

Viscosity behaviour of particles with non-adsorbing polymers Part III—experimental study

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Abstract

A series of well characterised *cis*-poly(isoprene) (PIP) polymers ($M_w = 1180, 8000, 28\,300, 31\,500, 86\,000, 115\,000$ and $130\,000$) have been added to dispersions of poly(12-hydroxystearic acid) (PHS) coated poly(methylmethacrylate) (PMMA) particles in dodecane. The ratio of particle size to adsorbed layer was also varied. For a given added polymer molecular weight, the polymer concentration in the continuous phase covered the dilute, semi-dilute and concentrated regimes as defined by the critical concentrations c^* and c^{**} . The viscosity behaviour of latex dispersions with added polymer were similar for all latex/polymer combinations except when polymer $M_w = 1180$ was added. In the latter case, the effect of adding polymer reduced both the viscosity and shear thinning behaviour. This supports the contention that the lower molecular weight polymer acts more like a diluent than a depletant. The behaviour of the viscosity ratio (the viscosity of the dispersion relative to that of the medium) as a function of polymer concentration increased with an increase in the polymer concentration until some critical concentration (c_{max}) for all polymers except for a polymer molecular weight 1180 Daltons. The addition of the polymer $M_w = 8000$ gave the highest viscosity ratio values in the polymer concentration range studied. It was found that the viscosity of all latex/polymer combinations decreased with an increase in temperature. The results suggest that the viscosity behaviour cannot be explained on the basis of a simple steric-elastic model and require a modified theoretical treatment.

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1. Introduction

This is the third in a series of papers reporting the rheological properties of a system containing quasi hard spheres and a non-adsorbing polymer. Experimental and theoretical studies have been undertaken on the effect of the depletion interactions on the phase separation and the viscoelastic properties of the systems [1,2]. The work presented here examines the unusual viscous flow behaviour of these systems.

Non-aqueous colloidal dispersions are encountered in many industrial formulations. In a number of applications exemplified by materials processing, non-aqueous colloidal dispersions must be formulated to display well-defined rheological behaviours. Many governments are now pushing for restrictions in the use of volatile organic compounds (VOCs) and solvents considered hazardous air pollutants

(HAPs) [3]. For instance, liquid coatings formulation must simultaneously meet VOC limitations and HAP restrictions by shifting to high solids, low-solvent coatings as well as water-borne coatings. Although, a lot of research is now concentrating on water-borne systems, non-aqueous systems will still continue to be used for sometime to come. So, non-aqueous formulations that meet existing and pending VOC and HAP regulations and offer the performance customers are willing to pay for are important to industry.

In many paint and pesticide formulations, thickeners such as hydroxyethylcellulose are added to control the rheology of the dispersion [4]. This is to reduce settling and ease of the application of the formulation. In certain formulations, the paint must be highly pseudoplastic or shear thinning and possibly thixotropic.

It is well established that the addition of non-adsorbing (free) polymer can cause several events to occur depending on the type, molecular weight and concentration of the polymer. Two phenomena of particular relevance have been documented and these are depletion flocculation and depletion

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restabilisation. Experiments and theory have shown that concentrations of free polymer comparable to that at which chain–chain overlap begins to occur (i.e. near the semi-dilute concentration, c^* , of the polymer solution) can induce flocculation, while relatively higher concentrations can impart stability [5].

Reynolds and Reid [6] have studied the rheological properties of a three-component system of concentrated sterically stabilised poly(methylmethacrylate) (PMMA) latex particles dispersed in non-aqueous non-adsorbing polymer solution. The average hydrodynamic diameter of the PMMA latex particles (i.e. core plus chemically grafted poly(12-hydroxystearic acid), PHS chains) was 180 nm. The adsorbed layer thickness δ was about 9 nm. The non-adsorbing polymer was poly(isobutylene) (PIB) of weight-average molecular weights (M_w) 380 000 and 2000, whose radius of gyration R_g in dodecane were estimated to be 32 and 2.6 nm, respectively. They observed that the rheology and phase behaviour were different for the two molecular weights. The rheological comparisons were mainly based on what they called the viscosity ratio, η_{ratio} , defined as the reduced viscosity of the dispersion with the added polymer to the polymer containing continuous phase at the same shear rate. η_{ratio} data were relatively higher for systems with added lower molecular weight PIB. In contrast to systems with added higher molecular weight *cis*-poly(isoprene) (PIP), the low molecular weight polymer exhibited not only shear thinning but also time-dependent rheological (thixotropic) behaviour indicating high degree of structure within the samples. The increase in η_{ratio} for the systems with added low molecular weight polymer was compared to the steric–elastic effect suggested by Choi and Krieger [7,8]. For PIB/dodecane continuous phase used, Reynolds and Reid envisaged that since the low molecular weight PIB was of comparable size to that of the PHS stabilising chains and when used at high concentration, it becomes the effective dispersion medium. The net effect of a concentrated dispersion will be to compress the PIB chains, thus giving rise to the steric–elastic repulsive force.

According to Choi and Krieger, the steric–elastic effect: (i) should be more marked with higher molecular weight polymers in solution and small particles; and (ii) causes an increase in viscosity of the dispersion with increase in temperature. This work is an extension of the work by Reynolds and Reid and attempts to address the two above issues.

2. Experiments

2.1. Preparation and characterisation of the dispersions

Five PMMA latices sterically stabilised with chemically grafted PHS chains were prepared using the method described by Antl et al. [9]. The PHS chains are terminally grafted at multiple points along the backbone of an insoluble anchor polymer PMMA. Three “comb-like” PHS stabilisers

Table 1
Particle characterisation data based on high shear viscometry experiments

Latex code	a (nm)	COV (%) ^a	Stabiliser code	δ (nm)	PHS chain (M_w)	a/δ
HK3	405	4.7	I	14	3100	29
HK4	267	5.8	I	14	3100	19
HK5	180	8.5	II	3.5	680	51
HK7	116	12.2	ICI	4	1800	29
HK8	156	9.2	ICI	6	1800	26

^a COV is the coefficient of variation = $100 \times \text{S.D. deviation/radius}$.

(code names I, II and ICI) of varying PHS chains degrees of polymerisation were used. Stabilisers I and II were prepared in the laboratory at Bristol University whereas stabiliser ICI was supplied by Dr. Neil Perrins, ICI Paints Division, Slough.

The particle core radius, a , was determined by transmission electron microscopy. The particles core volume fraction was derived by drying a sample of known weight and knowledge of the densities of PMMA core particles ($\rho = 1.18 \text{ g cm}^{-3}$) and dodecane ($\rho = 0.749 \text{ g cm}^{-3}$). The adsorbed layer thickness, δ , was determined by using the Saunders' method [10] and the method based on the Krieger–Dougherty viscosity–concentration relationship [11] suggested by Goodwin and Ottewill [12]. The details of these methods are described elsewhere [1,2,13]. The effective volume fraction, ϕ_e , is calculated using Eq. (1).

$$\phi_e = \phi \left(1 + \frac{\delta}{a} \right)^3 \quad (1)$$

The maximum packing fraction in the Krieger–Dougherty equation was iterated to give the best fit to all the data simultaneously. The two methods gave similar values of δ and the mean values are used in this paper. The particle characterisation data are given in Table 1. The maximum packing fraction was found to be $\phi_m \approx 0.6$ using this approach and this value provided a sensible relationship between the adsorbed layer thickness and the molecular weight of the PHS chains used in the synthesis. A packing fraction of $\phi_m = 0.605$ is adopted throughout this study which it is consistent with the packing of quasi hard spheres in layered flow.

2.2. Characterisation of the polymers

The added free polymer was *cis*-poly(isoprene) and was obtained from Polymer Laboratories, together with molecular weight characterisation data. PIP was chosen for three main reasons.

- It is soluble in dodecane (solubility parameters are not very different [14]).
- There is little or no adsorption of the polymer to the particles probably due to its low functionality.
- The polydispersity (ratio of weight–average to number average molecular weights, $M_w/M_n < 1.10$) was low over the molecular weight range of interest.

Table 2
Characteristic properties of PIP in dodecane

Polymer code	M_w (g mol ⁻¹)	M_v (g mol ⁻¹)	M_w/M_n	$[\eta]$ (cm ³ g ⁻¹)	R_g (nm)
P1K	1180	1203	1.08	3.61	1.1
P8K	8000	8308	1.03	11.19	3.2
P28K	28300	29103	1.03	26.86	7.0
P31K	31500	31257	1.03	28.23	7.7
P86K	86000	87862	1.02	58.30	14.5
P115K	115000	110000	1.02	68.37	17.4
P130K	130000	–	1.05	76.98 ^a	18.9

^a Extrapolated data using Eq. (2).

The density of the polymer was 0.91 g cm⁻³. The molecular weights were chosen such that there were situations whereby the polymer radius of gyration R_g is roughly equal to δ . As stated earlier, it is postulated that the steric–elastic effect is observed when this condition is fulfilled [4]. R_g values were derived from measured intrinsic viscosities. For a given polymer molecular weight, the relative solution viscosity of PIP in dodecane at 298 K was measured using capillary viscometry. This was performed at several polymer concentrations. These data were extrapolated linearly by the Huggins [15] and Kraemer [16] plots to find the intrinsic viscosity at infinite dilution $[\eta]$. This was performed for each molecular weight and the intrinsic viscosity was plotted using the Mark–Houwink equation allowing for the low molecular weight rigidity which gave:

$$[\eta] = 1.0 + 0.158M_v^{0.72} \text{ cm}^3 \text{ g}^{-1} \quad (2)$$

for $1180 \leq M_w \leq 115000$, where M_v is the viscosity average molecular weight. The intercept allows for the rigidity of the chain at low molecular weight. The power index 0.72 indicates that dodecane is a good solvent for PIP and the latter in solution exists as open flexible random coils [17,18]. Table 2 shows the molecular weight data supplied with the respective extrapolated intrinsic viscosities and calculated R_g values [1].

2.3. Viscosity measurements

The viscosity measurements were carried out using a Bohlin VOR rheometer. Three designs of the instrument geometry were used in this study: a cone and plate; a double concentric cylinder; and a bob and cup (single concentric cylinders).

The shear stress–shear rate dependence of the samples was determined using the viscometry mode. A known strain rate is applied and the resulting stress measured. The rheometer could be programmed to apply a range of shear rates to the sample and the shear stress at every shear rate determined. The viscosity as a function of shear rate is calculated from the ratio of stress to strain. Each viscometric run was commenced at the lowest shear rate and increased successively to higher shear rates to obtain a flow curve.

3. Results and discussions

3.1. Choice of particle volume fraction range

The high shear relative viscosity, $\eta_r(\infty)$, against volume fraction, ϕ , curves for the latex dispersions without added polymer are given in Fig. 1. The curves show that the viscosity starts to increase between $\phi = 0.35$ and $\phi = 0.55$. An average surface-to-surface distance, h , between the particles in the dispersion can be estimated from Eq. (3).

$$h = 2a \left(\left(\frac{\phi_m}{\phi} \right)^{1/3} - 1 \right) \quad (3)$$

Assuming layered flow $\phi_m = 0.605$ for hard spheres, an example of the calculated h values for $\phi = 0.50$ for the five lattices studied are given in Table 3. It is clear that h is generally greater than twice the adsorbed layer thickness (2δ) for each latex. It has been observed that sterically stabilised dispersions for which the ratio a/δ is small (i.e. soft particles), $\phi_m > 0.605$ [19]. However, according to Eq. (3), h will even be larger for larger ϕ_m . This means that h is greater than 2δ for all the lattices. The results suggest that the particle volume fraction range chosen is such that significant interpenetration of the steric layers are minimal at the concentrations interrogated here.

3.2. Choice of the polymer concentration range

The concentration of the polymer in this work is expressed in weight of polymer per unit volume of the solvent. For

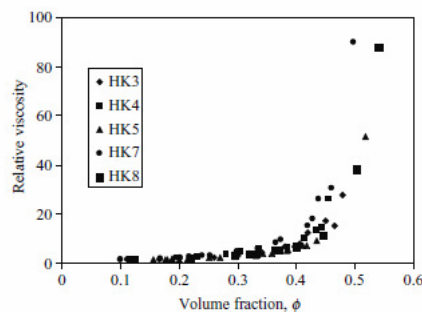


Fig. 1. High shear relative viscosity–volume fraction behaviour for PMMA lattices dispersed in dodecane.

Table 3
Surface-to-surface separations of latex particles at $\phi = 0.50$

Latex code	a (nm)	2δ (nm)	h (nm)
HK3	405	28	29
HK4	267	28	19
HK5	180	7	51
HK7	116	8	15
HK8	156	12	20

Table 4
Critical polymer concentrations calculated using Vincent et al. [21] model

Polymer code	M_w (g mol ⁻¹)	R_{g0} (nm)	R_g (nm)	c^* (g cm ⁻³)	c^{**} (g cm ⁻³)
P1K	1 180	1.0	1.1	0.261	1.44
P8K	8 000	2.9	3.2	0.0720	0.400
P28K	28 300	5.9	7.0	0.0243	0.168
P31K	31 500	6.4	7.7	0.0203	0.0147
P86K	86 000	11.0	14.5	0.00823	0.0789
P115K	115 000	12.8	17.4	0.00644	0.0670
P130K	130 000	13.7	18.9	0.00568	0.0617

instance, 0.01 g cm⁻³ means 0.01 g of PIP in 1 cm³ of dodecane.

According to polymer solution theory [20], there are three polymer concentration regimes often considered and these are dilute, semi-dilute and concentrated regimes. These regimes are separated by two critical concentrations. The first represents the concentration at which the polymer coils begin to touch or overlap and is often regarded as the onset of the semi-dilute regime or c^* . The second critical concentration represents the onset of the concentrated regime or c^{**} such that a more or less uniform segment density of polymer coils in solution is achieved. In the concentrated regime, the concentration of the solution has been increased sufficiently so that the dimensions of the coils shrink to their unperturbed values.

Various theoretical models have been suggested to estimate c^* and c^{**} [20]. For instance, the equations derived by Vincent et al. [21] for c^* and c^{**} are:

$$c^* = \frac{M_w}{b^* R_g^3 N_A} \quad (4a)$$

and;

$$c^{**} = \frac{M_w}{b^{**} R_{g0}^3 N_A} \quad (4b)$$

where R_{g0} and R_g are the unperturbed and perturbed radius of gyration, respectively, and b^* and b^{**} are constants that are equal to 5.63 and 1.36, respectively, for hexagonal close packing of polymer coils. N_A is the Avogadro's number. The calculated c^* and c^{**} using the above equations for the seven polymers are given in Table 4. The polymer concentrations ideally would be chosen such that the three concentration regimes were covered. However, this was not always possible due to insufficient availability of polymer samples and the difficulty experienced in dissolving the polymer to produce high polymer concentrations.

There is a critical concentration at which the free polymer concentration in a concentrated colloidal dispersion may start to induce depletion flocculation [5] and is referred to in this paper as c^+ . It has been observed that rheological parameters such as the yield stress, plastic viscosity and shear modulus [22] start to increase dramatically above c^+ . Furthermore, restabilisation of the dispersion has been claimed [5] to take place if the free polymer is added in sufficient

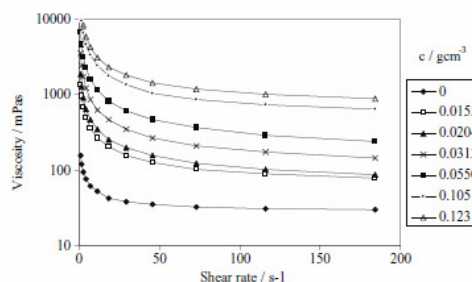


Fig. 2. Typical viscosity–shear rate behaviour of PMMA dispersions at various polymer concentrations when polymer $M_w = 8000$ was added (HK4+P86K, $\phi = 0.425$).

quantity to exceed the second critical polymer concentration which is referred to as c^{++} in this paper. Both depletion flocculation and restabilisation effects are reversible on dilution. It has been demonstrated that depletion flocculation commences at c^+ which is in excess of c^* [20]. As the polymer concentration is increased, restabilisation concentration c^{++} is reached, and it has been suggested that it occurs in the neighbourhood of c^{**} . It is important to stress that the object in this work is not to contest theoretical background of the equations used to estimate c^* and c^{**} but experimentally span a range of polymer concentrations. The calculated critical concentrations were used as a guide for the range of polymer concentrations prepared in this study.

3.3. Effect of polymer concentration and molecular weight on viscosity

The viscosity behaviour of PMMA latex dispersions with added PIP is discussed in two parts. The effect of the polymer concentration in all latex and polymer combinations showed the same trends for all molecular weights except for the addition of polymer P1K ($M_w = 1180$). Therefore, the effect of adding polymer P1K on dispersion viscosity is presented separately.

3.3.1. $M_w \geq 8000$

The effect of polymer concentration on viscosity was studied over a wide range of shear rates from as low as the instrument could detect up to as high as 1000 s⁻¹. The shear stress, σ , and correspondingly the viscosity, η , increased with an increase in polymer concentration. There is a linear relationship between shear stress and shear rate above shear rate of 46 s⁻¹ for the samples. Typical examples of the behaviour of η and η_{ratio} are plotted in Figs. 2 and 3, respectively, for latex HK4 with added polymers P86K and P115K. The viscosity ratio, η_{ratio} , of the systems at high shear rates for the dispersions with added polymer (i.e. shear rate region where both medium and dispersion viscosities were independent of shear rate) was similar to that of the

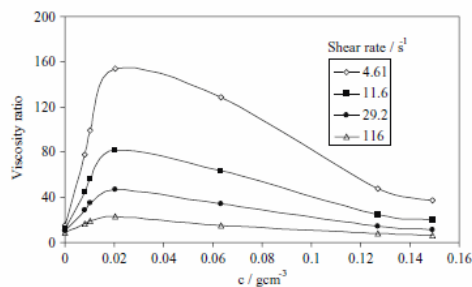


Fig. 3. Typical viscosity ratio–polymer concentration behaviour of PMMA dispersions at various shear rates when polymer $M_w \geq 8000$ was added (HK4+P115K, $\phi = 0.377$).

dispersion without added polymer. This suggests that the depletion flocculated network structures observed in quiescent conditions in the previous studies [1,2] were disrupted at high shear rates. Consequently the data reported here are mainly from the shear thinning region (i.e. this is at a shear rate below 120 s^{-1}).

The viscosity increased with increasing polymer concentration. However, η_{ratio} goes through a maximum with increasing polymer concentration. The behaviour of the viscosity ratio as function of polymer concentration and polymer molecular weight shows that both,

- the polymer concentration at which the maximum η_{ratio} occurs (c_{max}); and
- the magnitude of the maximum η_{ratio} in the region of c_{max} decreases with an increase in the molecular weight of the added polymer at any shear rate in the shear thinning region.

These points are further illustrated in Table 5 for latex systems of similar effective volume fraction defined by Eq. (1). It should be noted that the maximum η_{ratio} occurs in the semi-dilute polymer concentration regime (i.e. between c^* and c^{**}). The polymer P8K caused higher increases in η_{ratio} in this concentration range than the other polymers. Reynolds and Reid [6] observed similar increases in η_{ratio} when low molecular weight PIB ($M_w = 2000$) was added. However, they did not observe the decrease in η_{ratio} for both high and low molecular weight added polymers. This could be due to the fact that they did not achieve polymer con-

Table 5
Effect of polymer concentration on viscosity of latex/polymer ($\phi_e \sim 0.49 \pm 0.03$) systems at shear rate 11.7 s^{-1}

Latex code	ϕ	ϕ_e	M_w	$c_{\text{max}} (\text{g cm}^{-3})$	η (mPa s)	η_{ratio}
HK4	0.448	0.522	115 000	0.0210	468	99
HK4	0.425	0.495	86 000	0.0313	624	101
HK4	0.425	0.495	28 300	0.0728	783	121
HK7	0.416	0.460	8 000	0.343	9500	613

centrations as high as c^{**} . The increase in η_{ratio} is gentle as one moves from polymer P115K to polymer P28K and the sudden increase seem to occur between polymers P28K and P8K. η_{ratio} increases about five times around c_{max} by decreasing the added polymer molecular weight from $M_w = 115 000$ to $M_w = 8000$. It is important to realise that the dimensions of the polymer coil being comparable to the adsorbed layer thickness that Reynolds and Reid postulated to give an additional steric–elastic repulsive force seems to have no major significance in the observed increase in viscosity ratio. Otherwise, the combination of latex HK5 ($\delta = 3.5 \text{ nm}$) and polymer P8K ($R_g = 3.2 \text{ nm}$), for instance, would have shown marked increase in η_{ratio} . According to Choi and Krieger [8], the mechanism for the steric–elastic effect is such that it should be strongest for small particles (where the void spaces are small), and high molecular weight polymers. For a given polymer molecular weight at the same concentration, rheological parameters such as yield stress, plastic viscosity and viscosity ratio were observed to increase with decrease in particle size. Their increase is due to the surface area-to-volume ratio which increases with a decrease in particle size resulting in an increase in the net attraction between particles as explained by Tadros [22]. But for a given particle size, the low molecular weight polymer (i.e. P8K) gave a more marked increase in η_{ratio} which is contrary to the steric–elastic mechanism.

3.3.2. $M_w = 1180$

The viscosity and viscosity ratio behaviour of dispersions with added polymer PIK was different from that of the other latex/polymer systems studied. The polymer solutions in the shear rate range studied were assumed to be Newtonian as it was only possible to measure the viscosity at generally higher shear rates than used for the dispersions. There were no signs of shear thinning at high shear rates where the viscosity was measurable for the polymer solutions. The term viscosity ratio is used for this data although strictly each data set is not obtained at the same rate. This has no numerical consequence for the data. Both viscosity and viscosity ratio decreased with increase in polymer concentration. In fact, the latex dispersions without added polymer were found to exhibit more shear thinning character than the dispersions with added polymer. Figs. 4 and 5 show the effect of polymer concentration on viscosity and viscosity ratio, respectively. Clearly, the effect is such that the higher the polymer concentration the more Newtonian the dispersions became in the shear rate range studied.

The rheological behaviour of latex samples with added polymer PIK resemble that of a concentrated latex dispersion without added polymer as it is diluted down with solvent. In other words, the polymer seems to be acting as a “co-solvent” dispersing the particles. As the polymer concentration increased, it was observed visually that the dispersion became less and less viscous. This is the opposite of what was observed for samples with added higher molecular weight polymers. The samples have clearly lost their

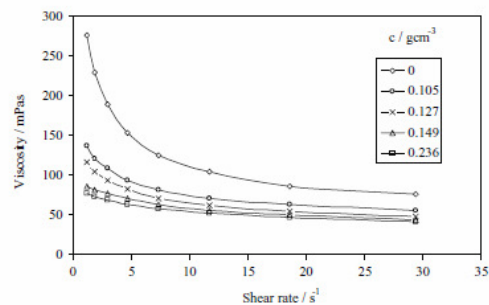


Fig. 4. Typical viscosity–shear rate behaviour of PMMA dispersions as a function of polymer concentration when polymer P1K was added (HK8+P1K, $\phi = 0.475$).

network structure as compared to the addition of the high molecular weight polymer. The results here are entirely consistent with the previous studies [1,2] and imply that the lowest molecular weight polymer does not induce an attractive depletion interaction between the particles.

3.4. Effect of temperature on viscosity

An increase in temperature caused a decrease in viscosity for all combinations of latex, polymer molecular weight and concentration. Choi and Krieger [8] showed that the viscosity increases with an increase in temperature for systems that show the steric–elastic effect because the elastic modulus of a polymer increases with an increase in temperature. In all particle/polymer combinations, the viscosity of the systems decreased with increase in temperature even for systems that were found to be highly elastic [1,13]. In the case of latex dispersions with added polymer P8K (huge increases in viscosity ratio were observed), the viscosity behaviour was the same as shown in Table 6. Polymer solutions and dispersions without added free polymer also showed a similar

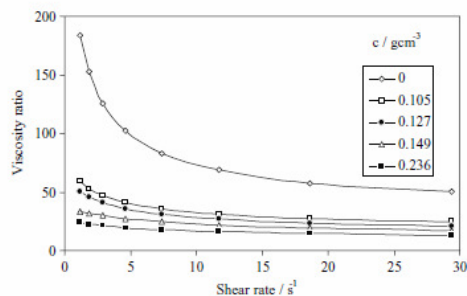


Fig. 5. Typical viscosity ratio–shear rate behaviour of PMMA dispersions as a function of polymer concentration when polymer P1K was added (HK8+P1K, $\phi = 0.475$).

Table 6
Effect of temperature on viscosity of latex HK7 ($\phi = 0.416$) with added polymer P8K ($M_w = 8000$)

Shear rate (s^{-1})	Viscosity (Pas)					
	0.0764 ($g\ cm^{-3}$)		0.149 ($g\ cm^{-3}$)		0.550 ($g\ cm^{-3}$)	
	25 °C	35 °C	25 °C	35 °C	25 °C	35 °C
1.85	0.311	0.186	6.97	4.60	43.7	35.7
4.64	0.237	0.155	3.34	2.32	20.3	17.2
11.7	0.185	0.125	1.78	1.21	10.5	8.39
29.4	0.144	0.102	0.925	0.656	5.11	4.41
73.5	0.120	0.088	0.506	0.379	2.49	2.19

trend when the data was plotted using a linearised form of the Arrhenius equation. The equation is defined in Eq. (5),

$$\eta = B e^{E/kT} \quad (5)$$

where E is the viscosity energy of activation, B , a constant, k , the Boltzmann constant and T , the absolute temperature [23]. The data from the polymer solutions and latex only gave a much better Arrhenius fit than that of systems with added polymer [13]. However, the results do show that the viscosity in all combinations of latex and polymer decreases with increases in temperature. These results simply suggest that the viscosity behaviour cannot be simply explained on the basis of the steric–elastic effect as earlier suggested [6].

4. Discussion

The results of this study clearly demarcate a difference in behaviour between the P1K polymer, the lowest molecular weight system, and the higher molecular weight polymers. In the previous papers in this series it was shown that no phase separation effects were seen with a polymer with a molecular weight of 1180 Da. The viscosity data here suggests the absence of any significant network structures when this polymer is added to a quasi hard sphere system. This supports the contention that the low molecular weight polymer acts more like a diluent than a depletent.

Previous studies in this series [1,2] of the phase behaviour and elasticity of the higher molecular weight systems have been investigated. These have proved amenable to a simple model based on a new description of the pair interactions between the particles. Essentially such systems show phase behaviour consistent with other literature data [24] and the phase separation behaviour (which was normalised to the viscosity [1,2]) consistent with attraction between the particles giving rise to non-ergodic behaviour [25].

The viscosity results presented in this paper and those of Reynolds and Reid [6] are much more difficult to explain. An initial impression of the data presented here is that it provides no clear support for the steric–elastic effect, the possibility of which has been explored using both temperature and concentration. If the effect is only significant when the equilibrium configuration of the polymer becomes restricted

by increasing concentrations or radius of gyration then this mechanism becomes important once the mean particle separation reduces below the equilibrium persistence length of the polymer. The conditions for the onset of chain compression are easy to approximate by equating $2R_g$ to the mean interparticle spacing. This calculation can be performed for the data in Table 5 and this shows that the mean particle separation in the high shear limit is insufficient to compress the polymer. Thus with this hypothesis the steric–elastic effect would be small in the high shear rate limit. However, the experimental data indicates a surprising increase over that of the polymer alone.

There is a speculative option which might offer the possibility of an explanation. Buscall [26] suggested that a flow curve of a dispersion can be related to the pair interactions. He proposed that as the shear rate is increased convective motion overcomes the Brownian motion of the particles and forces the particles closer together. The stress required to do this can be equated to the pair interaction between the particles and the viscosity to an effective volume fraction or spacing between the particles. Suppose the spirit of this idea is adopted as an explanation of the phenomena seen here. As the shear rate is increased the spatial arrangement of the particles changes [27]. Although Buscall did not allow for the effect it would be expected that the packing fraction would increase with increasing stress, thus the average spacing between particles increases. There is a competing effect which is the main process identified by Buscall. As the stress is increased the increased energy of particle collisions will cause the mean separation to reduce. Now if these ideas are extended to a system containing free polymer an interesting possibility arises which is that a polymer chain(s) could get trapped ‘transiently’ between particles as they ‘collide’. The extent of entrapment depends in part upon a balance of the change in spatial arrangement of the particles and the energetics of the collision. This could be thought of as giving rise to a dynamic steric–elastic effect. The two competing processes could give rise to a peak in the viscosity ratio. However, this simple idea is underpinned by very complex polymer-particle dynamics which would require a thorough theoretical treatment to elucidate. This idea prompts some questions, why, for example, does the lower molecular weight polymer lead to the greatest increase in the viscosity ratio? It could be explained by the chain being more rigid at lower molecular weights, or the possibility that more coils are trapped per collision with a low molecular weight polymer than with a high one. The response with temperature would be a complex balance of increased Brownian motion and increased chain elasticity. Thus temperature would not prove a simple test of the theory.

5. Summary

The shear thinning behaviour of PMMA dispersions with added polymer depends heavily on polymer molecu-

lar weight and concentration. There is a critical polymer molecular weight at which increasing the polymer concentration in a latex dispersion produces a dispersion which shows less shear thinning and thus a reduced interaction force between the particles. In light of the previous studies [1,2], it can be concluded that the low molecular weight added polymer fails to induce depletion flocculation. It is a diluent.

There is also a polymer molecular weight range which causes a relatively large increase in the viscosity ratios in the semi-dilute polymer concentration regime. In the semi-dilute and concentrated regimes, the viscosity of a polymer solution is higher so that the calculated viscosity ratio is reduced more than in the dilute regime. The large increases in viscosity ratio cannot readily be explained on the basis of the steric–elastic effect but a dynamic interpretation of this idea may give an explanation for the phenomena. The general behaviour (excluding magnitude) of the viscosity ratio seems to be independent of the ratio of the particle size to adsorbed layer thickness.

The phase behaviour of depletion systems have been widely studied and described by theoretical models. The rheological behaviour of such systems is far less well developed. It has been shown in previous publications that the elasticity can be predicted to an extent [1,2] with the general principles being reasonably well understood. The viscous flow behaviour contains subtle features which are puzzling and which have not received the attention they deserve. There is the possibility that the flow curve of these systems is uncovering generic information about concepts underpinning the nature and dynamics of mixed systems. This could prove of particular relevance to multicomponent blends with some interesting implications for commercial systems which are so often formed from complex mixtures.

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