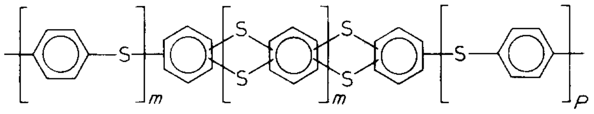
However, according to Behringer and co-workers[8], diaryl disulphides do not react with aromatic hydrocarbons in the presence of Lewis acids with the formation of the corresponding thiol and sulphide.

It is highly probable that the obtained polymer has a poly-*p*-phenylene sulphide structure the sequences of which are separated by cyclic sulphide type sequences.



Such a structure supposes its potential high thermal stability confirmed by the results of thermal gravimetric analysis (*Figure 3*).

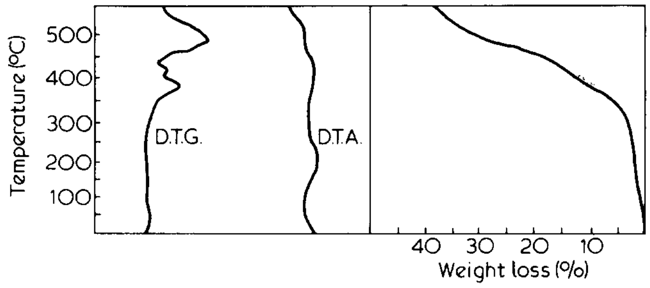


Figure 3 DTA and DTG curves of the obtained polymer

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Rheological study of particle interaction in a concentrated polymer dispersion

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INTRODUCTION

The influence of the purification procedure on the viscosity of polymer dispersions has been investigated[1,2]. However, data on particle interaction and the formation of the ordered structure of dispersed particles in well-defined systems are still not available[2,3]. Ferguson *et al.*[4] have suggested that the formation of an ordered structure of dispersed particles can adequately be followed by measuring the development of shear stress with time at constant shear. They also suggested that a dispersed system with ordered particle structure is characterized by a peak stress (static yield value) found at the onset of steady shear.

Here, we have used a Couette-type viscometer to study a well-characterized polystyrene latex. The formation of structure by the dispersed particles after purification has also been studied. In addition, we have attempted to calculate the Hamaker constant for particle interaction by using an equation developed by Albers and Overbeek[5].

EXPERIMENTAL

A monodisperse polystyrene dispersion (latex 206–2) was prepared by the direct polymerization of styrene by using potassium persulphate as initiator and an emulsifier (Aerosol MA, American Cyanamid CO., Wayne, NY, USA). The characteristics of the latex were as follows: particle arithmetic mean diameter 177.2 nm; standard deviation of distribution 4.7 nm; polydispersity ratio 1.006; electrophoretic mobility -5.50 nm s^{-1}V^{-1}cm; and zeta potential -77.5 mV. The preparation procedure, as well as all these parameters were defined and computed as described elsewhere[6].

The samples were extensively dialysed against distilled water (procedure, ref 7). The deionization procedure for the dialysed latex suspensions was carried out by the method of Vanderhoff *et al.*[2]. Initial concentrations were about 20% for the dialysed and about 5% the deionized latex. The concentration of the dialysed dispersions was increased to 50%, and that of the deionized samples to 30%, respectively, by vacuum evaporation. These concentrations were chosen as the upper limits, for above these limits considerable amounts of thick, dry film are found which prevent further study. Evaporation of deionized samples is somewhat simpler due to the absence of emulsifier which generally causes foaming. Solutions of sodium hydroxide, hydrochloric acid and sodium chloride were added instead of redestilled water in experiments where the variation of pH or ionic strength was needed.

A Haake–Rotovisko Couette-type rotational viscometer (Gebruder Haake, Berlin, BRD) and NV head were used. In order to ensure that all samples had been subjected to the same shear history the same loading procedure was employed in all experiments. Samples were pippetted into the stator of the viscometer and allowed to stand for 30 min to obtain the required temperature (20.0 ±0.05°C). The flow curves were measured by increasing the rate of shear, D, in 10 equal steps to a maximum value ('up' curves), and then decreasing the rate of shear in the same equal steps ('down' curves). The duration of shear at each step was 20 s. The readings from the instrument scale were constant even for the smallest D values.

The steady shear experiments were carried out at a constant shear rate of $0.16\ s^{-1}$ by using a reduction gear box ZG 100.

pH values were determined using a pH-meter immediately after viscosity measurements.

RESULTS AND DISCUSSION

The dependence of shear stress on rate of shear for the dispersions prepared (dialysed and deionized) at various concentrations was measured. The rheograms obtained are shown in *Figure 1*. The pH value of the dispersions ranged from 5.20 to 5.35. The influence of repeated purification procedure was also investigated. The deionized samples exhibited shear thinning behaviour at a concentration of 10%. The 'up' and 'down' curves were identical and are represented by a single line for each sample. Since no evidence of a thixotropic hysteresis loop was obtained, the systems measured can be considered as having a short thixotropic recovery times.

The effect of pH on the minimal viscosity (i.e. at $D = 2620\ s^{-1}$) of the 10% deionized sample at constant ionic strength (5.0×10^{-2} mol dm^{-3}) is shown in *Figure 2*. This effect is the same as that obtained for dispersions of much lower concentrations[6]. Although there are difficulties in the interpretation of the viscosity data obtained in a Couette-type viscometer when coagulation takes place, it would appear that a decrease in pH leads to destabilization of a dispersion. Consequently, coagulation of initially separated particles causes an increase in viscosity. We believe the limiting pH value at which destabilization takes place to be characteristic of a given system. The steady shear experiment with the 20% dispersions at a low shear rate ($D = 0.16\ s^{-1}$) showed that the shear stress build-up was dependent on observation time. *Figure 3* shows the difference between the dialysed and deionized samples, as well as the effect of additional rest-time on the onset and numerical value of the peak stress (static yield value). One sample was allowed to stand for 35 min, the other for 60 min. Practically identical equilibrium values for both deionized samples were established after the peak values.

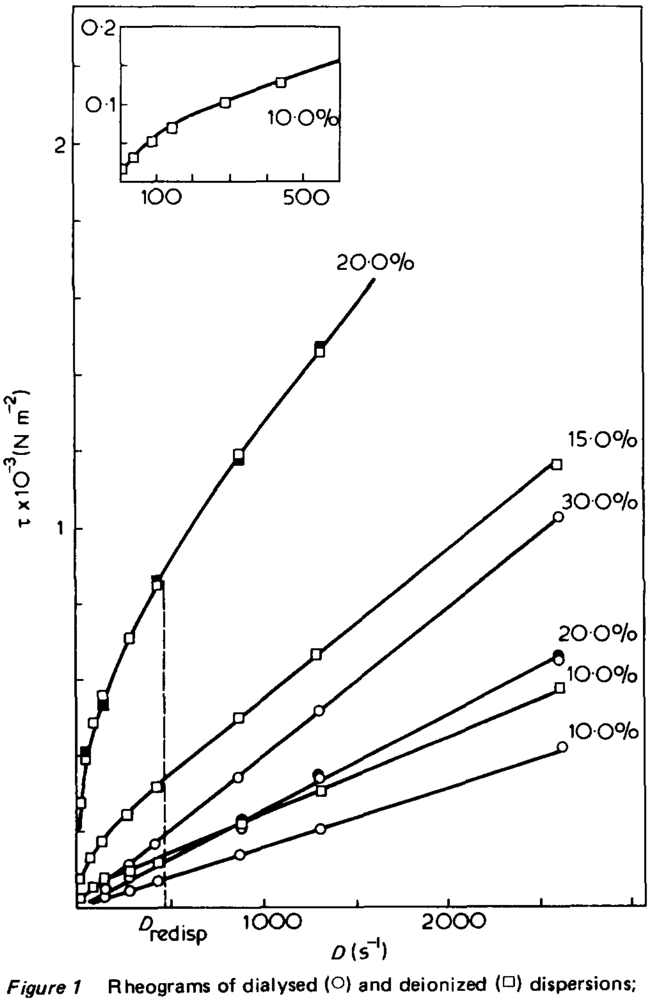

Figure 1 Rheograms of dialysed (○) and deionized (□) dispersions; (●, ■) repeated purification procedures; pH 5.20–5.35

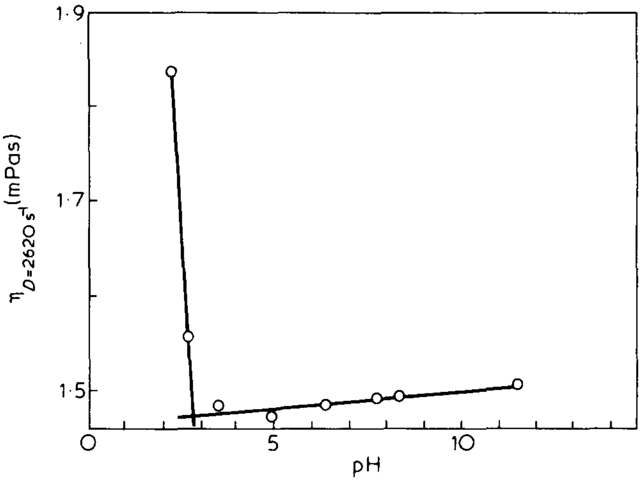

Figure 2 Minimal viscosities (at $D = 2620\ s^{-1}$) vs. pH values; $\mu = 5.0 \times 10^{-2}$ mol l^{-1}

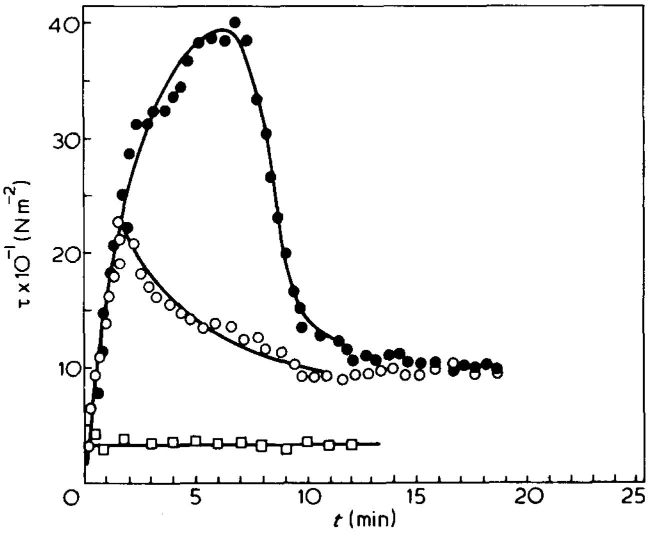

Figure 3 Dependence of shear stress on time of measurement at constant rate of shear ($0.16\ s^{-1}$); □, dialysed sample – rest time 60 min; ○, deionized sample – rest time 35 min; ●, deionized sample – rest time 60 min

Vanderhoff *et al.*[2] have shown that polymer latices treated with ion-exchange resins exhibit different interference colours. This is due to the diffraction of light from 'liquid crystals', i.e. from particle aggregates packed in ordered arrays. These are caused by deionization which removes emulsifiers and electrolytes from the system and increases the thickness of the double layer. Eventually the distance between the particles reaches the light diffraction region. Hachisu *et al.* have studied the ordered structure in monodisperse latex dispersions using a modified metallurgic microscope and have found in most cases a two-dimensional hexagonal lattice oriented parallel to the vessel wall. However, in some other cases cubic particle orientation, dislocation of ordered structure and sometimes microcrystals and even Brownian motion were found[3]. Summarizing both findings (*Figure 3*) it can be concluded that the observed peak values indeed reflect structuring within the system. Interference colours increased with the standing time of the sample; the same was true for the static yield value. These effects were not observed either for dialysed samples, or for deionized samples with concentrations lower than 20%. Hachisu *et al.* have found considerable ordering at much lower concentrations (even at ~0.55%); hence, a possible explanation is that the available rate of shear of the Haake instrument is still too high, leading to a disruption of the structure initially formed.

Albers and Overbeek[5] have explained non-Newtonian behaviour as being a result of agglomeration and structure formation in dispersions at low shear rates. The particle aggregates break down with increasing rate of shear over a wide range of shear until eventually redispersion is complete. For a monodisperse system, the critical shear rate is given by the equation:

$$D_{\mathrm{redisp}}=\frac{A}{36\pi\eta a\, d^2 \sin(2\alpha_{\mathrm{crit}})}$$

where A is the Hamaker (London–van der Waals) constant, η is the dispersion viscosity, a is the dispersed particle radius (86.6 nm in our case), d is the minimum distance between the surfaces of two particles, and α_{crit} is the critical angle for redispersion of an agglomerate. Albers and Overbeck take 30° for the critical angle claiming that the precise value of α_{crit} is of little importance to the problem.

When D_{redisp} is known it is possible to calculate the other parameters from rheological measurements. It would be particularly interesting to calculate the Hamaker constant, because this value is not well known for polystyrene dispersion due to difficulties associated with its determination (there are, however, a number of literature data showing theoretical calculation and experimental determination of the constant which was frequently determined by the coagulation method using a foreign electrolyte). To calculate Hamaker constant it is necessary to assume the values for dispersion viscosity, the minimum distance, and finally the D_{redisp}. We have used 20% deionized dispersion, because Albers and Overbeek had suggested that concentrations between 10% and 20% were suitable. The method of Gillespie[9] was used to determine the viscosity of the latex suspension, because it presumably corresponds to the viscosity of a non-agglomerated suspension, and was found to be 7.1 mPa s. The minimum distance between the surfaces of two particles is twice the difference between the effective particle radius, a_{eff}, and the particle radius obtained using electron microscopy [i.e., $d=2(a_{\mathrm{eff}}-a)$]. The relationship between a_{eff} and a is: $fa^3=a^3_{\mathrm{eff}}$, where, f, the correction factor is indicative of the double layer interaction. Our data were analysed by the method of Vanderfoff *et al.* who rewrote Mooney's equation[2]. We obtained a value for the correction factor of the deionized sample as 2.460, and consequently $a_{\mathrm{eff}}=119.4$ nm. Therefore, the minimum distance between the two particle is 61.6 nm. The critical shear rate, D_{redisp}, was obtained by a direct reading form the rheogram (*Figure 1*) and was equal to 450 s^{-1}.

The value of Hamaker constant was calculated to be 8.5×10^{-20} J. There, it would be interesting to compare the value calculated on the basis of rheological measurement presented here with other results. A paper by Force and Matijevic[10] gives a review of various investigations, and, according to them, experimental values ranged from 1×10^{-21} to 1.1×10^{-20} J, while corresponding theoretical values ranged from 5×10^{-21} to 9×10^{-20} J. This indicates the validity of Albers and Overbeek's explanation of non-Newtonian behaviour in dispersions, and, perhaps, provides a method for obtaining the values of Hamaker constant by measurement of viscosity.

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