

## SUMMARY.

The following programme of experimental work, survey work and theory has been undertaken in preparation for this thesis.

### Experimental .

Fractionated solutions of Polystyrene in benzene and toluene were irradiated with ultrasonics at frequencies of 1 Megacycle/s and 25 Kilocycles/s. It is noted that most published data referred to the effect of the lower ultrasonic frequencies on high polymer solutions (10 - 500 kcs.) From the cavitation theory of Moltingk and Neppiras, a greater cavitation severity and resulting degradation would be expected at the lower frequencies. The degradation curves obtained by Langton and Vaughan established that the rate and extent of degradation at 1 Megacycle/s was comparable to that obtained at the lower frequencies. The experiments at 25 kilocycles/s were made to verify other published results. Polystyrene/benzene was also irradiated at 1 Megacycle using various crystal voltages, and results obtained were found to be in agreement with other data.

Fractionated Polymethyl methacrylate in toluene <sup>were irradiated</sup> and chloroform/ at 1 Megacycle and 25 Kilocycles/s, and most of the degradation curves were in agreement with other

published data. Anomalous results were obtained for a solution in chloroform of one fraction obtained from a sample of 'Diakon' PMMA moulding granules. These results were considered to indicate that the fraction chosen was of very low M.Wt. , possibly being of the order of the limiting degree of polymerisation  $P_f$  of this polymer/solvent system.

The ultrasonic power entering the test solutions was measured for the 25 Kilocycle and 1 Megacycle equipment. A calorimetric method was employed, and the process for obtaining  $\left(\frac{d\theta}{dt}\right)_0$  , the temperature gradient at zero excess temperature, was improved in later calibrations. The low powers found to be entering the solutions lead the author to an improved design of the irradiation cell.

#### Survey.

A critical survey of the published work was made, and it was found that the experimental results given in this thesis were in general agreement with other published data. The graphical method, used to obtain the final D.P.  $\left(\overline{P}_w\right)_\infty$  from the degradation curves, was examined and a more accurate method used to calculate the present results. Recalculations were also made from the data published by Jellinek, Mostafa, and Melville and Murray. It was found that this method was not

applicable to the calculation of final M.Wt. from Mostafa's data , and this was attributed to the polydispersity of his sample.

The Schmid equation representing the degradation process in terms of D.P. and the rate of breakage of bonds was examined, and three other simple rate equations considered. These equations were integrated and the integrated forms tested for agreement with experimental data. It was found that one of the equations gave a better fit than the Schmid equation. Rate equations proposed by D. Ovenall and his co-workers were discussed, and these authors' theories examined.

#### Theoretical.

The degradation theories proposed by Schmidt, Jellinek and Mostafa, and Ovenall et. al. were considered, and the underlying theory of a vibrating stretched string examined. The weakness of such theories was noted, and alternative mechanisms considered. It was concluded that no satisfactory agreement could be obtained between stretched string theory and experimental data without considering sub-harmonics of a high order, or evaluating the theory in terms of non-linear motion ( which would present mathematical difficulties). This lead to the consideration of a cavitation degradation theory in which bonds were

broken in the macromolecule as a result of cavitation bursts in the vicinity of the molecule. This theory has been considered by Dooberman and other workers.

The writer proposes that the polymer molecules (or aggregates) themselves act as nuclei for cavitation.

The threshold nucleus size for cavitation and the pressures in the region of a collapsing cavity are calculated, and it is found that the expected size-range for cavitable nuclei is of the same order of size as the macromolecules present in the solution.

It therefore appears reasonable to assume that the polymer molecules act as nuclei around which cavitation bubbles form. It is shown in the latter part of this thesis that there is very good qualitative agreement in favour of this theory. This initiation process, together with the cavitation forces, is proposed as a theory to explain the phenomena of ultrasonic degradation of polymers in solution.