Solution behaviour of a random copolymer of poly(isobutyl methacrylate–t-butylaminoethyl methacrylate): 2. Viscosity and light scattering intensity studies*

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(*Received 13 November 1989; revised 22 December 1989; accepted 16 January 1990*)

Random copolymers of poly(isobutyl methacrylate–t-butylaminoethyl methacrylate) with $M_w \sim 2.4 \times 10^6$ g mol^{-1} could be shown to form more expanded coils in the very dilute solution regime ($\lesssim 10^{-5}$ g ml^{-1}) due to intramolecular repulsion, to associate in most solvents in the dilute solution regime ($\sim 10^{-4}$ g ml^{-1}) where inter- and intramolecular interactions are present, and to aggregate further in semidilute/concentrated solution regimes where intermolecular interactions dominate. The formation of larger aggregates in semidilute/concentrated solutions is responsible for its effectiveness as a polymer additive. At the same time, the rheological properties, such as the shear-rate dependence of the viscosity, tend to become more sensitive to concentration and temperature variations.

(Keywords: solution behaviour; random copolymer; viscosity; light scattering)

INTRODUCTION

Random copolymers of (isobutyl methacrylate and t-butylaminoethyl methacrylate (poly(iBMA–tBAEMA)) have been used successfully as polymer additives for lubricants and coating materials in order to influence the fluid viscosity in polar and aprotic solvents under different conditions. However, poly(iBMA–tBAEMA) has been very difficult to characterize because of its aggregation behaviour due to intramolecular/intermolecular interactions, which are responsible for its utility as a polymer additive in the first place. The solution behaviour of poly(iBMA–tBAEMA) has recently been investigated by means of laser light scattering (LLS)[1]. The key to such a successful LLS study is the coincidental isorefractive nature of homopolymers of poly(iBMA) and poly(tBAEMA) and of the random copolymer poly(iBMA–tBAEMA). Thus, as far as LLS is concerned, measurements of absolute scattered intensity together with those of refractive index increments could yield estimates of the weight-average molar mass of the aggregates (here we retain the notation M_w for convenience), its *z*-average root-mean-square radius of gyration (R_g, instead of an apparent value), as well as interparticle interactions in terms of the second virial coefficient A_2. Poly(iBMA–tBAEMA) solutions in a variety of solvents may not yield the same mass weight because the degree of association (due to intermolecular interactions), as well as intramolecular interactions at even dilute concentrations, could depend on the solvent quality. In fact, most of the solvents tested, such as isopropylamine (IPA), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAA) and a solvent mixture of TMEDA and 3-heptanone (HTN) with a molar ratio of [TMEDA]/[HTN] = 0.4/0.6, show aggregation behaviour for the polymer solution in all the solvents (except perhaps for IPA). The weight-average molar mass of the particles (in 10^6 g mol^{-1}) is 2.42, 5.86, 8.52, 9.08 and 13.6 in the above solvents, respectively. The small refractive index increment differences ($\sim$0.001–0.003) among the homopolymers and the random copolymer could not account for the large molar mass differences exhibited by the poly(iBMA–tBAEMA) in different solvents ranging from IPA to a solvent mixture of TMEDA/HTN. So, we were forced to come to the conclusion that poly(iBMA–tBAEMA) could have different degrees of aggregation in different solvents. There could be composition inhomogeneities as a function of molecular weight in the random copolymer varying from one lot to another. Consequently, there could be quantitative differences in the degree of aggregation for random copolymers with the same overall copolymer composition. Nevertheless,

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* Dedicated to Professor Walther Burchard on the occasion of his 60th birthday

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the qualitative nature of the solution behaviour of poly(iBMA–tBAEMA) was clearly established.

We further tested our hypothesis by making light scattering measurements at very dilute solution concentrations. Indeed we observed a break-up of the supramolecular polymer formation in the Zimm plots and estimated the single-polymer weight-average molecular weight to be in the neighbourhood of $2.4\times10^6\,\mathrm{g\,mol^{-1}}$, in agreement with an estimate from aqueous size-exclusion chromatography (s.e.c.) in which aggregation could be removed by chemical means and that based on poly(iBMA–tBAEMA) in IPA. There was no reason *a priori* why the aggregated random copolymer should break up into smaller fragments over the very dilute concentration range that was accessible to LLS. However, the fact that we did not observe a break-up based on changes in the absolute scattered intensity, the apparent radius of gyration and the apparent hydrodynamic radius strengthened our supposition that the random copolymers formed aggregated supramolecules in most solvents due to strong intermolecular interactions dominated by the presence of pendent aminoalkyl groups.

In this paper, we report results of our viscosity studies, together with additional LLS measurements at very dilute solution concentrations, in order to provide further evidence on the supramolecular formation of poly(iBMA–tBAEMA) at dilute and semidilute solution concentrations. In our viscosity studies, we used poly(iBMA), whose chemical structure is quite similar to that of the copolymer except for the pendent aminoalkyl group, as our reference for comparison purposes.

EXPERIMENTAL METHODS

Materials

The random copolymer of poly(iBMA–tBAEMA) with a molar ratio of iBMA/tBAEMA of 77/23 (by ^{13}C n.m.r.) was prepared by emulsion polymerization and purchased from Polyscience (Lot No. CM1-120). The homopolymer poly(iBMA) was prepared by emulsion polymerization and purchased from Rohm and Haas Co. (Lot No. 39015-23).

The weight-average molecular weight for poly(iBMA–tBAEMA) was estimated to be $2.4\times10^6\,\mathrm{g\,mol^{-1}}$ by aqueous s.e.c. and LLS. The weight-average molecular weight for poly(iBMA) was determined to be $1.7\times10^6\,\mathrm{g\,mol^{-1}}$ by LLS. All solvents were of high quality (Aldrich Chemical Co.) and freshly distilled before solution preparation.

For dilute solutions, the polymer was dissolved in solvents at ~60°C (with occasional stirring) for about four days and then equilibrated at room temperature for an additional period of at least three days.

Viscosity measurement

The viscosities of semidilute and concentrated polymer solutions were determined with a magnetic needle rheometer developed by our research group at Stony Brook[2,3]. The magnetic needle was constructed by enclosing a small magnetic bar inside a precision quartz capillary tubing of 1 mm o.d. and 0.9 mm i.d. The density of the quartz-enclosed magnetic needle could be made to specific values depending on the magnitude of solution density and of solution viscosity. The magnetic force F_M on a stationary magnetic needle levitated in a stationary fluid is:

$$F_M(v=0)=F_g-F_b \tag{1}$$

where F_g ($=mg$) is the gravitational force; $-F_b$ ($=mg\rho_l/\rho_s$) is the buoyancy force, with ρ_l and ρ_s being the densities of the liquid and of the magnetic needle, respectively. When the fluid is moving past (e.g. up at a constant velocity v) the stationary (levitated) magnetic needle, an additional viscoelastic force F_e (or drag force) acts on the needle. Then:

$$F_M(v)=F_g-F_b+F_e \tag{2}$$

The variation in the magnetic force, $\Delta F_M=F_M(v)-F_M(0)$, is proportional to the product of the velocity v and the fluid viscosity η. The shear rate can be calculated according to the equation[3]:

$$\dot{\gamma}=(2v/d)(b^2-1)/[b^2(\ln b-1)+\ln b+1] \tag{3}$$

where $b=D/d$ with D and d being the diameters of the sample cell and the needle, respectively. The sample chamber in the magnetic needle rheometer could be controlled to within 0.05°C.

At dilute polymer solution concentrations, the viscosities were measured using an Ubbelohde viscometer in a water bath with temperature controlled to ±0.005°C. The flow time could be determined by a fibre-optic viscosity timer with a precision of 0.001 s (ref. 4). However, as a 0.005°C fluctuation in temperature corresponds to a viscosity change of about 0.005 s for our capillary viscometer, we have retained 0.01 s or about one part in 10^5 as the precision of our viscosity measurements using the capillary viscometer for the copolymer at dilute and very dilute solution concentrations.

All dilute polymer solutions were centrifuged at 3000*g* for 3 h prior to viscosity measurements.

The reduced viscosity (or viscosity number), defined as $\eta_{sp}/C=(\eta-\eta_0)/(\eta_0 C)$, was used throughout this paper, where η, η_0 and C are the solution viscosity, the solvent viscosity and the polymer concentration ($\mathrm{g\,ml^{-1}}$), respectively.

Light scattering

The light scattering spectrometer[5] used an argon-ion laser operating at 0.1 W and $\lambda_0=488\,\mathrm{nm}$. The angular range covered was between 15° and 135° and photon counting was used for light-scattering intensity measurements.

RESULTS AND DISCUSSION

Two reasons prompted us to use viscosity measurements in addition to our light scattering studies. Although we claimed only a small refractive index difference (0.001–0.003) among the homopolymers (poly(iBMA) and poly(t-BAEMA)) and the copolymer (poly(iBMA–tBAEMA)), inhomogeneities in the segmental length of monomer types (iBMA and tBAEMA) and the sequencing of the monomers could produce local variations of the refractive index increment for copolymers with the same overall chemical composition. Fortunately, the effect of non-perfect matching of the refractive index increment within the copolymer chain was not sufficient to influence estimates of the molar mass of copolymer aggregates in different solvents. Nevertheless, another independent

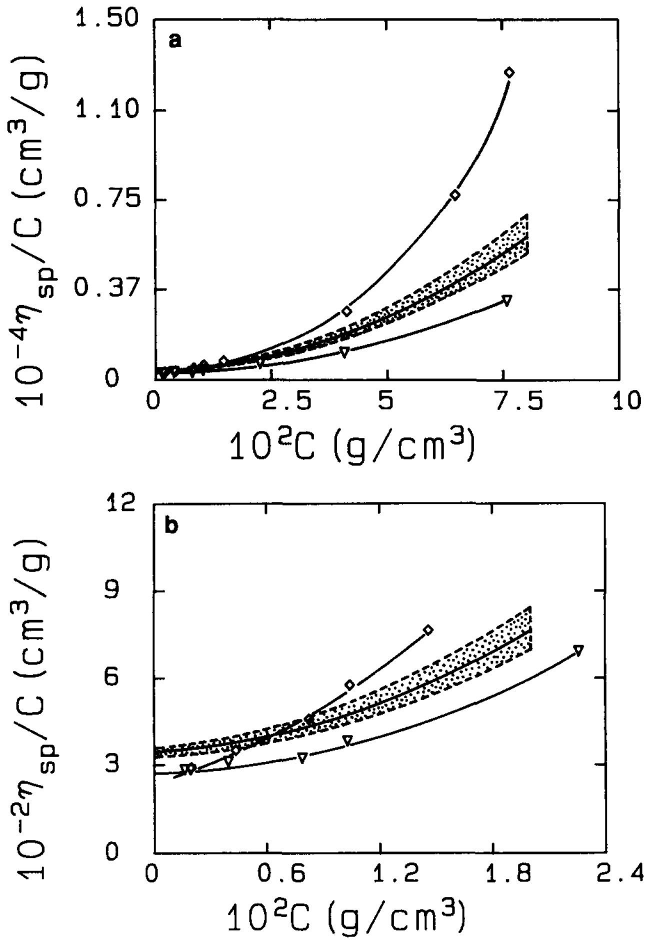

Figure 1 Reduced viscosity–polymer concentration profiles of poly(iBMA) (▽) with $M_w = 1.7 \times 10^6\,\mathrm{g\,mol^{-1}}$ and poly(iBMA–tBAEMA) (◇) with $M_w = 2.4 \times 10^6\,\mathrm{g\,mol^{-1}}$ in TMEDA at 30±0.05°C. Broken curves denote a scaled reduced viscosity–polymer concentration profile of poly(iBMA) having the same molecular weight as that of poly(iBMA–tBAEMA) by means of equations (4) and (5). (a) Over the entire experimental concentration range. (b) Magnified view at dilute concentrations

experiment, which is not affected by refractive index increments of the copolymer and of the monomers, should strengthen our interpretation of the solution behaviour of poly(iBMA–tBAEMA). Secondly, the copolymer is a polymer additive. Some rheological behaviour of the copolymer solution over a broad range of concentrations may provide us with a better understanding of its practical utility.

Figure 1a shows a plot of reduced viscosity *versus* polymer concentration for poly(iBMA–tBAEMA) and poly(iBMA) in TMEDA at 30±0.05°C. As the molecular weights of the random copolymer, poly(iBMA–tBAEMA), and of the homopolymer, poly(iBMA), were not identical, we tried to scale the reduced viscosity of poly(iBMA) from $M_w = 1.7 \times 10^6$ to $2.4 \times 10^6\,\mathrm{g\,mol^{-1}}$. By assuming the hydrodynamic radius $R_h \sim M^{\alpha}$ with $\alpha \sim 0.5$, we can fit the empirical equation[6]:

$$\eta_{sp} = a_1(V_e/M)C + a_2(V_e/M)^2C^2 + a_3(V_e/M)^3C^3 + \cdots \quad (4)$$

where V_e ($\equiv (4\pi/3)R_h^3$) is the effective hydrodynamic volume of the polymer solute, M is the molecular weight, C is the polymer concentration and a_i are constants. A least-squares fitting of the experimental η_{sp} *versus* C yields:

$$\eta_{sp}/C = 0.22M^{0.5} + 1.88 \times 10^{-3}MC + 2.17 \times 10^{-4}M^{3/2}C^2 \quad (5)$$

Thus, we could estimate η_{sp} for poly(iBMA) if $M_w = 2.4 \times 10^6\,\mathrm{g\,mol^{-1}}$.

The broken curves in *Figure 1* tried to take into account possible errors in estimating the magnitude of α. If we took $\alpha \sim 0.46$, which is comparable to the conformation of the copolymer aggregates[1], the cross-over would take place at a lower concentration ($< 6\,\mathrm{mg\,ml^{-1}}$). If we considered TMEDA to be a fairly good solvent for poly(iBMA) and took $\alpha \sim 0.55$, the cross-over would take place at a higher concentration ($> 6\,\mathrm{mg\,ml^{-1}}$). We could even observe a cross-over in η_{sp}/C between poly(iBMA) and poly(iBMA–tBAEMA) without adjusting the molecular weight of poly(iBMA). In any case, in a plot of η_{sp}/C *versus* C at dilute concentrations, as shown in *Figure 1b*, we observed a cross-over in η_{sp}/C at $C \sim 6\,\mathrm{mg\,ml^{-1}}$ for poly(iBMA) and poly(iBMA–tBAEMA). It should be noted that the overlap concentration $C^* \sim 4\,\mathrm{mg\,ml^{-1}}$ for poly(iBMA–tBAEMA)[1]. A lower value of η_{sp}/C would suggest a decrease in M provided that the polymer conformation remained unchanged or, conversely, if the molar mass were to remain relatively unchanged, a lower value of η_{sp}/C could suggest a contraction in the polymer size. Thus, the cross-over could suggest an increase in the intramolecular interactions in the dilute solution regime for the random copolymer because we made a comparison of the copolymer with a homopolymer of the same molecular weight. At higher concentrations, the random copolymer would tend to associate to form apparently larger aggregates yielding higher η_{sp}/C values.

Figure 2a shows plots of η_{sp}/C *versus* C for poly(iBMA–tBAEMA) in TMEDA, DMAA and IPA at 30±0.05°C. A cross-over at a higher concentration of $\sim 20\,\mathrm{mg\,ml^{-1}}$ (or $\sim 25\,\mathrm{mg\,ml^{-1}}$) (see *Figure 2b* in comparison with the cross-over behaviour in *Figure 1b*) between the curve of TMEDA (or DMAA) and that of IPA was observed. This cross-over behaviour, which took place at a higher concentration ($20\,\mathrm{mg\,ml^{-1}} > C^*$), further demonstrated that the magnitude of intramolecular interactions for poly(iBMA–tBAEMA) in IPA was weaker than those of the same random polymer in TMEDA and DMAA when the copolymers began to overlap, i.e. at concentrations $C^* \lesssim C \lesssim 20\,\mathrm{mg\,ml^{-1}}$. At higher semidilute and concentrated solutions, the random copolymers in TMEDA and in DMAA aggregate more strongly by intermolecular interactions, yielding higher η_{sp}/C values than those of the same random copolymer in IPA.

The aggregated random copolymer, like micelles, could fall apart to form single-polymer solutions at extremely dilute concentrations. Following the observations made by laser light scattering in which a break-up of the supramolecular aggregates occurred at very dilute concentrations ($\sim 10^{-5}\,\mathrm{g\,ml^{-1}}$ or ~ 100 times more dilute than the concentrations shown in *Figure 1b*), we carried out the viscosity studies at concentrations $\sim 10^{-5}\,\mathrm{g\,ml^{-1}}$. *Figure 3* shows reduced viscosity–polymer concentration profiles of poly(iBMA–tBAEMA) in IPA, TMEDA and DMAA. We used the reduced viscosity of poly(iBMA) in TMEDA as a reference. The η_{sp}/C values for poly(iBMA) in TMEDA and poly(iBMA–tBAEMA) in IPA were comparable, especially if we were to take into account

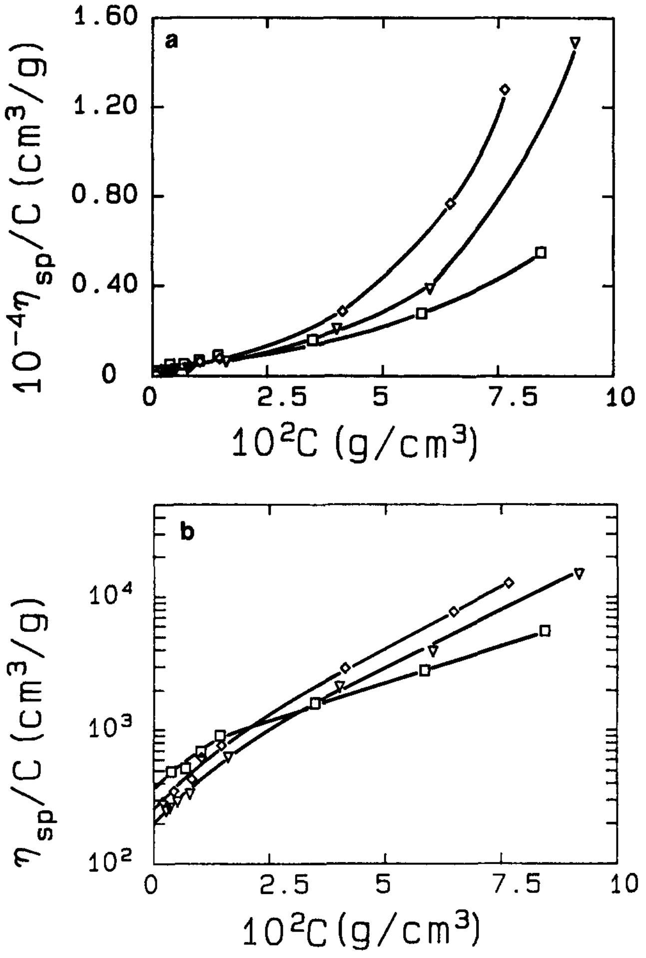

Figure 2 (a) Reduced viscosity–polymer concentration profiles of poly(iBMA–tBAEMA) in TMEDA (◇), DMAA (▽) and IPA (□) at 30±0.05°C. (b) A cross-over was observed in a plot of log(η_{sp}/C) *versus* *C*

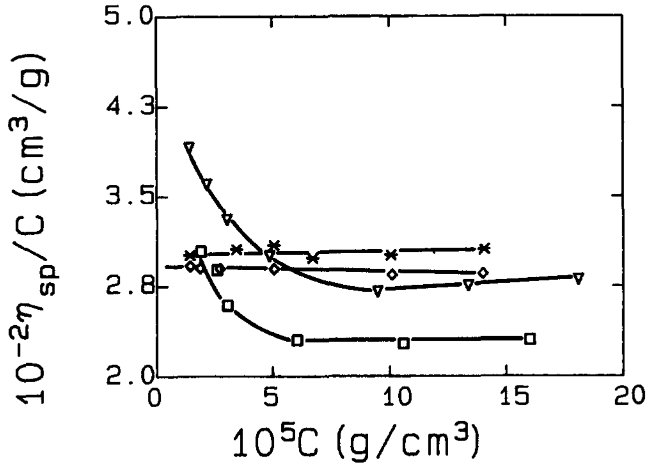

Figure 3 Reduced viscosity–polymer concentration profiles of poly(iBMA–tBAEMA) in IPA (✱), TMEDA (▽) and DMAA (□) and poly(iBMA) (◇) in TMEDA at 30±0.005°C. The marked upsweeps in the reduced viscosity at very low concentrations of poly(iBMA–tBAEMA) in TMEDA and DMAA are quite similar to ionomer behaviour in polar solvents in the dilute solution regime

the slightly lower molecular weight for the homopolymer poly(iBMA) with $M_w = 1.7 \times 10^6$ g mol^{-1}. In *Figure 3*, the upturn for the copolymer took place at a higher concentration in TMEDA than that in DMAA, signifying stronger intermolecular interactions for the copolymer in DMAA. This observation is in agreement with the fact that the copolymer forms larger aggregates in DMAA than in TMEDA. The upward sweep occurred over the same concentration range as observed in a plot of HC/R_{vv} *versus* *C* (see *Figure 7*) by means of absolute light scattering intensity measurements, with *H* and R_{vv} being an optical constant and the excess Rayleigh ratio for vertically polarized incident and scattered light. Apart from a break-up of the aggregates as signified by an increase in the magnitude of η_{sp}/C, the sharp increase of η_{sp}/C at very dilute concentrations with magnitudes far above those of the homopolymer and the same copolymer in IPA (a solvent showing a small amount of aggregation, if any, as demonstrated by light scattering) suggests that the copolymer must have expanded in size due to stronger intramolecular repulsions by the pendent aminoalkyl groups in the copolymer in TMEDA and in DMAA when compared with those in IPA.

Estimates of molecular parameters of poly(iBMA–tBAEMA) in different solvents (IPA, TMEDA and DMAA) show that the molecular weight of the copolymer in different solvents becomes comparable in the limit of infinite dilution, but the sizes of the copolymer expand in TMEDA and in DMAA, as listed in *Tables 1* and *2* and shown schematically in *Figure 4*. The values of R_g

Table 1 Molecular parameters of poly(iBMA–tBAEMA) in different solvents in the dilute solution regime (~10^{-4} g cm^{-3}) (after ref. 1)

	IPA	TMEDA	DMAA
M_w (10^6 g mol^{-1})	2.42	5.86	9.08
R_g (nm)	95	131	162
R_h (nm)	65	100	120

Table 2 Estimates of molecular parameters of poly(iBMA–tBAEMA) in different solvents in the very dilute solution regime (~10^{-5} g cm^{-3})

	IPA	TMEDA	DMAA
M_w (10^6 g mol^{-1})	~2.5	~3.1	~3.1
R_g (nm)	97	110	112
[η] (cm^3 g^{-1})	300	400	>300

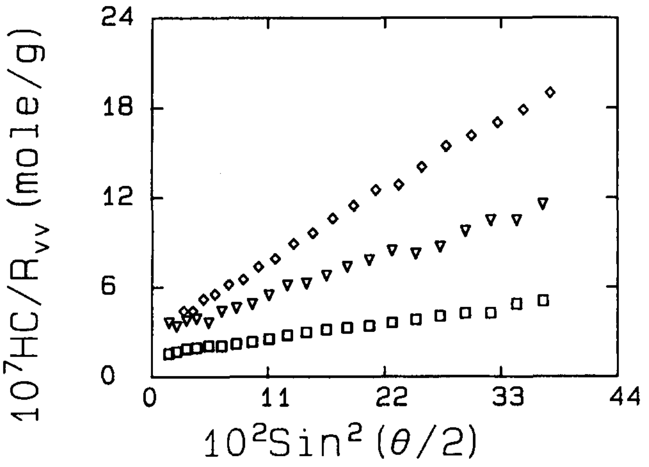

Figure 4 Angular dependence of scattered intensity of very dilute solutions of poly(iBMA–tBAEMA) in IPA (◇) at $C = 4.1 \times 10^{-5}$ g cm^{-3}, TMEDA (▽) at $C = 5.0 \times 10^{-5}$ g cm^{-3}, and DMAA (□) at $C = 1.4 \times 10^{-5}$ g cm^{-3}. The R_g values of the copolymer in each solution are listed in *Table 2*. The R_g values in TMEDA and in DMAA were found to follow the same R_g *versus* *M* relation as shown in *Figure 5*

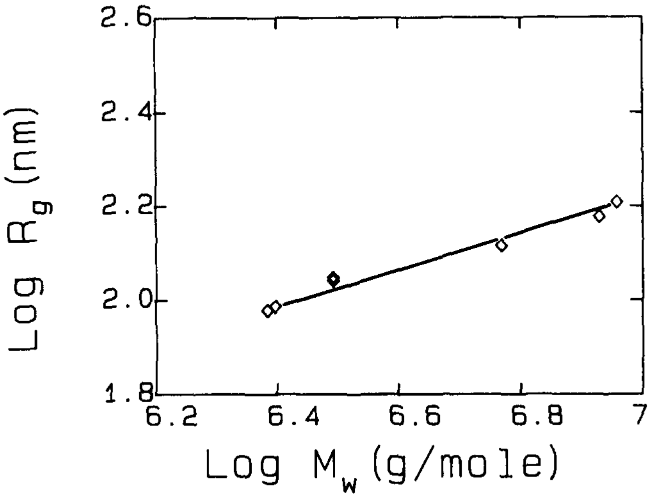

Figure 5 Log–lot plot of R_g *versus* M_w for poly(iBMA–tBAEMA) in different solvents by extrapolation from dilute and very dilute solution regimes

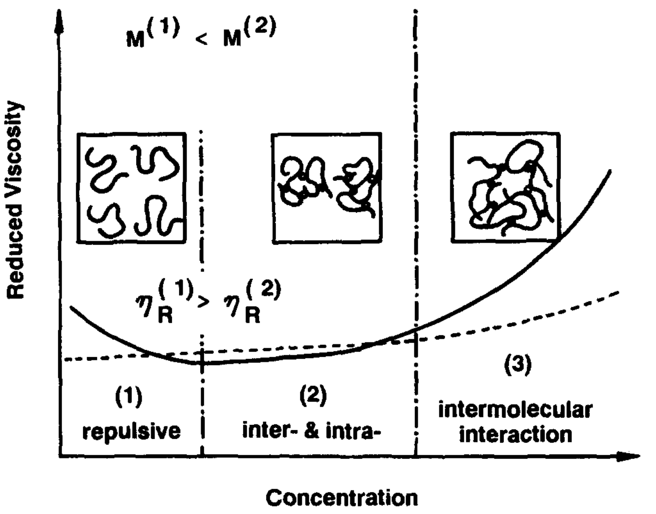

Figure 6 Schematic representation of intra- and intermolecular interactions in the three concentration regimes of very dilute, dilute and semidilute/concentrated solutions. The full curve represents a typical curve of reduced viscosity as a function of concentration for the random copolymer, poly(iBMA–tBAEMA), suggesting an ionomer-like solution behaviour. The broken curve represents the normal reduced viscosity behaviour of a homopolymer, poly(iBMA)

obtained by extrapolation to infinite dilution suggested slightly higher values than those of the same copolymer in IPA. They did not conflict with the supposition that at very dilute concentrations the sizes of the copolymer were larger in those solvents which promoted stronger inter- (and intra-) molecular interactions.

An interesting plot is shown in *Figure 5*, in which a log–log plot of R_g *versus* M_w (i.e. the molar mass of the particle) reveals a linear relation, obeying $R_g \propto M_w^{0.46}$, for the same copolymer in different solvents with R_g and M_w values being determined in two separate regimes (dilute and very dilute). The low α ($=0.46$) value seems to imply that the copolymer forms fairly contracted coils, as Gaussian coils would yield $\alpha = 0.5$ at theta condition. In *Figure 5*, we neglected the coil size differences in different solvents and considered all effects to be due to intermolecular association.

A schematic representation of intra- and intermolecular interactions in the three solution regimes of very dilute, dilute and semidilute/concentrated solutions is shown in *Figure 6*. The full curve represents a typical curve of reduced viscosity as a function of concentration for the random copolymer, poly(iBMA–tBAEMA), suggesting an ionomer-like solution behaviour.[7,8] The broken curve represents the normal reduced viscosity behaviour of a homopolymer, poly(iBMA), which is our reference polymer. At high semidilute/concentrated concentrations, as shown in *Figures 1* and *2* and region (3) in *Figure 6*, the reduced viscosity for the copolymer is about a factor 10 higher than the homopolymer without the pendent aminoalkyl groups. More importantly, one can achieve an effective reduced viscosity by using smaller amounts of the copolymer when compared with the homopolymer. This behaviour was achieved mainly by the formation of larger aggregates due to intermolecular interactions, resulting in a lowering of the overlap concentration. Near the overlap concentration, a cross-over could occur, as shown in *Figures 1b* and *2b* and region (2) in *Figure 6*. The cross-over suggested the presence of intramolecular interactions, making the polymer aggregates more contracted when compared with that of the homopolymer. The copolymers at dilute concentrations were aggregates because light scattering studies showed a higher molecular weight than that of the unassociated copolymer whose single-molecule molecular weight could be estimated by extrapolation to infinite dilution using measurements at very dilute solution concentrations ($\sim 10^{-5}\,\mathrm{g\,ml^{-1}}$) for the copolymer in interacting solvents such as TMEDA and DMAA and at dilute solution concentrations ($\sim 10^{-4}\,\mathrm{g\,ml^{-1}}$) for the copolymer in IPA. In IPA, the copolymer exhibited weaker intermolecular interactions. Independently, the same single-molecule molecular weight was determined by aqueous size-exclusion chromatography. Thus, at dilute solution concentrations, the copolymer had a higher effective molar mass than the unassociated copolymer. Yet, the reduced viscosity was lower. These observations strongly suggested the presence of intramolecular association, as well as intermolecular association.

The solvent effect dominated region (1) in *Figure 6* in the very dilute concentration range ($\sim 10^{-5}\,\mathrm{g\,ml^{-1}}$) where the aggregation began to fall apart, as shown by the switch-over in slope in a $HC/R_{vv}(0)$ *versus* C plot in *Figure 7*. In the very dilute solution regime, the reduced

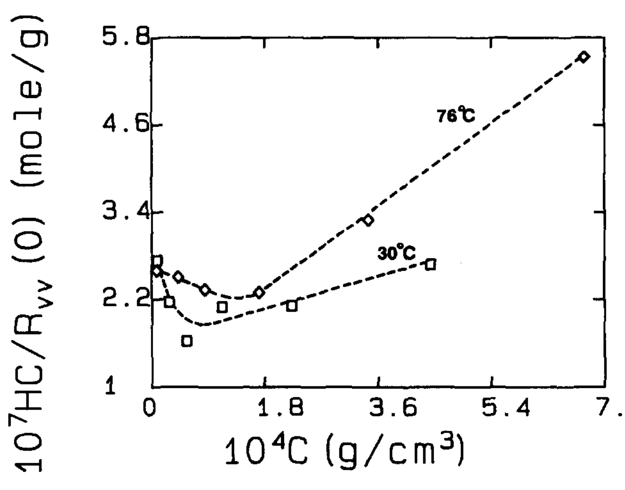

Figure 7 Temperature effect on excess scattered intensity of poly(iBMA–tBAEMA) after extrapolation to $\theta = 0°$ in TMEDA in the dilute and very dilute concentration regimes. The two upward curves terminate at about the same value on the y axis at infinite dilution

viscosity of the copolymer in TMEDA or DMAA increased and became greater than that of the homopolymer of lower or comparable molecular weight or that of the copolymer in IPA, signifying an expansion of the polymer coil due to intramolecular charge-like repulsion. It should be emphasized that the interactions between the copolymer and the solvent were non-ideal. *Figure 8* shows a plot of the reduced viscosity of poly(iBMA–tBAEMA) as a function of the composition of co-solvent TMEDA/MCH (2-methylcyclohexanol) at a copolymer concentration of $2 \times 10^{-2}\,\mathrm{g\,ml^{-1}}$ at 30±0.05°C. A minimum in reduced viscosity was observed at a weight fraction of TMEDA of ~0.5.

In order to make a further test of our supposition of inter- and intramolecular interactions, we examined the temperature dependence of the viscosity, as the aggregation behaviour should be influenced by temperature. *Figure 9a* shows a plot of viscosity as a function of temperature for poly(iBMA–tBAEMA) at $C = 4.10 \times 10^{-2}\,\mathrm{g\,ml^{-1}}$ and poly(iBMA) at $C = 4.07 \times 10^{-2}\,\mathrm{g\,ml^{-1}}$, in TMEDA. The nearly flattened curve of poly(iBMA) is typical of a polymer in a relatively good solvent, i.e. the solution viscosity decreases with increasing temperature. In contrast to this behaviour, the change of viscosity with temperature for poly(iBMA–tBAEMA) is considerably larger. The stronger negative slope could be attributed to a decrease in the degree of aggregation as well as the solvent viscosity decrease with increasing temperature. In *Figure 9b*, the reduced viscosity shows an increase with temperature for the homopolymer, suggesting an expansion of the polymer coil at higher temperatures because of an improvement in solvent quality. On the other hand, the dominating effect for the copolymer must be a decrease in the degree of aggregation, resulting in a sharper decrease in the reduced viscosity with increasing temperature. The same effect can be observed from a slightly different viewpoint by means of *Figure 10,* which shows the temperature effect on the viscosity–concentration relationship of poly(iBMA–tBAEMA) in TMEDA at 30°C and at 60°C. The viscosity–concentration curve shifts down towards the curve for poly(iBMA) in TMEDA at 30°C. The behaviour strengthens our supposition that intermolecular association could be reduced by a temperature increase. On closer examination of *Figure 7,* we note that the switch-over (or the minimum) occurred at a higher concentration for the 76°C curve, suggesting that aggregation occurred at a higher polymer concentration at higher temperatures in the very dilute solution regime. The shallower slope in the very dilute solution regime

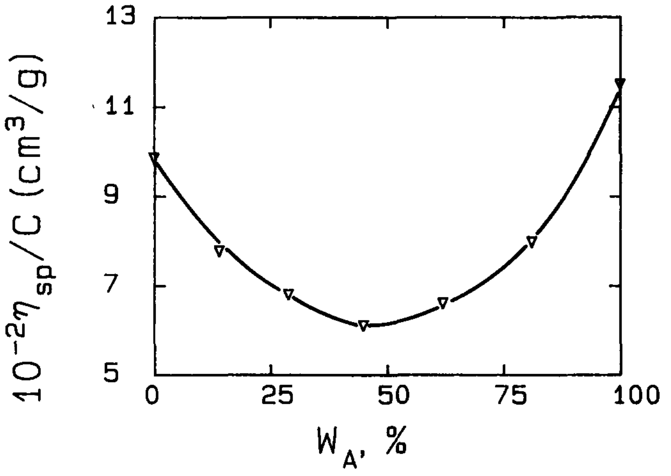

Figure 8 Reduced viscosity of poly(iBMA–tBAEMA) as a function of the composition of co-solvent TMEDA/MCH at a copolymer concentration of $2 \times 10^{-2}\,\mathrm{g\,ml^{-1}}$ at 30±0.05°C. W_A is the weight fraction of solvent TMEDA

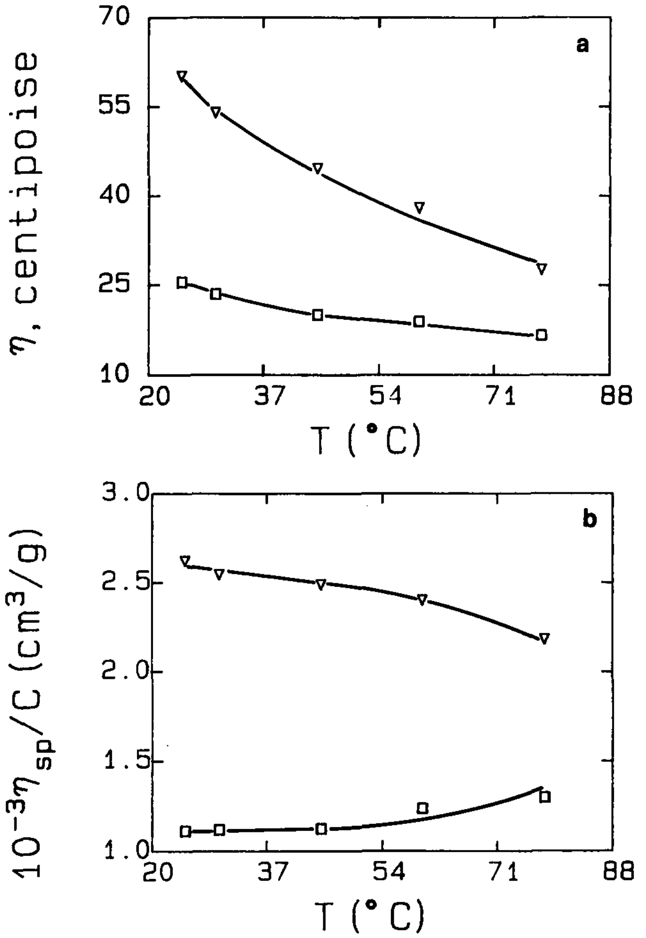

Figure 9 (a) Viscosity as a function of temperature for poly(iBMA–tBAEMA) (▽) at $C = 4.10 \times 10^{-2}\,\mathrm{g\,ml^{-1}}$, and poly(iBMA) (□) at $C = 4.07 \times 10^{-2}\,\mathrm{g\,ml^{-1}}$, in TMEDA. (b) Reduced viscosity as a function of temperature for poly(iBMA–tBAEMA) (▽) at $C = 4.10 \times 10^{-2}\,\mathrm{g\,ml^{-1}}$, and poly(iBMA) (□) at $C = 4.07 \times 10^{-2}\,\mathrm{g\,ml^{-1}}$, in TMEDA

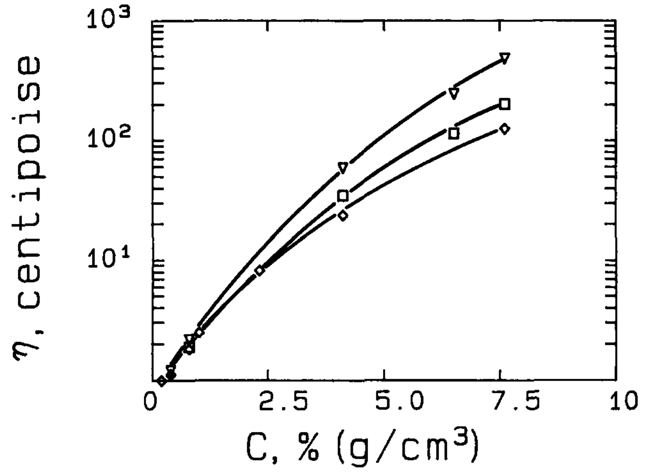

Figure 10 Temperature effect on viscosity–concentration relationship of poly(iBMA–tBAEMA) in TMEDA at 30°C (▽) and at 60°C (□). When the temperature is increased, the viscosity–concentration curve shifts down towards the curve for poly(iBMA) in TMEDA at 30°C (◇). The behaviour strengthens the supposition that intermolecular association could be reduced by a temperature increase

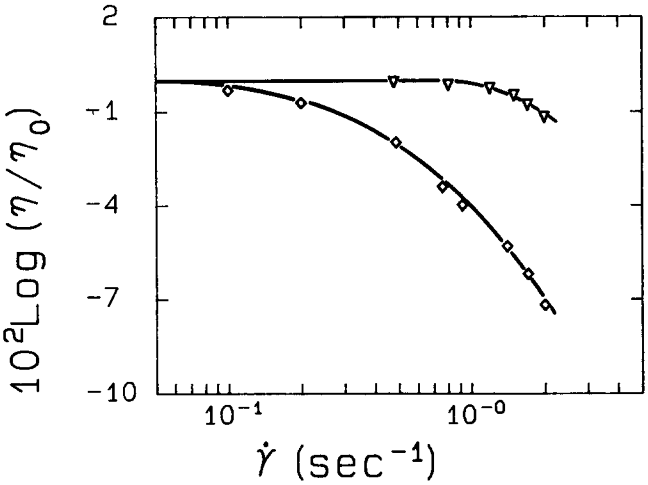

Figure 11 Shear-rate dependence of viscosity normalized to zero shear rate for poly(iBMA–tBAEMA) in DMAA at 25±0.05°C, at $C=0.096\,\mathrm{g\,ml^{-1}}$ (▽) and $C=0.117\,\mathrm{g\,ml^{-1}}$ (◇). The concentration effect on the transition from non-Newtonian to Newtonian behaviour is quite large. The higher the concentration, the lower the shear rate at which non-Newtonian behaviour begins

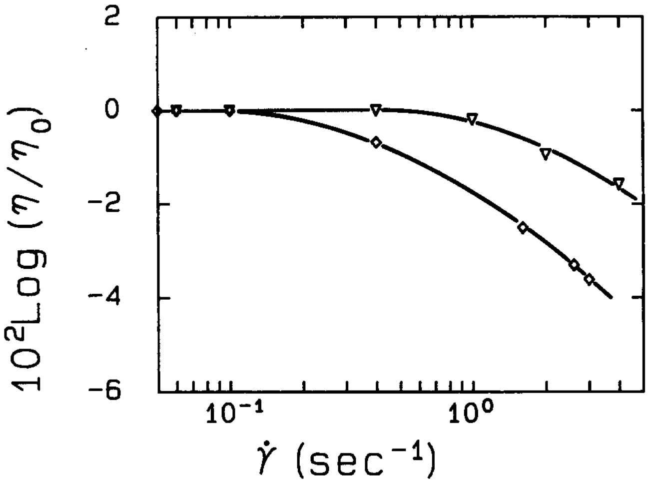

Figure 12 Shear-rate dependence of viscosity normalized to zero shear rate for poly(iBMA) (▽) at $C=0.108\,\mathrm{g\,ml^{-1}}$, and for poly(iBMA–tBAEMA) (◇) at $C=0.108\,\mathrm{g\,ml^{-1}}$, in DMAA at 25±0.05°C

and steeper slope in the dilute solution regime at 76°C when compared with those at lower temperatures (say 30°C) also imply a better solvent quality at 76°C (than at 30°C) in TMEDA.

In our discussions so far, we have used the viscosity extrapolated to zero shear rate. As a polymer additive, it is also essential to realize the shear-rate dependence of viscosity at different polymer concentrations. *Figures 11* and *12* show the shear-rate dependence of poly(iBMA–tBAEMA) at two different concentrations and in comparison with the homopolymer. At higher polymer concentrations, non-Newtonian behaviour begins at a lower polymer concentration. The copolymer also shows stronger shear-rate dependence when compared with the homopolymer.

CONCLUSIONS

By combining light scattering with viscosity measurements, we have been able to strengthen our supposition that the copolymer poly(iBMA–tBAEMA) forms more expanded coils at very dilute solution concentrations ($\lesssim 10^{-5}\,\mathrm{g\,ml^{-1}}$). The degree of aggregation depends on the solvent nature. Copolymer solutions in most solvents form supramolecules even in the dilute solution regime. Then the degree of aggregation increases with increasing concentration. The use of such copolymers as a viscosity additive is mainly due to polymer aggregation by intermolecular interactions. Such aggregates are more susceptible to shear and have a stronger shear-rate dependence. Similarly, the aggregation also depends on temperature and has a stronger temperature effect when compared with our reference homopolymer, poly(iBMA).

ACKNOWLEDGEMENT

We gratefully acknowledge support of this work by the US Army Research Office (DAAL0387K0136).

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