Communications to the Editor

Effects of an Ionomer Additive on the Rheological Properties of a Random Copolymer Poly(isobutyl methacrylate–(*tert*-butylamino)ethyl methacrylate)

I. Introduction. The random copolymer poly(isobutyl methacrylate–(*tert*-butylamino)ethyl methacrylate) (poly(iBMA–tBAEMA)) is a useful polymer additive, which, for example, can be used in motor oils as a viscosity enhancer because of its ability to alter the rheological properties in a variety of organic solvents. A considerable body of patents concerning the preparation and the properties of this class of polymers has been reviewed.[1,2] Our recent light scattering and viscosity studies[3,4] of poly(iBMA–tBAEMA) in polar and nonpolar solvents at room temperture have revealed an aggregation phenomenon in most solvents spanning a large range of concentration from the dilute to the semidilute solution regimes. The coexistence of intra- and intermolecular interactions could most likely be attributed to the interactions between the "basic" amino groups on the side chains and the carboxylate groups. Such interactions could be responsible for the intramolecular, as well as the intermolecular, aggregation behavior.

A stronger intermolecular interaction could be achieved by chemically introducing a small amount of acidic groups to the copolymer chains or by physically adding an ionomer to the base-containing copolymer. The latter concept has been successfully demonstrated by incorporating a small amount of styrene sulfonic acid onto a polystyrene (PS) chain and a similar quantity of 4-vinylpyridine onto a poly(ethyl acrylate) (PEA) chain. The chemical changes improved the compatibility of these two incompatible polymers in bulk.[5] For a mixture of a base-containing polymer A and an acid-containing polymer B in solution, it appears that these polymeric acid–polymeric base associations could be manipulated to create a new family of thickening agents. To our knowledge, no demonstration on a system that involves aprotic dipolar solvents, a high molecular weight polymeric base, and an ionomer, such as the sulfonated polystyrenes, has been formally reported.

This paper is concerned with the rheological properties of mixtures of poly(iBMA–tBAEMA) with ionomers containing low levels of a transition-metal-neutralized sulfonate group (or sulfonic acid groups) in a polar solvent in order to improve the thickening efficiency of poly(iBMA–tBAEMA) through coordination-type and acid–base pair interactions. The effect on the viscosity enhancement of poly(iBMA–tBAEMA) in combination with these ionomers was examined as a function of polymer composition, concentration, temperature, and shear rate using the copolymer as the reference.

II. Experimental Section. II.1. Samples. The random copolymer poly(iBMA–tBAEMA) (lot no. CM1-120) was prepared by emulsion polymerization and purchased from Polyscience. The lot investigated was obtained from the latex-phase blend of several independent emulsion polymerizations. Therefore, the molecular weight distribution (MWD) might not necessarily be characteristic of a single free-radical emulsion polymerization reaction. Aqueous size-exclusion chromatography (SEC) and light scattering measurements in isopropylamine (IPA)[3] provided an estimate of the copolymer weight-average molecular weight to be 2.7×10^6 and 2.4×10^6, respectively. The molar ratio of iBMA to tBAEMA was 77/23 as determined by ^{13}C NMR.

Anionically polymerized polystyrene was purchased from Polymer Laboratories Ltd. with a weight-average molecular weight 1.05×10^5. The preparation of free acid sulfonated polystyrene (HSPS) and the zinc salt form of sulfonated polystyrene (ZnSPS) from the anionically polymerized polystyrene was described in ref 6. The sulfur content for both acid and zinc salt forms was 4.7 mol % as determined by Dietert sulfur analysis.

Starting solutions were prepared by dissolving separately each sample in a redistilled solvent, *N,N*-dimethylacetamide (DMAA) (purchased from Aldrich Chemical Co.), at 50 °C for a couple of weeks and then kept at room temperature for 1 week. The solutions of poly(iBMA–tBAEMA)/ionomer were obtained by mixing the homogeneous solutions of each polymer component and then kept at room temperature with occasional agitation for 5 days in order to ensure that the solution mixtures have been equilibrated.

II.2. Viscosity Measurement. Viscosity measurements were performed by using a magnetic sphere/needle rheometer[7,8] permitting viscosity measurements over a range from 0.7 to 1×10^6 cP with shear rates varying from 1×10^{-2} to 10^1 s^{-1}. Temperature was controlled to within 0.01 °C. In most cases, the viscosity values were converted into the reduced viscosity defined by $\eta_{sp}/C = (\eta - \eta_0)/(\eta_0 C)$, where η_0 is the solvent viscosity and η is the solution viscosity at concentration C.

III. Results and Discussion. According to the principle of coordination-type and acid–base pair interactions, an intermolecular interaction in a binary polymer solution between polymer B containing acidic groups and polymer A containing basic groups could take place and give rise to noncovalent associative cross-linking among polymers A and B. In spite of the resulting gel formation in many cases, this idea could be employed to develop a polymer thickener by mixing a polymer containing a basic group, such as the amino group, with an appropriate amount of an ionomer in a *moderately* sulfonated acid form or salt form. Figure 1 shows a reduced viscosity–polymer composition diagram for the mixture of poly(iBMA–tBAEMA) (polymer A) and ZnSPS (polymer B) at a total concentration of 1.00×10^{-2} g/mL in DMAA at 30 °C. DMAA is a good solvent for both polymer A and polymer B around room temperature. The reduced viscosities for polymer A and polymer B are $\sim 5.7 \times 10^2$ and 1.1×10^2 mL/g, respectively. Over a very broad range in polymer composition, as schematically shown by the shadowed area in Figure 1, the appearance of gellike precipitates upon mixing of the two pure A and B solutions is observed. This phenomenon suggests the formation of polymer networks as a result of strong cross-linking between polymer A and polymer B, since the precipitates are no longer soluble in DMAA at room temperature. By mixing the two polymer solutions that are supposed to interact with each other, uneven local cross-linking could

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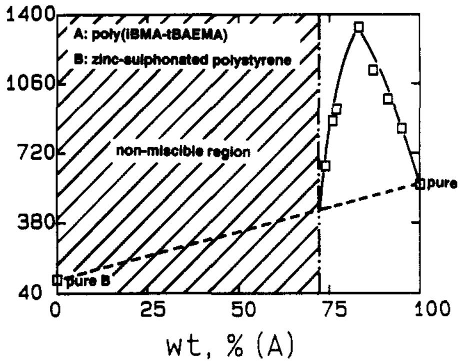

Figure 1. Reduced viscosity–polymer composition diagram of a mixture of poly(iBMA–tBAEMA) with a zinc salt form of sulfonated polystyrene in DMAA at $C = 1.00 \times 10^{-2}$ g/mL and 30 ± 0.01 °C. Shadowed area represents the nonmiscible region where a gellike precipitate is formed. The maximum of the reduced viscosity at a polymer mixture composition of about 83% of component A indicates a most effective cross-linking in terms of intermolecular interactions among polymers A and B in solution at this concentration. The dashed shade suggests that the immiscible region near pure B has not been established.

yield a gellike second phase, which is precipitated, rather than a homogeneous gel. If there is no interaction between polymer A and polymer B for the binary polymer solution, the reduced viscosity should follow the dashed straight line between points of pure A and pure B as illustrated in Figure 1. However, the reduced viscosity of the mixtures exhibits a peak covering a polymer composition region of ~70–100% of polymer A by weight. The reduced viscosity in this region is significantly altered according to the mixing ratio. At the maximum reduced viscosity (83% of polymer A by weight), the reduced viscosity is increased by a factor of 2.4 as compared with that of pure A. Theoretically, only ~5% of the basic groups on the poly(iBMA–tBAEMA) chain have reacted statistically with the transition-metal-neutralized sulfonate group on the ionomer at the maximum reduced viscosity. This maximum could suggest a most effective polymer composition for the mixture of poly(iBMA–tBAEMA)/(4.7 mol %) ZnSPS in DMAA in order to achieve a thickening effect at room temperature with a minimum amount of *total* polymer additive.

The polymer solution mixtures in this article are referred to near this optimum composition, i.e., copolymer/ionomer = 4/1 (w/w), unless stated otherwise. The concentration dependence of the reduced viscosity for the mixtures of poly(iBMA–tBAEMA)/ZnSPS and of poly(iBMA–tBAEMA)/HPS in DMAA at a copolymer/ionomer mixing ratio of 4/1 (w/w) is shown in Figure 2a. By comparison of the curves for the mixtures (hollow squares, poly(iBMA–tBAEMA)/ZnSPS; hollow inverse triangles, poly(iBMA–tBAEMA)/HSPS) with the curve for the pure poly(iBMA–tBAEMA) (hollow diamonds), a sharper increase in the reduced viscosity of mixture solutions with increasing concentration was observed. Specifically, the mixture solution of poly(iBMA–tBAEMA)/ZnSPS shows a larger viscosity enhancement effect than the mixture of poly(iBMA–tBAEMA)/HSPS when the total polymer concentration is above ~7.0×10^{-3} g/mL. This might be interpreted in terms of the strength of the interactions in forming a zinc/amine complex between poly(iBMA–tBAEMA) and ZnSPS in DMAA. In particular, a crossover of the curves between the mixtures and poly(iBMA–tBAEMA) *at a very low concentration* (~7.0×10^{-3} g/mL) is clearly demonstrated. Below this point, both mixtures show an even lower reduced viscosity than that of pure poly(iBMA–tBAEMA). As a matter of fact, the sample ZnSPS or HSPS, when prevented from functioning as a linking agent, can decrease the reduced viscosity of the poly(iBMA–tBAEMA) solution since both ionomers have a fairly low average molecular weight and would essentially be diluents. Also, the increased intramolecular interaction of poly(iBMA–tBAEMA) bridged by ionomers at very low concentrations is another possible factor responsible for the dramatic change in the reduced viscosity.

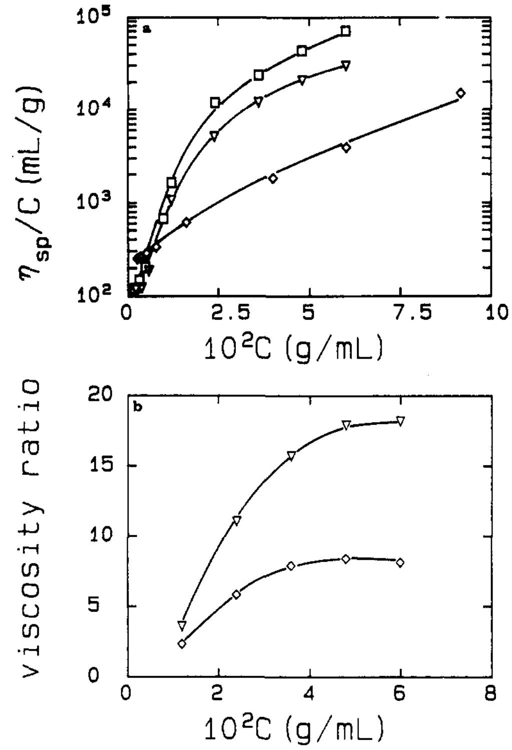

Figure 2. (a) Reduced viscosity–concentration profiles of poly(iBMA–tBAEMA) (hollow diamonds), of a mixture of poly(iBMA–tBAEMA)/ZnSPS at a mixing ratio of 4/1 (w/w) (hollow squares), and of a mixture of poly(iBMA–tBAEMA)/HSPS at a mixing ratio of 4/1 (w/w) (hollow inverse triangles) in DMAA at 30 ± 0.01 °C. (b) Plots of the viscosity ratio of the polymer mixtures over one of its components, poly(iBMA–tBAEMA). Hollow inverse triangles and hollow diamonds denote the behavior of the mixture of poly(iBMA–tBAEMA)/ZnSPS and of the mixture of poly(iBMA–tBAEMA)/HSPS, respectively.

The reduced viscosity ratio of solution mixtures over the poly(iBMA–tBAEMA) solution as a function of concentration is shown in Figure 2b. As the concentration is above ~0.01 g/mL, the reduced viscosity ratios for poly(iBMA–tBAEMA)/ZnSPS solution (hollow inverse triangles) and poly(iBMA–tBAEMA)/HSPS solution (hollow diamonds) increase dramatically, finally approaching a plateau at a concentration of ~0.05 g/mL where the reduced viscosities for poly(iBMA–tBAEMA)/ZnSPS and poly(iBMA–tBAEMA)/HSPS solutions are about 18 and 8 times that of poly(iBMA–tBAEMA) solution, respectively.

Parts a and b of Figure 3 show the effects of temperature on the solution viscosity of poly(iBMA–tBAEMA) (hollow diamond) and of the mixture of poly(iBMA–tBAEMA)/ZnSPS (hollow inverse triangles) over a temperature range of 25–75 °C in DMAA. It can be seen that the solution mixture is about 1 order of magnitude larger than the poly(iBMA–tBAEMA) solution in the viscosity amplitude throughout the entire temperature range investigated (see Figure 3b). The viscosity of poly(iBMA–tBAEMA)/ZnSPS solution decreases faster than that of the poly(iBMA–tBAEMA) solution with increasing temperature, implying that the intermolecular association between poly-

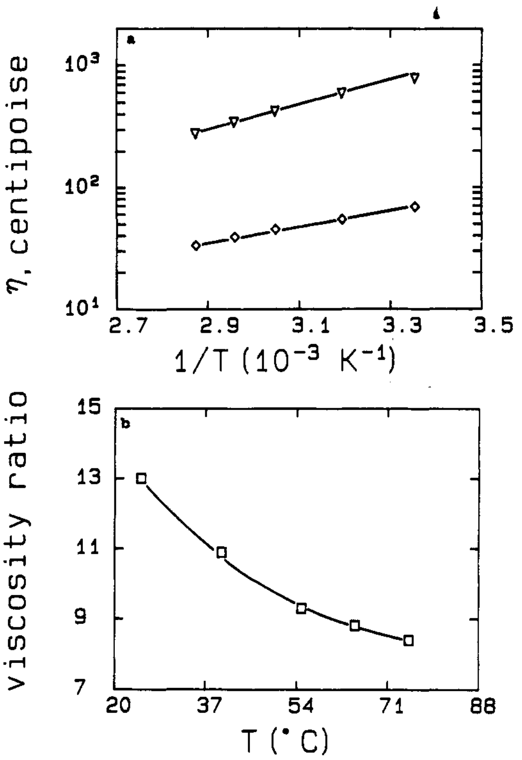

Figure 3. (a) Temperature effect on the viscosity of poly(iBMA-tBAEMA) (hollow diamonds) and of a mixture of poly(iBMA-tBAEMA)/ZnSPS (hollow inverse triangles) at a mixing ratio of 4/1 (w/w) in DMAA at $C = 4.00 \times 10^{-2}$ g/mL. (b) Temperature effect on the viscosity ratio of the mixture of poly(iBMA-tBAEMA)/ZnSPS over one of its components, poly(iBMA-tBAEMA).

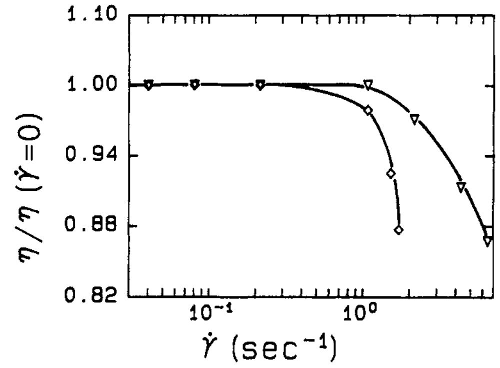

Figure 4. Shear rate dependence of viscosity normalized to zero shear rate for poly(iBMA-tBAEMA) (hollow inverse triangles) and for a mixture of poly(iBMA-tBAEMA)/ZnSPS (hollow diamonds) at a mixing ratio of 4/1 (w/w) in DMAA at $C = 6.00 \times 10^{-2}$ g/mL and 30 ± 0.01 °C.

(iBMA-tBAEMA) and ionomer is more readily broken apart by increasing the temperature than the intermolecular association between poly(iBMA-tBAEMA) itself. The temperature dependence of the viscosity for both the mixture and the pure polymer solution, as shown in Figure 3a, can be represented essentially by an Arrhenius equation. The activation energy, ΔE, calculated by using the Arrhenius equation for the mixture and the pure polymer solution is 4.3 and 2.9 kcal/mol, respectively.

Figure 4 shows the shear rate dependence of the viscosity for the mixture of poly(iBMA-tBAEMA)/ZnSPS (hollow diamonds) and poly(iBMA-tBAEMA) (hollow inverse triangles) at $C = 6.00 \times 10^{-2}$ g/mL in DMAA at 30 °C. It is obvious that the non-Newtonian behavior for the polymer mixture solution appears at a lower shear rate when compared with that for the pure polymer solution. Moreover, it is interesting to note that another characteristic of this polymer mixture is the more dramatic decrease in viscosity at a shear rate higher than $1\ s^{-1}$. The power law coefficients in a log-log plot of $\eta(\dot{\gamma})/\eta(\dot{\gamma}=0)$ versus $\dot{\gamma}$ (s^{-1}) were estimated based on the three high shear rate data points, and these values are 1.14×10^{-2} and 7.30×10^{-2} for poly(iBMA-tBAEMA) and poly(iBMA-tBAEMA)/ZnSPS, respectively.

IV. Conclusion. On the basis of coordination-type and acid-base pair interactions, an effective ionomer additive for poly(iBMA-tBAEMA) solutions in order to improve the thickening efficiency has been explored. The viscosity enhancement effect is dependent on the polymer composition, concentration, temperature, and shear rate. An optimum polymer composition for viscosity enhancement was found to be around 83% by weight of poly(iBMA-tBAEMA) for a 4.7 mol % ZnSPS in DMAA. On the other hand, a broad region for gellike precipitate formation was found when poly(iBMA-tBAEMA) was ≤70% by weight in DMAA at room temperature. The reduced viscosity of poly(iBMA-tBAEMA) in DMAA at a concentration of about 0.06 g/mL could be increased by a factor of 18 by introducing a small amount of ionomer solution. The zinc salt form of the ionomer is more effecive than the acid form of the ionomer in increasing the thickening efficiency for the poly(iBMA-tBAEMA) solution. The mixture of poly(iBMA-tBAEMA)/ZnSPS solution manifested a stronger temperature and shear rate dependence than poly(iBMA-tBAEMA).

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