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Solution Behavior of Lightly Sulfonated Polystyrene and Poly(styrene-*co*-4-vinylpyridine) Complexes in Dimethylformamide

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ABSTRACT: The solution behavior of blends of lightly sulfonated polystyrene (SPS) and poly(styrene-*co*-4-vinylpyridine) (PSVP) was studied as a function of blend composition, copolymer composition, the SPS counterion, and solvent polarity. Complexation between PSVP and metal-neutralized SPS occurred in dimethylformamide (DMF) solutions, but no intermolecular interactions were noticeable for blends containing the sulfonic acid derivative. A maximum in the viscosity occurred at a vinylpyridine to sulfonate ratio of ca. 6:1. This ratio was found to be relatively independent of solvent polarity, composition of the copolymers, and the cation used. The magnitude of the viscosity maximum, however, increased with decreasing solvent polarity and with increasing functionality of the two polymers. Transition metal cations formed the strongest interactions as judged by the largest viscosity increase. The viscosity of blends using the alkali and alkaline earth metal salts of SPS decreased with increasing electrostatic field strength (q/r) of the cation. The solution viscosity for the blends in a mixed solvent of toluene/methanol (95/5 v/v) was thixotropic, but the viscosity increased slowly when the shear deformation was stopped.

Introduction

By promoting intermolecular interactions between specific functional groups on two polymers, it is possible to form miscible or partially miscible blends from polymers that would otherwise be immiscible. When ionomers are used, the interactions depend on the counterion, the concentration of the ionic species, and the structure and concentration of functional groups on the other polymer.[1-4] Specific interactions that have been employed in blends containing ionomers have included ion-dipole,[5] acid-base,[6] and transition metal complexation.[7]

With regard to the work discussed in the present paper, refs 4, 7, and 8 are particularly relevant. Peiffer et al.[8] studied the melt viscosities of blends of poly(styrene-*co*-4-vinylpyridine) (PSVP) and sulfonated poly(ethylene-*co*-propylene-*co*-ethylidenenorbornene) (SEPDM). The viscosity of blends in which a transition metal salt of SEPDM was used resulted in higher melt viscosities than comparable blends containing non-transition-metal salts, and this was attributed to the formation of a coordination complex between the transition metal salt of the SEPDM and the vinylpyridine group of the PSVP. Studies of the solution behavior of similar blends in nonpolar solvents yielded the same conclusion.[4] Sen and co-workers[7] reported improved miscibility for blends of PSVP and the zinc and copper salts of α,ω-dicarboxylpolybutadiene in which a transition metal complex was formed between the two polymers.

All of the previously reported studies of miscibility enhancement due to interactions involving ionomers have used polymers with structurally dissimilar backbones, which generally exhibit phase separation in solution or in the bulk. Thus, the effect of the ionic interactions is complicated by the inherent thermodynamic repulsion between the two polymers. Moreover, the previous solution studies[3,4] were carried out in nonpolar solvents, and it is well-known that ionomers aggregate in these solvents, even in dilute solution. This also may complicate the interpretation of the solution behavior of blends in that aggregation of ionomers and intermolecular complexation between an ionomer and another functionalized polymer have similar effects on the solution behavior. Obviously, more studies of this nature are needed to fully understand how specific interactions can be exploited to control polymer blend miscibility and solution behavior.

This paper discusses the effect of metal cations on the intermolecular interactions and miscibility in a blend of two ionomers, one having a cation attached to the chain and the other having an anion attached to the chain. To avoid or, at least, reduce the complication of the thermodynamic repulsion of the two ionomer backbones, the two ionomers used, lightly sulfonated polystyrene and PSVP, had predominantly polystyrene backbones. A polar, ionizing solvent, dimethylformamide (DMF), was used to eliminate the typical ionic associations that occur in simple ionomer systems. The presence and qualitative assessment of intermolecular interactions were judged by solution viscosity studies and the glass transition temperature(s) of the neat blends.

Experimental Section

Lightly sulfonated polystyrene (SPS) and its various metal salts were prepared by the procedure described by Makowski et al.[9] The starting polystyrene was a commercial product of Dow Chemical Co. with $M_n = 106\,000$ and $M_w = 288\,000$, as determined by gel permeation chromatography (GPC). The sulfonation level was determined by titration of SPS in toluene/methanol (90/10 v/v) solution to a phenolphthalein end point with methanolic sodium hydroxide. The metal sulfonate derivatives were prepared by neutralizing SPS in toluene/methanol with a 20% excess of the appropriate metal hydroxide or metal acetate. The neutralized polymers were precipitated in a large excess of ethanol, filtered, washed several times with ethanol, and dried for a week under vacuum at 70 °C. The nomenclature used for the SPS salts is $x.y$-MSPS, where $x.y$ is the sulfonation level in mol % of substituted styrene monomers and M is the counterion used.

PSVP was synthesized by a free-radical emulsion copolymerization.[10] Styrene was washed with 10% sodium hydroxide to remove the inhibitor and then with distilled water, and the 4-vinylpyridine was vacuum-distilled at 5 mmHg and 30 °C. Potassium persulfate was used as the initiator, sodium lauryl sulfate as a surfactant, and dodecylthiol as a chain-transfer agent; all were used as received. The reaction was carried out for 24 h and terminated with hydroquinone. The copolymer was precipitated in acetone, washed with methanol, and dried under vacuum at 50 °C for a week. The vinylpyridine (VP) content was

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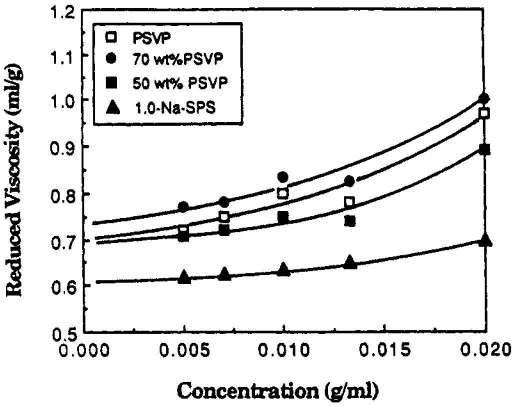

Figure 1. Reduced viscosity vs polymer concentration for 1.0-NaSPS/PSVP (3 mol % VP) blends in DMF.

determined by nitrogen analysis, and the molecular weight was determined by GPC. Two PSVP copolymers were prepared: one contained 3.4 mol % VP and had $M_n = 142\,000$, $M_w = 291\,000$, and the other contained 12 mol % VP and had $M_n = 103\,000$, $M_w = 265\,000$. Blends were prepared by adding a PSVP/DMF solution dropwise to a DMF solution to SPS under constant stirring. Reduced viscosities of the solutions were measured at 30 °C with a Ubbelohde viscometer. In all cases, the flow times were greater than 100 s, and no kinetic energy corrections were made.

Films of the blends were cast from solution at ambient temperature and dried to constant mass under vacuum at 50 °C. Glass transition temperatures (T_g) were measured with a Perkin-Elmer DSC 7 differential scanning calorimeter using a heating rate of 20 °C/min.

Results and Discussion

Solution Behavior of SPS/PSVP Blends. Typical solution viscosity curves for several blends of 1.0-NaSPS and PSVP (3 mol %) are shown in Figure 1. For a solution of two polymers without specific interactions between the polymers, the reduced viscosity, $\eta_{r,m}$, can be calculated as a weighted average of the viscosities of the individual components

$$\eta_{r,m} = (c_A\eta_{r,A} + c_B\eta_{r,B})/c_0 \qquad (1)$$

where $\eta_{r,A}$ and $\eta_{r,B}$ are the reduced viscosities of polymer A and polymer B at concentration $c_0 = c_A + c_B$. When there are specific intermolecular interactions, the solution viscosity of the blend will generally be higher than given by eq 1. The contribution of the interaction to the reduced viscosity is $\eta_{r,i}$, where

$$\eta_{r,i} = \eta_{r,exp} - \eta_{r,m} \qquad (2)$$

Alternatively, one can define a viscosity enhancement factor, R

$$R = \eta_{r,i}/\eta_{r,m} \qquad (3)$$

where $\eta_{r,exp}$ is the experimentally measured reduced viscosity, $\eta_{r,m}$ is given by eq 1, and R is the relative change of the viscosity due specifically to interactions.

Figure 2 shows R as a function of the mole fraction of VP groups in the blend (mole fraction is based on the total number of VP and sulfonate functional groups; thus, a mole fraction of 0 corresponds to a solution of only SPS and a mole fraction of 1.0 corresponds to a PSVP solution) for 2.0% (g/mL) solutions of blends of PSVP and four different 1.0-MSPS salts (M = H, K, Mg, and Cu) in DMF. Since the backbones of both polymers were essentially polystyrene, there should be little thermodynamic repulsion between the different polymers, therefore, R is a direct measure of the magnitude of the intermolecular interactions that occur in these systems.

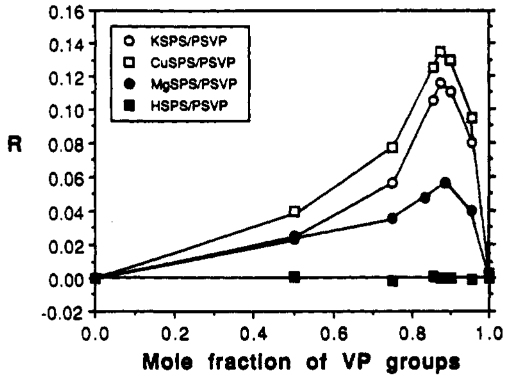

Figure 2. Composition dependence of R for 2% solutions of blends of 1.0-MSPS/PSVP (3 mol % VP) in DMF for various salts of SPS.

For the mixture of 1.0-HSPS and PSVP, the reduced viscosity of a 2.0% (g/mL) solution of the polymers in DMF was a simple weighted average of the viscosities of the component; i.e., eq 1 was valid and $R = 0$ over the entire range of composition. This result indicates that no significant amount of interpolymer interactions or complexation occurred in that system. In contrast, blends of PSVP with the different metal salts of 1.0-MSPS exhibited positive deviation from eq 1; i.e., $R > 0$, and a maximum in R occurred at a mole fraction of VP ≈ 0.85, which corresponded to $[\mathrm{VP}]/[\mathrm{SO_3^-}] \approx 6$.

For SPS/PSVP mixtures, one might expect two competitive interactions: (1) interpolymer complexation between the pyridine and metal sulfonate groups and (2) association of the uncomplexed ionic pairs of the SPS. The latter interaction depends strongly on the solvent polarity and is not favored in solvents capable of ionizing the ion pair, such as DMF.[11] Caution is necessary when interpreting changes in the reduced viscosity of ionomer solutions when highly ionizing solvents such as DMF are used. For example, it is well documented that solutions of SPS in DMF exhibit polyelectrolyte behavior, which is manifest by an increase in the viscosity at very low polymer concentrations.[2] In that case, a viscosity increase is caused by intramolecular repulsions of the solvated, i.e., unshielded, anions along the polymer backbone, which tend to expand the hydrodynamic volume of the chain. However, at the 2.0% (g/mL) polymer concentration used in the present study, sufficient overlap of the chains occurs so that the solution viscosity is expected to be dominated by *inter*molecular effects rather than *intra*molecular ones.

The increase in viscosity of the PSVP/SPS solutions is thought to be due to a competition of the VP groups with DMF for association with the sulfonate salt. That is, a soluble interpolymer complex was formed. Insoluble complexes were formed when the polymer concentration was increased significantly beyond 2% or the sulfonate content of the SPS was increased to 6 mol % for the Ca or Mg salts. These complexes dissolved, however, when the solution was heated to ca. 70 °C.

Strong interpolymer associations only occurred when metal-neutralized SPS was used. DMF effectively inhibited interactions between PSVP and HSPS, but was less efficient when neutralized ionomers were used. In addition, a strong effect of the choice of cation was observed; see Figure 2. The specific interaction that occurred in these systems is believed to be complexation of the electron-deficient nitrogen of the vinylpyridine group with the electron-rich oxygen of the sulfonate anion; see Figure 3. This interaction depends on the solvation of the cation, i.e., separation of the ion pair by the solvent.

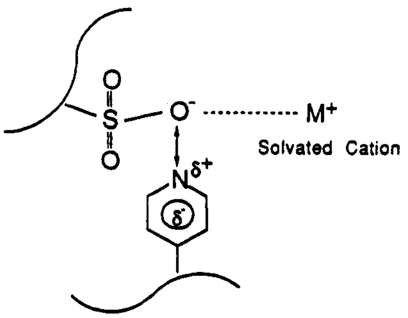

Figure 3. Schematic of intermolecular complex formed between MSPS and PSVP in DMF.

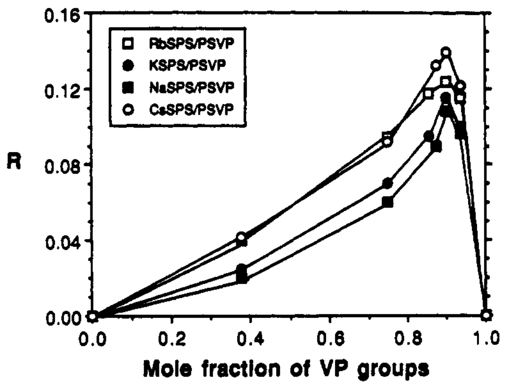

Figure 4. Composition dependence of R for 2% solutions of blends of 1.0-MSPS/PSVP (3 mol % VP) in DMF for SPS alkali metal salts.

The better is the separation, the weaker is the polarization of the anion by the cation and the more nucleophilic is the oxygen carrying the anion charge. Differences in the strength of the ion pair, then, are expected to result in differences in the strength of the VP–sulfonate complexes and are manifest by variations in the viscosities for the complexes using different metal cations. This will be discussed further in the following section.

Lundberg et al.[4] reported that interactions occurred in PSVP/ZnSEPDM blends in nonpolar solvents such as xylene. However, viscosity measurements indicated that no specific interactions between the two polymers occurred when alkali or alkaline earth metal neutralized SEPDM was used. In that system, the nonpolar solvent favors the formation of the ion pair. Thus, the electronegativity on the anion oxygen is considerably lower than in the situation where the ion pair is solvated, and complexation between the oxygen and the VP nitrogen does not occur to any great extent. The enhancement of the viscosity with the transition metal cation neutralized SEPDM was due to direct complexation of the transition metal with the VP group. This occurs because of interactions of the d electrons of the cation with the nitrogen of the VP group.

Influence of Metal Cation. The effect of the metal cation on R is shown in Figures 4–6 for alkali metal, alkaline earth metal, and transition metal salts, respectively. For the alkali metal series (Figure 4), the solution viscosity increased in the order Na < K < Rb < Cs. The larger the cation, the stronger was the interaction with the pyridine group. Similar trends were observed for the alkaline earth and transition metal cations, as shown in Figures 5 and 6. In those cases, the enhancement of the solution viscosity of the blends was Mg < Ca < Ba for alkaline earth metal and Mn < Fe < Ni < Cu for transition metal.

The R data corresponding to the viscosity maxima in Figures 4–6 for the three classes of cations are replotted in Figure 7 as a function of the electrostatic field strength

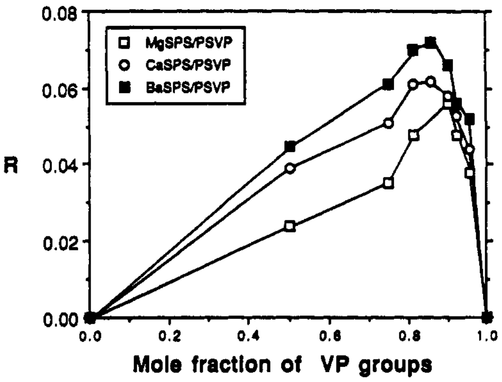

Figure 5. Composition dependence of R for 2% solutions of blends of 1.0–MSPS/PSVP (3 mol % VP) in DMF for SPS alkaline earth metal salts.

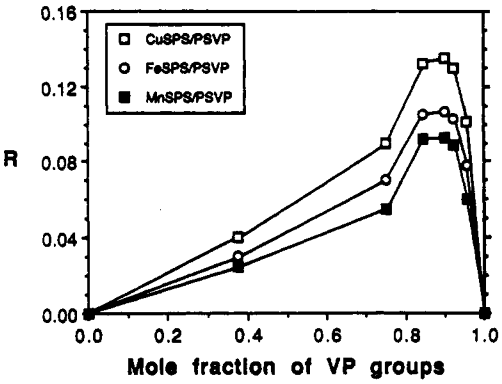

Figure 6. Composition dependence of R for 2% solutions of blends of 1.0-MSPS/PSVP (3 mol % VP) in DMF for SPS transition metal salts.

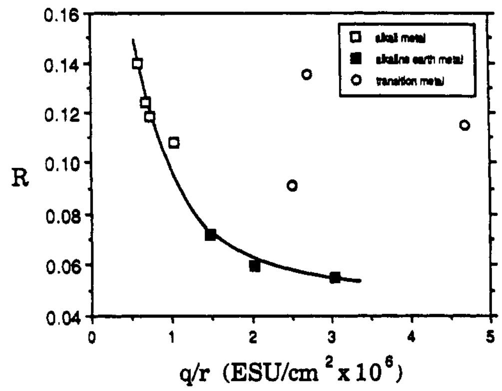

Figure 7. Maximum values of R from Figures 2–4 plotted against q/r.

of the cation, $E = q/r$, where q is the cation charge and r is the ionic radius. The values for the alkali and alkaline earth metal cations formed a single curve. The values of R for the transition metal salts, however, were generally higher for a given value of q/r, indicating that complexation occurred to a greater extent for those salts.

The results shown in Figures 4–6 are consistent with the proposed interpolymer complex shown in Figure 3. For the alkali and alkaline earth metal salts, the extent of solvation of the metal sulfonate ion pair by DMF is expected to increase as E decreases. A corresponding increase in the nucleophilicity of the anion oxygen promotes complexation with the VP, which increases R. The deviation of the transition metal salts from the curve in Figure 7 is most likely a consequence of the availability of their d electrons. Similar effects have been observed in the hydrogen-bonding behavior of metal sulfonate groups.[12] That is, the strength of the interactions for non-

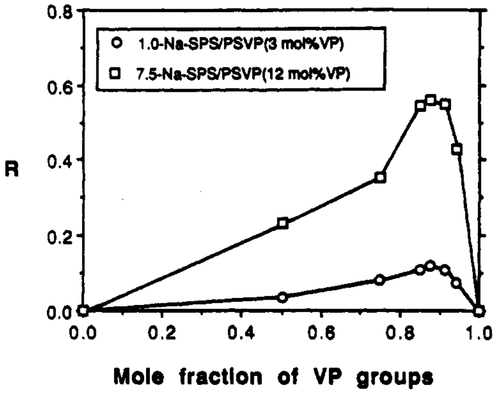

Figure 8. Effect of the two copolymer compositions on R for 2% solutions of blends of NaSPS and PSVP in DMF.

transition-metal salts can be explained on the basis of the electrostatic field of the cation, while for transition metal cations, coordination-type bonding is generally stronger than would be expected from their electrostatic field strength.

Complex Stoichiometry. The composition for the maximum in R, ca. 0.85 mole fraction of VP, was relatively independent of the salt used, cf. Figures 4–6. This corresponded to a VP to sulfonate ratio of ca. 6:1. The functional group stoichiometry at maximum in R was also relatively insensitive to the composition of the copolymer used. Figure 8 shows the R vs composition curves for 2% solutions involving blends formed from two different copolymers of PSVP and SPS. Although the value of R_{max} increased when the level of functionalization of the copolymers was increased, the position of R_{max} in both systems occurred at about the same VP/sulfonate ratio.

Agnew[13] reported that for zinc halide–poly(4-vinylpyridine) complexes, two VP's coordinated with one metal cation. Peiffer et al.[8] proposed that for PSVP/SEPDM blends the complex involves only one VP per sulfonate group due to steric hindrance of the polymer chains attached to the functional groups. The viscosity data for the PSVP/SPS solutions, however, suggest a stoichiometry of six VP's per sulfonate group. Bekturov and Bimendina[14] and Tsuchida and Abe[15] have reviewed interpolymer complexes in solutions of homopolymers and copolymers. The composition of the complexes, expressed as the molar ratio of the interacting monomer units, was usually 1:1 or nearly equimolar. There have, however, been a number of reported polyelectrolyte complexes for which the anion/cation ratios were 4:1 to 9:1.[15] Those mostly involved aqueous solutions of poly(carboxylic acids) with poly(ionenes). The reasons proposed for the unusually high stoichiometry included that differences in the charge densities of the polycation and polyanion led to various degrees of dissociation of the poly(carboxylic acids), that the hydrophobicity of the polycation, i.e., ionene, affected the stability of the complex, and that steric hindrance around the ionic sites and the conformation of the chains affected the efficiency of complexation. Although some of these explanations might also apply to the SPS/PSVP/DMF systems, it is still not clear why the stoichiometry of 6:1 should be relatively independent of the composition of the copolymers and the cation used. Similarly, the competition of DMF with the VP for complexation with the sulfonate anion might be responsible for the seemingly high complex composition, but as discussed in the next section, the 6:1 stoichiometry was also observed in other solvents.

Another explanation may relate to the VP distribution in the PSVP copolymers. That is, if the PSVP were relative blocky, the ability of each VP in a blocky sequence to associate with sulfonate groups randomly placed on the SPS chain would be reduced. Although this might explain the invariance of the position of the viscosity maximum, there is no evidence that the PSVP were other than random copolymers.

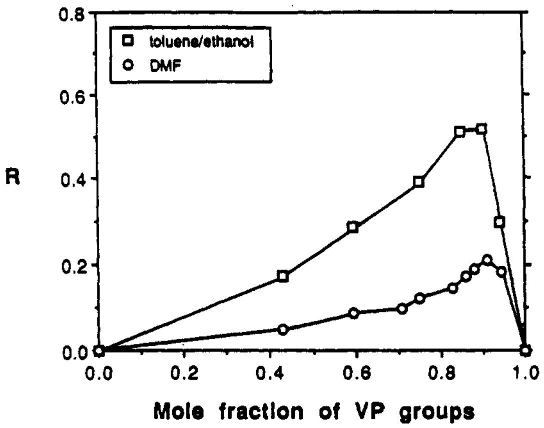

Figure 9. Effect of the solvent on R for 2% solutions of 2.8-ZnSPS/PSVP (3 mol % VP).

Solvent Effects. R data for ZnSPS/PSVP (3 mol % VP) solutions in DMF and in a mixed solvent of toluene and ethanol (95/5 v/v) are shown in Figure 9. Compared with DMF, the mixed solvent was a relatively nonpolar solvent, though the ethanol preferentially associates with the sulfonate group and, to a great extent, solvates ion–dipole interactions involving the sulfonate ion pair. The enhancement of viscosity for the toluene/ethanol solutions was much greater than for the DMF solutions, but the maximum viscosity occurred at a similar VP composition. Thus, the solvent polarity influenced the solution viscosity, but not the stoichiometry of the interactions. It appears that the ethanol is also effective at solvating the ion pair, which is not surprising, and, as a result, complex formation between the VP and the anion oxygen is promoted. The extent of complexation, as judged by the relative values of R, was greater in the toluene/ethanol solvent. This is probably a consequence of the lower overall dielectric constant of the mixed solvent, which yields a stronger potential for the interactions.

One should note that the complex behavior described here is fundamentally different from that described by Lundberg et al.[4] for ZnSEPDM/PSVP and MSPS/PSVP blends in xylene. As discussed earlier, a maximum in the solution viscosity of ZnSEPDM/PSVP in xylene was observed at a complex stoichiometry of [VP]/[sulfonate] = 1. In that case, however, the complex formed between the VP nitrogen and the zinc cation. Similarly, for ZnSPS/PSVP blends in xylene, a transition metal complex formed, and this resulted in gelation of the solution at relatively low polymer concentration, <1%. From the limited data reported in ref 4 for that system, no maximum in the viscosity with changing blend composition was observed; the viscosity increased monotonically with increasing sulfonate concentration.

In contrast to the complexes reported in the present paper, no interactions were observed by Lundberg et al. for the NaSPS/PSVP blend in xylene. That result is consistent with the inability of relatively nonpolar xylene to solvate the ion pair. As a result, the cation decreases the nucleophilic nature of the anion oxygen, and no complex occurs due to the absence of d-shell electrons.

The viscosities of SPS/PSVP in tetrahydrofuran (THF) were also measured, and the R vs composition curves for

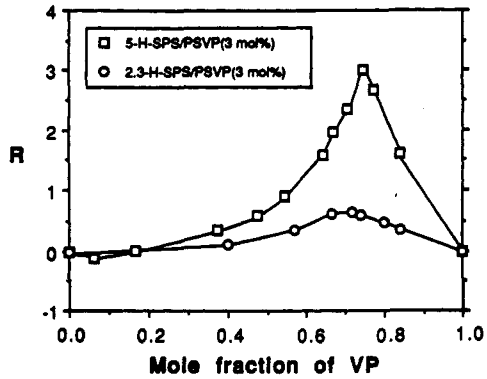

Figure 10. Composition dependence of R for 2% solutions of blends of 2.3-HSPS/PSVP (3 mol % VP) and 5.0-HSPS/PSVP (3 mol % VP) in THF.

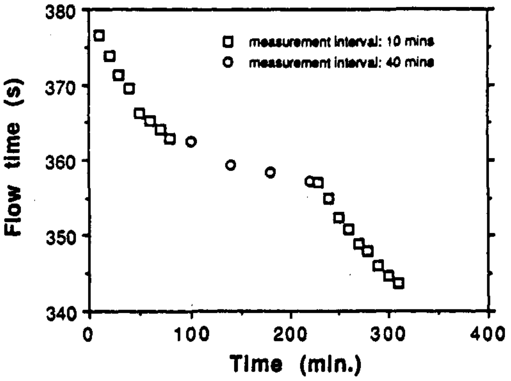

Figure 11. Capillary flow time for successive determinations for 2% solutions of 2.8-ZnSPS/PSVP (12 mol % VP) in toluene/ethanol (95/5 v/v).

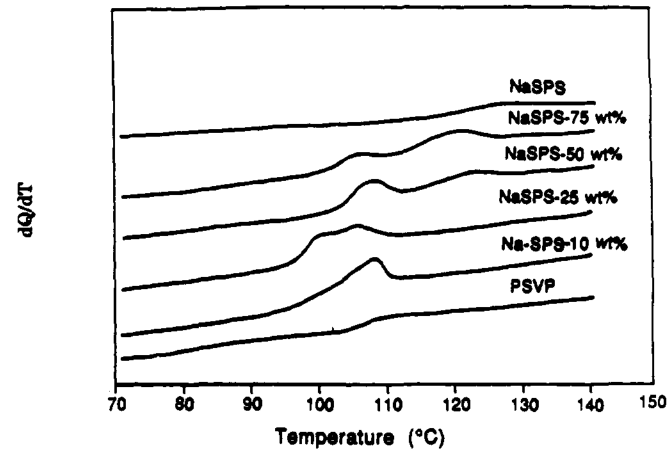

Figure 12. DSC thermograms of 7.5-NaSPS/PSVP (12 mol % VP) blends.

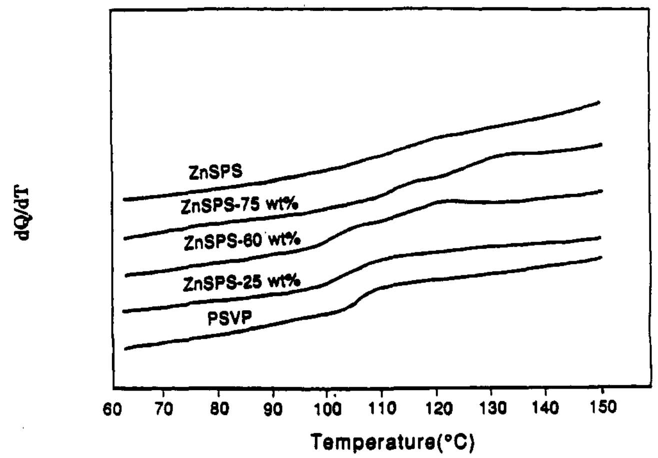

Figure 13. DSC thermograms of 7.5-ZnSPS/PSVP (12 mol % VP) blends.

two different HSPS blends are given in Figure 10. The maximum in R occurred at a VP/sulfonate ratio of ca. 2:1 to 3:1, considerably lower than in the DMF and toluene/methanol solutions. This, together with the results of Lundberg et al.[4] for xylene solutions, strongly suggests that the 6:1 complex stoichiometry observed in the DMF and toluene/methanol solutions was due to competition by complexation of the solvent with the polymers and not to the actual complex composition. That is, the amino group of DMF can coordinate with the sulfonate anion and methanol can hydrogen bond to it. Apparently, a large excess of VP groups is needed in these solvents to maximize the complexation of the VP and sulfonate groups.

In the case of HSPS/PSVP in THF (Figure 10) proton transfer occurs and a polysalt complex is formed. That the stoichiometry at which the maximum in viscosity was observed was higher than 1:1 may reflect the ability of THF oxygen to associate with the electron-deficient nitrogen of VP. Thus, again, an excess of VP functionality is required to achieve a maximum in the polymer association.

Thixotropic behavior, i.e., a time-dependent solution viscosity, was observed for a 2% polymer solution containing 75 wt % PSVP (12 mol % VP) and 25 wt % 2.8-ZnSPS in toluene/ethanol (95/5 v/v) (Figure 11). When capillary measurements were made over a period of ca. 5 h, the viscosity, which is proportional to the flow time, decreased with each succeeding determination. The relative amount of the viscosity decrease between measurements depended on the time interval between measurements. For example, the rate of viscosity decrease was much less when the measurements were made at 40-min intervals than at 10-min intervals. The thixotropic behavior is probably due to degradation of the complex. When the shear deformation was stopped, however, the complex re-formed. The data in Figure 11 suggest that the relaxation time of the dissociated complex, i.e., the characteristic time needed to re-form the complex, was of the order of 1 h.

Complexed Polymers in the Bulk. Since the backbones of the two polymers used in this study were similar, one might expect that intermolecular interactions between the two polymers might yield miscible blends. Blends cast from DMF solution at ambient temperature, however, exhibited two T_g's, hence two phases, as shown by the DSC curves in Figures 12 and 13 for 7.5-NaSPS/PSVP (12 mol % VP) and 7.5-ZnSPS/PSVP (12 mol % VP), respectively. The cast films were transparent, which may have resulted from either similar refractive indices of the two component polymers or a very small dispersed phase size, i.e., $\ll 1\ \mu m$. The phase separation is believed to result from the relatively poor solubility of the complexed polymers in DMF and precipitation from the solution at high polymer concentrations as the solvent evaporated. This solvent-induced phase separation was eliminated by annealing the samples above T_g; e.g., after annealing the blend for 10 min at 250 °C, only one T_g was observed by DSC.

Both T_g's were composition dependent, which indicates that interactions between the two polymers did lead to some phase mixing. In fact, at the higher PSVP concentrations, i.e., 75 wt % in the case of the ZnSPS and 90 wt % for the NaSPS, only a single broad T_g was observed. That result was consistent with the solution data that showed that the maximum degree of complexation occurred at a relatively high PSVP concentration. This result suggests that the complex formed in the DMF solution is preserved in the dried film. The composition dependence of the two T_g's was stronger for the blends containing ZnSPS compared to those containing NaSPS, which confirms that the transition metal salt complexes more strongly with VP than the non-transition-metal salts.

Conclusions

The solution behavior of blends of SPS and PSVP ionomers in DMF—a polar solvent—indicated that intermolecular complexation occurred only when metal sulfonate derivatives of SPS were used. The maximum effect on the viscosity of complexation occurred at a VP to sulfonate ratio of ca. 6:1, which was relatively independent of copolymer composition and the choice of the cation.

For alkali and alkaline earth metal salts, the magnitude of the viscosity increased with decreasing electrostatic field strength of the cation. Transition metal salts yielded the greatest viscosity enhancements, but there was not a direct correspondence between the viscosity and the electrostatic field strength. The choice of solvent also affected the magnitude of the viscosity enhancement; the viscosity increased with decreasing solvent polarity. The solutions were thixotropic due to shear-induced breakup of the intermolecular complexes. Once the shear was removed, however, the structure recovered on the time scale of about an hour.

Bulk samples of the PSVP/MSPS blends (where M = metal cation) cast from DMF exhibited two T_g's, characteristic of a phase separation morphology. Both T_g's were composition dependent, which indicates some miscibility. Blends of PSVP and HSPS prepared in the same manner were miscible, which was probably due to the absence of strong interactions between these polymers in DMF, which allowed the polymers to remain in solution as the polymer concentration increased during evaporation of the solvent.

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