAA/EHA(60:40)0.184 at various levels of addition

ous

295



Fi Fig. 7.52 : Variation of η/η_0 with time for NR latex containing polymer MAA/EHA(50:50)0.033 at various levels of addition

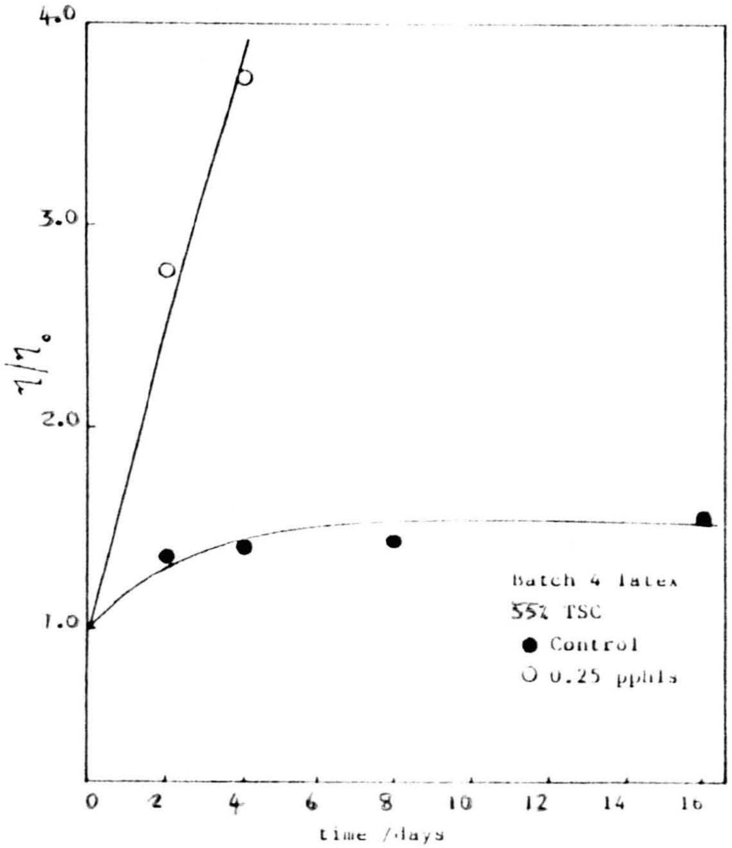


Fig. 7.53 : Variation of η/η_0 with time for NR latex containing polymer MAA/EHA(50:50)0.099 at various levels of addition

addition is increased. This observation suggests that the ability of the more hydrophilic polymers to enhance the colloid stability of latex outweighs their ability to sensitise latex towards zinc ions as their concentration in latex is increased, and that the ability of the more hydrophobic polymers to adsorb on the particle surfaces and hence to form complexes with the proteinaceous substances whose zinc derivatives are relatively unhydrated increase as their concentration in latex is increased.

CHAPTER EIGHT

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

8.1 Introduction

It has been found that such characteristics of synthetic hydrophilic polymers as molecular weight, composition distribution and hydrophilicity are dependent upon the method used for their preparation. It has also been found that certain properties of NR latex can be modified by the addition of hydrophilic polymers, and that the extent to which these properties is modified depends upon the characteristics of the added polymers. This chapter summarises conclusions which have been drawn from this investigation, and makes suggestions for further work.

8.2 Effects of preparative method upon characteristics of polymers

8.2.1 Effects upon intrinsic viscosity

The intrinsic viscosities of the polymers of Type 1, i.e., the polymers prepared by a conventional solution polymerisation process, were found to be higher than those of the polymers of Type 2, i.e., the polymers prepared under the conditions of monomer starvation. This difference is believed to be a consequence of differences in the variation of concentration of initiator with time of polymerisation reaction during the preparation of these two types of polymers.

8.2.2 Effects upon composition distribution

The composition distribution of polymers of Type 1 were found to be wider than those of the polymers of Type 2. It is believed that polymers of Type 1 show a wider compositional distribution than do polymers of Type 2 because, in a conventional solution polymerisation process, it is possible that the polymer molecules formed during the initial stages of polymerisation are rich in the more reactive monomer, and polymer molecules formed during the final stages of polymerisation are rich in the less reactive monomer. Thus the overall polymer formed in the reaction has a wide distribution of composition, depending on the difference in reactivity between the two monomers. The polymers prepared under the conditions of monomer starvation have a narrow distribution of composition because in this method the monomer mixture was added to the reaction system continuously at a rate which is beleived to be less than the rate of polymerisation.

8.2.3 Effects upon hydrophilicity

The polymers of low molecular weight of Type 1 were found to be less hydrophilic than the corresponding polymers of Type 2, whereas the polymers of high molecular weight of Type 1 were found to be more hydrophilic than the corresponding polymers of Type 2. It is suggested that the polymers of low molecular weight of Type 1 prepared using high concentrations of initiator, contain polymer molecules which are rich in the less reactive monomer, EHA, formed towards the end of the polymerisation reaction, and hence are less hydrophilic than the corresponding polymers of Type 2. On the other hand, the polymers of high molecular weight of Type 1 prepared using low concentra-tions of initiator, do not contain the polymer molecules which would form towards the end of the polymerisation reaction, because of incomplete conversion. They are, therefore, more hydrophilic than the corresponding polymers of Type 2.

8.3 Effects of polymers of Type 1 upon some properties of NR latex

8.3.1 Effects upon mechanical stability and viscosity

All the polymers of Type 1 enhanced the mechanical stability and viscosity of NR latex at all the levels of addition investigated, although in some cases the effects were small. In both cases, the magnitude of the enhancement depended upon both the molecular weight and the hydrophilicity of the added polymer, as well as upon the level at which it was present. The ability of the added polymer to enhance both MST and viscosity increased as the molecular weight of the added polymer increased. This was attributed to the enhanced adsorption of added polymer at the rubber/water interface with increasing molecular weight. The extent of the enhancement of viscosity was found to increase with increasing hydrophilicity of the added polymer. It was suggested that this might be a consequence of the enhancement of both the viscosity of the dispersion medium and the effective hydrodynamic size of the particles as the hydrophilicity of the polymer was increased. The hydrophobicity of the added polymer was found to have an interesting effect upon the enhancement of MST. It was observed that, as the hydrophobicity of the added polymer was increased, at any given level of addition, the extent of the enhancement of MST first increased and then decreased with further increase in hydrophobicity. This is not surprising, as it is known that if a polymer is to be effective as a steric stabiliser, it should contain adequate amounts of both anchor groups and stabilising moieties. Amongst the polymers of low molecular weight investigated, the polymer MAA/EHA(70:30)B was found to be the most effective in enhancing the MST of NR latex.

8.3.2 Effects upon chemical stability

The effects of polymers of Type 1 upon the chemical stability of NR latex were found to parallel their effects upon the MST of NR latex. These observations have been interpreted in a similar manner to those for the effects upon the MST of NR latex

8.3.3 Effects upon zinc-oxide thickening

The addition of polymers of Type 1 affected the rate of zinc-oxide thickening of NR latex. The extent to which the added polymer influenced the rate of zinc-oxide thickening depended upon the molecular weight and hydrophobicity of the added polymer. At low levels of additions, all the polymers of low molecular weight investigated retarded zinc-oxide thickening, but the extent of the retardation was found to depend upon the hydrophilicity of the added polymer. The retardation of zinc-oxide thickening is attributed to the stabilisation of latex particles against zinc ions by the adsorbed polymer. At high levels of addition, the less hydrophilic polymers of low molecular weight accelerated zinc-oxide thickening and this is tentatively attributed to the formation of complexes with proteinaceous substances perhaps by hydrophobic association at the rubber/water interface, such complexes forming zinc derivatives which are relatively unhydrated. Most of the linear polymers of high molecular weight were found to be more effective in accelerating zinc-oxide thickening than were the corresponding linear polymers of low molecular weight. It is suggested that this is a consequence of the higher tendencies of the former to adsorb at the rubber/water interface than the latter. The effects of branched polymers upon the rate of zinc-oxide thickening of NR latex were found to be similar to those of the linear polymers of high molecular weight. Furthermore, it appeared that the effect of composition of added polymer upon the of zinc-oxide thickening of NR latex was far more important than that of the molecular weight of the added polymer.

8.3.4 Effects upon zinc-ammine heat-sensitivity

The effects of some linear polymers of low molecular weight of Type 1 upon the zinc-ammine heat-sensitivity of NR latex were found to parallel the effects upon the zinc-oxide thickening of NR latex. However, it was not possible to state with certainty that the effects of linear polymers of high molecular weight of Type 1 parallel their effects upon zinc-oxide thickening.

8.3.5 Effects upon heat-sensitivity

An investigation of the possibility of using some of the polymers of Type 1 as replacements for PVME as heat sensitisers for NR latex revealed that these polymers were not suitable as replacements for PVME as heat sensitisers for NR latex, at least under the conditions investigated.

8.3.6 Effects upon creaming

Some polymers of Type 1 were found to induce the creaming of NR latex. The extent of creaming was found to depend upon the hydrophilicity and the molecular weight of the added polymer. It is suggested that the ability of an added polymer to induce creaming of NR latex is dependent upon both its solubility in the dispersion medium and its tendency to adsorb at the rubber/water interface.

8.4 Effects of polymers of Type 2 upon some properties of NR latex

8.4.1 Effects upon mechanical stability and viscosity

The effects of polymers of Type 2 upon the MST and viscosity of NR latex were found to be, in general, similar to those of the polymers of Type 1. All the polymers of Type 2 investigated enhanced the MST and viscosity of NR latex at all the levels investigated. The magnitude of the enhancement depended upon both the molecular weight and the hydrophobicity of the added polymer, as well as upon the level of addition. The ability of the added polymer to enhance the viscosity of latex was found to increase as the molecular weight of the added polymer increased. However, unlike polymers of Type 1, the ability of the added polymer to enhance MST of latex was found first to increase and then decrease with increasing molecular weight of the added polymer. The initial increase in the enhancement of MST with increasing molecular weight of the added polymer is attributed to enhanced adsorption of the added polymer at the rubber/water interface with increasing molecular weight. The most likely explanation for the subsequent decrease in the extent of the enhancement of MST with further increase in the molecular weight is the decrease in the number of loops of the adsorbed polymer at the expense of the number of tails with increasing molecular weight. It may also be a consequence of the extension of hydrophobic parts of the polymer into the dispersion medium, such extension discouraging the extension of neighbouring hydrophilic parts into the dispersion medium. The effects of increasing hydrophobicity of added polymers of Type 2 upon the extent of the enhancement of MST were found to be similar to those of polymers of Type 1, even though it was not possible to decide the composition of the polymer which brought about the highest enhancement of MST amongst the polymers of Type 2 investigated.

The pattern of variation of the viscosity of NR latex with the level of added polymer was found to depend upon the hydrophobicity of the added polymer. As the concentration of added polymers of groups MAA/EHA(60:40) and AA/EHA(60:40) increased, the extent of the enhancement of viscosity first increased, then passed through a maximum, and decreased, passed through a minimum and then again increased with further increase in the concentration of the polymer. On the other hand, the viscosity of latex to which the more hydrophilic polymers had been added was found to increase with increasing level of addition. This observation perhaps indicates that the more hydrophobic polymers may be capable of inducing interparticle bridging at low levels of addition, and that the more hydrophilic polymers increase the viscosity of NR latex mainly by dissolving in the dispersion medium. As the more hydrophilic polymers were more capable of enhancing the viscosity of NR latex than were the more hydrophobic polymers, it was concluded that the adsorption of the added polymer at the rubber/water interface tends to reduce the extent to which the viscosity is enhanced.

8.4.2 Effects upon zinc-oxide thickening

The effects of polymers of Type 2 upon the zinc-oxide thickening were generally similar to those of the polymers of Type 1. The polymers of low molecular weight were found to be in general less effective in accelerating the zinc-oxide thickening of NR latex than are the corresponding polymers of high molecular weight. The difference was particularly marked with more hydrophobic polymers at high levels of addition. This is tentatively attributed to their higher tendency to adsorb at the rubber/water interface and perhaps to form complexes with proteinaceous substances whose zinc derivatives are relatively unhydrated.

The ability of the added polymers to accelerate the zinc-oxide thickening of NR latex first decreased, then passed through a minimum and then increased as the hydrophobicity of the polymer increased. The ability of the more hydrophilic polymers to accelerate zinc-oxide thickening is attributed to their ability to sensitise the latex towards zinc ions by forming insoluble zinc derivatives. It was observed that the ability of the more hydrophilic polymers to accelerate zinc-oxide thickening decreased as the concentration of added polymer increased. It is thought that this may be a consequence of the increase in the ability of these polymers to enhance the colloid stability of NR latex with increasing concentration. The ability of the more hydrophobic polymers to enhance the zinc-oxide thickening of latex increased with increasing concentration of the added polymer, and this is again attributed to the increase in the tendency of the added polymer to adsorb at the rubber/water interface and perhaps to form complexes with proteinaceous substances whose zinc derivatives are relatively unhydrated.

8.5 Suggestions for further work

The investigation of the effects of added hydrophilic polymers upon some properties of NR latex has yielded many interesting results, and has indicated that there is clearly great scope for further work. The following appear to be the more obvious areas where further research is desirable:

1. All the polymers used in this investigation were of relatively low molecular weight. Further work using water-soluble polymers of a wide range of molecular weight is therefore desirable.

2. It has been found that the ability of an added polymer to enhance the MST and viscosity of NR latex did not depend upon the nature of the stabilising moieties, amongst the stabilising moieties investigated. However, further work should be carried out on this aspect before coming to a definite conclusion. For this purpose, it would be desirable to investigate the polymers which contain other substituted acrylic-acid monomers such as n-propyl acrylic acid and n-hexyl acrylic acid, or other hydrophilic monomers such as itaconic acid or vinylsulphonic acid.

3. The effects of the nature of the anchor group of the added polymer upon the ability of the added polymer to influence the properties of NR latex might also be interesting to investigate in greater detail. Monomers such as n-tetradecyl acrylate and n-octadecyl acrylate would be of interest for this purpose.

4. An investigation of the effects of block and graft copolymers of various combinations of hydrophilic and hydrophobic monomers upon the properties of NR latex might also be of interest.

5. Finally, a systematic investigation of the effects of well-defined linear, branched, block, and graft copolymers of various hydrophilic and hydrophobic monomers upon the properties of well-defined model latices might provide a better understanding of the behaviour of added hydrophilic polymers in latices.

APPENDIX 1

The equation for variation of initiator concentration with time of reaction for solution polymerisations carried out according to the Method 2 was derived with the assistence of Dr. A.C.Haynes of LSPT as follows:

Let the initial solution of initiator in monomers and solvent comprise I moles of initiator dissolved in M dm^3 of the mixture of monomers and solvent. Let the volume of solvent in the reaction vessel be S dm^3. The initiator solution is added to the solvent in the reaction vessel at a uniform rate over a period of time from $t=0$ to $t=t^*$, so the rates of additon of initiator to the reaction system are

$$\frac{dI}{dt} = \frac{I}{t^*}, \quad = i \qquad \text{for } o \leqslant t \leqslant t^* \qquad (1)$$

and

$$\frac{dI}{dt} = 0 \qquad \text{for } t > t^* \qquad (2)$$

and the rates of addition of monomers+solvent is

$$\frac{dM}{dt} = \frac{M}{t^*}, \quad = m \qquad \text{for } 0 \leqslant t \leqslant t^* \qquad (3)$$

and

$$\frac{dM}{dt} = 0 \qquad \text{for } t > t^* \qquad (4)$$

Let C^a denote the total amount of initiator (moles) which has been added to the reaction vessel at time t divided by the total volume (dm^3) of reaction system at time t. This is not , of course, the actual concentration of initiator in the reaction system at time t, because initiator begins to decompose as soon as it is added to the reaction system. Thus

$$C^a = 0 \qquad \text{for } t=0 \qquad (5)$$

$$C^a = it/S+mt, \qquad \text{for } 0 \leqslant t \leqslant t^* \qquad (6)$$

When $t > t^*$, C^a has the constant value

$$C^{a*} = \frac{it^*}{S+mt^*} = \frac{I}{S+M} \qquad (7)$$

From equation (6), the rate of increase of C^a with time is given by

$$\frac{dC^a}{dt} = \frac{iS}{(S+mt)^2} \qquad \text{for } 0 \leqslant t \leqslant t^* \qquad (8)$$

For $t > t^*$, dC^a/dt is zero.

Let C denote the actual concentration of initiator in the reaction system at time t. Thus,

$$C = 0 \qquad \text{for } t < 0 \qquad (9)$$

The rate of increase of C with time is given by

$$\frac{dC}{dt} = \frac{dC^a}{dt} - \left(\frac{dC}{dt}\right)_{decomp} \qquad \text{for } 0 \leqslant t \leqslant t^* \qquad (10)$$

where $(dc/dt)_{decomp}$ is the rate at which the initiator is decomposing at time t. The rate of decomposition of initiator is given by

$$\left(\frac{dC}{dt}\right)_{decomp} = kC \qquad (11)$$

where k is the dissociation constant of the initiator.

Combining equations (8), (10) and (110) gives

$$\frac{dC}{dt} = \frac{iS}{(S+mt)^2} - kC \tag{12}$$

This is the differential equation for the variation of C with t in the interval $0 \leqslant t \leqslant t^*$. At times greater than t^*, the variation of C with time is given by

$$\frac{dC}{dt} = \left(\frac{dC}{dt}\right)_{decomp} = -kC, \quad \text{for } t > t^* \tag{13}$$

The solution of equation (13) is

$$C = C^* e^{-k(t-t^*)}, \quad \text{for } t > t^* \tag{14}$$

where C^* is the initiator concentration at time $t=t^*$. The variation of C with t over the interval $0 \leqslant t \leqslant t^*$ is obtained by solving the differential equation (12). The solution for equation (12) is

$$C = Ae^{-kt} + e^{-kt} \int \frac{iS}{(S+mt)^2} e^{kt}\, dt \tag{15}$$

where A is a constant.

The integral on the right hand side of the equation (15) can be evaluated as follows:

$$\int \frac{iS}{(S+mt)^2} e^{kt}\, dt = \int \frac{IS}{S^2[1+(mt/S)]^2} e^{kt}\, dt \tag{16}$$

Put $i/S = a$ and $m/S = b$

Then

$$\int \frac{i/S}{[1+(mt/S)]^2} e^{kt}\, dt = \int \frac{a}{(1+bt)^2} e^{kt}\, dt \tag{17}$$

Now put $U = 1 + bt$

Then $t = U-1/b$, $dt/dU = 1/b$, $dt = dU/db$

Now the equation (17) can be rearranged to give

$$\int \frac{a}{(1+bt)^2} e^{kt}\, dt = a \int \frac{e^{\alpha U-\alpha}}{bu^2}\, dU \tag{18}$$

$$= a \int \frac{e^{\alpha U}}{be^{\alpha} U^2}\, dU \tag{19}$$

where $\alpha = k/b$

$$\int \frac{e^{\alpha U}}{be^{\alpha} U^2}\, dU = \beta \int \frac{e^{\alpha U}}{U^2}\, dU \tag{20}$$

where $\beta = 1/be^{\alpha}$

$$\int \frac{e^{\alpha U}}{U^2}\, dU = - \frac{e^{\alpha U}}{U} + \alpha \int \frac{e^{\alpha U}}{U}\, dU \tag{21}$$

$$\int \frac{e^{\alpha U}}{U}\, dU = \log U + \alpha U + \frac{\alpha^2 U^2}{2.2!} + \frac{\alpha^3 U^3}{3.3!} + \ldots \ldots + \frac{\alpha^n U^n}{n.n!} \qquad \ldots .(22)$$

Combining equations (19), (20), (21) and (22) gives

$$a \int \frac{e^{\alpha U}}{be^{\alpha} U^2}\, dU = \frac{-a\beta e^{\alpha U}}{U} + a\beta\alpha[\log U + \alpha U + \frac{\alpha^2 U^2}{2.2!} + \ldots \ldots . + \frac{\alpha^n U^n}{n.n!} \tag{23}$$

Now the equation (12) can be written as

$$C = Ae^{-kt} - \frac{a\beta e^{\alpha U-kt}}{U} + a\beta\alpha e^{-kt} [\log U + \alpha U + \frac{\alpha^2 U^2}{2.2!} + \ldots . \ldots . + \frac{\alpha^n U^n}{n.n!} \qquad \ldots .(24)$$

But $\alpha U\text{-}kt = \frac{k}{b}(1+bt)\text{-}kt = \frac{k}{b} = \alpha$

$$C = Ae^{-kt} - \frac{a\beta e^{\alpha}}{U} + a\beta\alpha e^{-kt}\,[\log U + \alpha U + \frac{\alpha^2U^2}{2.2!} + \ldots\ldots + \frac{\alpha^nU^n}{n.n!} \qquad \ldots.(24)$$

APPENDIX 2

The computer programme used for the calculation of variation of initiator concentration in the preparation of polymers by Method 2 was as foolows:

```
10  P = 0.02078
20  Q = 2.822x10^-3
30  K = 1.5x10^-4
40  L = 0.02078
50  Y = 2.822x10^-3
60  V = 4.7745x10^-5
70  W = 3.1414
80  Input "Time";time
90  U = 1+V*Time
100 For x = 1 to 40
110 T = 1
120 For N = 1 to x
130 T = T*N
140 Next N
150 Alpha = (w^x)/(x*T)
160 Beta = (w^x)*(U^x)/(x*T)
170 Sum = Sum+Alpha
180 Total = Total+Beta
190 IF Alpha < 0.0005 then go to 220
200 IF Beta < 0.005 then go to 220
210 Next X
220 Print "too small"
230 Print "sum";sum
240 Print "Total";total
250 A=P-Q*sum
250 Print A
270 S=Total+log(U)/2.3025
280 Print S
290 C = [A*exp(-K*Time)]-[L/U]+[[Y*exp[-K*Time]]*S
300 Print C
310 END
```

REFERENCES

1. Tunniclife, M.E., Trans IRI, 1954, 30, 97
2. Smith, R.H., Biochem.J., 1954, 56, 240; 1954, 57, 130
3. Lucas, F.F., Ind. Eng. Chem., 1938, 30, 146
4. Saunders, F.L., and Sanders, J.W., J. Colloid Sci., 1956, 11, 260
5. Frantz, G.C., Sanders, J.W. and Saunders, F.L., Ind. Eng. Chem., 1957, 49(9), 1449
6. Gillespie, T., J. Colloid Sci., 1960, 15, 313
7. Sperry, P.R., Hopfenberg, H.B. and Thomas, N.L., J. Colloid interface Sci., 1981, 82(1), 62
8. Tan, K.Y., Ph.D. Thesis, Polytechnic of North London, 1982
9. Ash, S.G. and Clayfield, E.J., J. Colloid Interface Sci., 1976, 55(3), 645
10. Blackley, *D.C., Salleh, B.N.M. and Twaits, R., Plast.* Rubb.: Mater. Appl., 1977, 2, 117
11. Blackley, D.C. and Chua, K.S., Plast. Rubb. Process. Appl., 1981, 1, 73
12. Kronberg, B., Sjoblom, E., Ehrenborg, L. and Stenius, P., Polymer preprints, 1985, 26(1), 236
13. Oldack, R.C., The Firestone Tire and Rubber Company, U.S. Patent No. 4,379,095, 1985 Apr. 5
14. Belbin, D., Buscall, R., Mumme-Young, C.A. and Shankey, J.M., Polymer Latex 2, (Proc. Int. Conf., London, 1985) 7
15. Gregory, J., Trans. Faraday Soc., 1969, 65, 2260

16. Gregory, J., J. Colloid Interface Sci., 1973, 42(2), 448

17. Gregory, J., J. Colloid Interface Sci., 1976, 55(1), 35

18. Gregory, J. and Sheiham, I., Brit. Polym. J., 1974, 6, 47

19. Ries, H.E. and Meyers, B.L., J. Appl. Polym. Sci., 1971, 15, 2023

20. Lauzon, R.V. and Schimidt, D.D., J. Appl. Polym. Sci., 1974, 18, 3319

21. Ho, C.H. and Howard, G.J., " The Effects of Polymers on Dispersion Properties " (Proc. Int. Sym. 1981), Ed. Tadros, T.F., 343

22. Sinn, G., PB 13,359, 1940 March 6

23. Sinn, G., Latices and Dispersions Symposium, Hastings, 1974 May

24. Blackley, D.C., High Polymer Latices, Applied Science Publishers Ltd., London, 1966

25. Cockbain, E.G, Trans. Inst. Rubb. Ind., 1956, 32, 97

26. Brachel, H., Esser., H., Muller, E., US Patent No. 3,062, 768, 1972 Nov. 6

27. Stoner, G., Azorlosa, J.L., Albus, C.P., US 2,842,606, 1958 July 8

28. Stoner, G., Azorlosa, J.L., Albus, C.P., US 2,805,210, 1957 Sept. 3

29. Bayer, BP 859,027, 1961 Jan. 18

30. Woods, T.J., Proc. Int. Polym. Latex Conf., London,1978

31. Gorton, A.D.T, and Pendle T.D., NR Technology, 1981,11(1), 1

32. Brown, G.L. and Garrett, B.S., , J. Appl. Polym. Sci., 1959, 1(3), 283

33. White, W.W., Ind. Eng. Chem., Prod. Res. Dev., 1962, 1(3), 220

34. Swinyard, P.E. and Gorton, A.D.T., NR Technology, 1983, 14(2), 35

35. Twiss, D.S. and Carpenter, A.S., Proc. Rubb. Tech. Conf. London 2, 1938, 81

36. Noble, R.J., " Latex in Industry ", Palmerton Publishing Co. 1936

37. Stamberger, P., " The Colloid Chemistry of Rubber" London, 1929, 30

38. Baker, H.C., Trans IRI, 1937, 13, 70

39. Vester, C.F., Proc. Rubb. Tech. Conf. London, 1938, 126

40. Bondy, C., Trans. Faraday Soc., 1939, 35, 1093

41. Saunders, F.L., J. Colloid Interface Sci., 1968, 28 (3/4), 475

42. Brodnyan, J.G. and Kelly, F.L., J. Polym. Sci., part C, 1969, 27, 263

43. Garvey, M.J., Tadros, Th.F. and Vincent, B., J. Colloid Interface Sci., 1974, 49(1), 57

44. Cowell, C. and Vincent, B., " The Effects of Polymers on Dispersion Properties ", Acedamic Press, London, 1981, 60

45. Tadros, Th.F., Polymer Latex 2, (Proc. Int. Conf., London, 1985), 6

46. Boomgard, Th. Van den., King, T.A., Tadros, Th.F., Tang, H. and Vincent, B., J. Colloid Interface Sci.,

1978, 66(1), 68

47. Tadros, Th.F., and Vincent, B., J. Phys. Chem., 1980, 84, 1575
48. Tadros, Th.F., and Vincent, B., J. Colloid Interface Sci., 1979, 72,(3), 505
49. Krongberg, B., Kall, L. and Stenius, P., J. Dispersion Sci. Tech., 1981, 2, 215
50. Encyclopaedia Brittanica, 1968, 12, 257; 1968, 17, 38
51. Heller, W. and Pugh, T.L., J. Chem. Phys., 1954, 22, 1778
52. Napper, D.H., J. Colloid Interface Sci.,1977, 58(2), 390
53. Napper, D.H., J. Colloid Interface Sci., 1970, 32(1), 106
54. Dawkins, J.V. and Taylor, G., Colloid Polym. Sci., 1980, 258, 79
55. Cowell, C., Li-in-on, R. and Vincent, B., J. Chem. Soc. Faraday Trans. 1, 1978, 74, 337
56. Lambe, R., Tadros, Th. F. and Vincent, B., J. Colloid Interface Sci., 1978, 66(1), 77
57. Everett, D.H. and Stageman, J.F., Colloid Polym. Sci. 1977, 255, 293
58. Feigin, R.I., Dodd, J. and Napper, D.H., Colloid Polym. Sci., 1981, 259, 1027
59. Croucher, M.D. and Hair, M.L., J. Colloid Interface Sci., 1981, 81, 257
60. Cowell, J. and Vincent, B., J. Colloid Interface Sci., 1982, 87, 518

61. Clarke, J. and Vincent, B., J. Chem. Soc. Faraday Trans. 1, 1981, 77, 1831

62. Everett, D.H. and Stageman, J.F., Faraday Disc. Chem. Soc., 1978, 65, 230; 1978, 65, 314

63. Napper, D.H., " Polymeric Stabilization of Colloidal Dispersions ", Acedamic Press, London1983

64. Dobbie, J.W., Evans, R., Gibson, D.V. Smitham, J.B. and Napper, D.H., J. Colloid Interface Sci., 1973, 45(3), 557

65. Tadros, Th.F. and Winn, " The Effects of Polymers on Dispersion Properties ", Acedamic Press, London,1981,1

66. Verwey, E.G.W. and Overbeek, J.Th.G., " Theory of Stability of Lyophobic Colloids", Elsevier, Amsterdam, 1948

67. Shaw, D.J., " Introduction to Colloid and Surface Chemistry ", Butterworth , London, 1970

68. Ottewill, R.H., J. Colloid Interface Sci., 1977, 58(2), 357

69. Ottewill, R.H., Prog. Colloid Polym. Sci., 1976, 59, 14

70. Smoluchowski, M.V., Z. Phys. Chem., 1917, 92, 129

71. London, F., Trans. Faraday Soc., 1937, 33, 8

72. Keesom, W.H., Phys. Z., 1921, 22, 129

73. Debye, F., Phys. Z., 1920, 21, 178

74. Slater, J.C. and Kirkwood, J.G., Phys. Review, 1931, 37,682

75. Hamaker, H.C., Physica, 1937, 4, 1058

76. De Boer, J.H., Trans. Faraday Soc., 1967, 32, 10

77. Gregory, J., J. Colloid Interface Sci., 1981, 83, 138

78. Helmholtz, H., Ann. Discuss. Physik. d. Cheme., 1879, 7, 337

79. Gouy, G., Ann. Phys., 1917, 9(9), 129

80. Chapman, D.L., Phil. Mag., 1913, 25, 475

81. Stern, O., Electrochem, 1924, 30, 508

82. Derjaguin, B. and Landau, L., Acta Phys. Chem., 1941, 14, 633

83. Vold, M.J., J. Colloid Sci., 1961, 16, 1

84. Crowl, V.T. and Malati, M.A., Discuss. Faraday Soc., 1966, 42, 301

85. Wiese, G.R. and Healy, T.W., Discuss. Faraday. Soc., 1969, 45, 490

86. Van Arkel, A.E. and Krupt, H.R., Rec. Trav. Chim., 1920,39, 656

87. Tuorilla, P., Kolloid Chem. Beih., 1922, 22, 191

88. Ottewill, R.H. and Wilkins, Trans. Faraday Soc., 1962, 58, 608

89. Higushi, W.J., Okada, R., Stelter, G.A. and Lamberger, A.P., J. Amer. Pharm. Ass., 1963, 52, 49

90. Lewis, K.E. and Parfitt, G.D., Trans. Faraday Soc., 1966, 62, 1652

91. Mcgown, D.N.L. and Parfitt, G.D., J. Phys. Chem., 1967, 71, 449

92. Spielman, L.A., J. Colloid Interface Sci., 1970, 33, 562

93. Honig, E.P., Robbersen, G.J. and Wiersema, P.H., J. Colloid Interface Sci., 1971,36, 97

94. Lichtenbelt, J.W.Th., Pathmansanoharan, C. and Wiersema, P.H., J. Colloid Interface Sci., 1974, 49, 281

95. Fuchs, N., Z. Phys., 1934, 89, 736

96. Ottewill, R.H. and Shaw, J.N., Discuss. Faraday Soc., 1966, 42, 154

97. Ash, S.G., " Colloid Science Specialist Periodical Reports ", (Ed. Everett, D.H.), Chem. Soc., 1973, 1, 103

98. Barrett, K.E.J., " Dispersion Polymerisation in Organic Media ", Wiley Inter Science, New York, 1975

99. Lipatov, Y.S. and Sergeeva, L.M., " Adsorption of Polymers ", Wiley, New York, 1974

100. Vincent, B., Adv. Colloid Interface Sci., 1974, 4, 193

101. Vincent, B., Adv. Colloid Interface Sci., 1974, 4, 104

102. Hoeve, C.A.J., J. Phys. Chem., 1965, 47, 3007; 1966, 44, 1505

103. Meir, D.J., J. Phys. Chem., 1967, 71, 1861

104. Hesselink, F.Th., J. Phys. Chem., 1969, 73, 3488; 1971, 75, 65

105. Scheutjens, J.M.H. and Fleer, G.J., J. Phys. Chem., 1979, 83, 1619

106. Mackor, E.L., J. Colloid Sci., 1951, 6, 490

107. Van Der Waarden, M., J. Colloid Sci., 1951, 6, 443

108. Mackor, E.L. and Van Der Waarden, M., J. Colloid Sci. 1951, 7, 535

109. Clayfield, F.J. and Lumb, E.C., J. Colloid Interface Sci., 1966, 22, 269

110. Hesselink, F.Th., Vrij, A. and Overbeek, J.Th.G., J. Phys. Chem., 1971, 75, 2094

111. Fischer, F.W., Kolloid Z., 1958, 160, 120

112. Napper, D.H., Ind. Eng. Chem., Prod. Res. Dev., 1970, 9, 467

113. Evans, R., Davison, J.B. and Napper, D.H., J. Polym. Sci., Part B Polym. Lett., J. Polym. Sci., 1972, 10, 449

114. Napper, D.H., Trans. Faraday Soc., 1968, 64, 1701

115. Napper, D.H., J. Colloid Interface Sci., 1977, 58, 390

116. Everett, D.H. and Stageman, J., J. Discuss. Faraday Soc., 1978, 65, 230

117. Overbeek, J.Th.G., Adv. Colloid Interface Sci., 1982, 16, 17

118. Frens, G. and Overbeek, J.Th.G., J. Colloid Interface Sci., 1972, 38, 376

119. Frens, G. and Overbeek, J.Th.G., Kolloid Z., 1969, 233 922, J. Colloid Interface Sci., 1971, 36, 286

120. Johnson, G.A., Lecchini, S.M.A., Smith, E.G., Clifford J. and Pethica, B.A., Discuss. Faraday Soc., 1966, 42, 120

121. Johnson, G.A., Goldfrab, J. and Pethica, B.A., Trans. Faraday Soc., 1965, 61, 2321

122. Thomas, H.C. and Cremers, A., J. Phys. Chem., 1970, 74, 1072

123. Faucett, A.S., Pafitt, G.D. and Smith, A.C., Nature, 1964, 204, 775

124. Churayer, N.H., Sobolev, V.D. and Zorin, Z.M., Special

Discuss. Faraday Soc., 1970, No. 1, 213

125. Hongardy, J., Serratosa, J.M., Stone, W. and Van Olphan, H., Special Discuss. Faraday Soc., 1970, No. 1 194

126. Feigin, R.I. and Napper, D.H., J. Colloid Interface Sci., 1980, 75, 525

127. Mason, J.C., in Polymer Hand Book, 2nd edition, Brandrup , J and Immergut, E.H., Eds., Wiley, New York, 1975, p. 11.3

128. Polymer Hand Book, 2nd edition, Brandrup , J and Immergut, E.H., Eds., Wiley, New York, 1975, p. 1V.2

129. Mayer, V.E., Polym. Preprints, 1964, 5, 60

130. Paxton, T.R., J. Polym. Sci., Part B Polym. Lett., 1963, 73 B(1), 766

131. Blackley, D.C. and Emengo, F.N., Kautsch. Gummi. Kunstst., 1984, 37(8), 675

132. Pok, C., M.Sc. Thesis, CNAA, 1987