Miscibility of Polystyrene-Based Ionomers with Poly(2,6-dibromo-1,4-phenylene oxide)

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ABSTRACT: Blends of poly(2,6-dibromo-1,4-phenylene oxide) (PDBrPO) with 4.8 mol % sulfonated polystyrene (4.8SPS), Na-neutralized 1.7 mol % sulfonated polystyrene (Na1.7SPS), Mn-neutralized 3.8 mol % sulfonated polystyrene (Mn3.8SPS), and Zn-neutralized 3.8 mol % sulfonated polystyrene (Zn3.8SPS) ionomers were investigated for their miscibilities with varying compositions by dilute solution viscometry (DSV), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). Δb, μ, and α parameters by W. R. Krigbaum and F. J. Wall (J Polym Sci 1950, 5, 505), K. K. Chee (Eur Polym J 1990, 4, 423), and Z. Sun et al. (Eur Polym J 1992, 28, 1259), respectively, were calculated from DSV data to determine miscibility. Na1.7SPS is immiscible with PDBrPO in no relation to the blend compositions. On the other hand, the increasing extent of miscibility of the blends reflected by the data is as follows: 4.8SPS < Mn3.8SPS < Zn3.8SPS. DSC and SEM results are also in agreement with the DSV data except for the α parameter, which showed some disagreements with Δb and μ parameters in a few blends. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3558–3567, 2001

Key words: poly(2,6-dibromo 1,4-phenylene oxide); sulfonated polystyrene ionomers; polymer blends; compatibility

INTRODUCTION

The miscibility of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with homo- and copolymers of halogen-substituted styrene derivatives was investigated extensively.[1–9] PPO is, in fact, a polyether and several blends of polyethers with appropriate ionomers show enhanced miscibility as a function of ionic group content.[10,11] This is attributed to ion–dipole interactions between the ion pairs in the ionomer and the ether oxygen in the polyether.

A blend with the nonneutralized ionomer similarly shows enhanced miscibility due to hydrogen-bonding interactions. Enhanced miscibility is not observed in the blends of poly(2,6-dibromo-1,4-phenylene oxide) (PDBrPO) and 4.8 mol % sulfonated polystyrene (4.8SPS) in this work because of an effective decrease in the electronegativity of the ether oxygen of PPO due to the 2,6-bromine substituents rather than methyl substituents. We examined the effects of the introduction of bromine and cationic groups on the miscibility with varying compositions of each component. It was shown that the presence of ionic groups can increase the miscibility of blends of PDBrPO/SPS ionomers. Na-neutralized groups are immiscible independent of composition. Acid groups are slightly miscible (only in 85% 4.8SPS/15%PDBrPO blend); Mn-neutralized groups are partially miscible, and Zn-neutralized groups are completely miscible with PDBrPO.
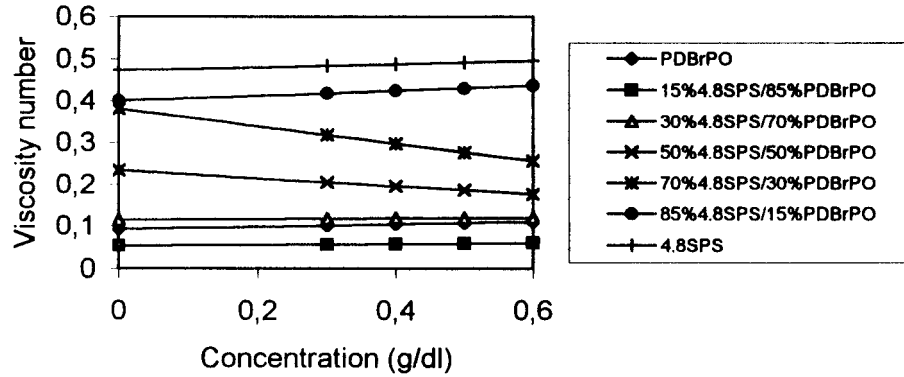
Figure 1 Viscosity number versus concentration relationship for 4.8SPS/PDBrPO system.

The compatibility of solutions were characterized by a viscometry technique by using the Krigbaum and Wall parameter, Δb.[12] Basically, DSV hinges on the classical Huggins equation[13] that expresses the specific viscosity (η_{sp}) of the polymer as a function of the concentration C

$$\eta_{sp}/C = [\eta] + K[\eta]^2 C \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity, K is the Huggins coefficient, and $K[\eta]^2$ is the interaction term and is represented by b after this point. The specific viscosity, $\eta_{sp,m}$, of a mixed polymer solution was expressed as

$$\eta_{sp,m} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2$$
$$+ b_{22}C_2^2 + 2b_{12}C_1C_2 \qquad (2)$$

where $[\eta_1]$ and $[\eta_2]$ are the intrinsic viscosities of components 1 and 2, C_1 and C_2 are the concentrations in mixed polymer solutions, b_{11} and b_{22} are self-interaction parameters that are the slopes of viscosity number versus concentration relationships of pure components, respectively, and b_{12} is the interaction coefficient for the mixture. For mathematical convenience, Krigbaum and Wall[12] defined the interspecific interaction coefficient b_{12}^* as

$$b_{12}^* = (b_{11}b_{22})^{0.5} \qquad (3)$$

However, the definition of the interspecific interaction coefficient according to eq. (3), which is not valid for systems that have negative values for b_{11} and b_{22}. Therefore, the modification by

Williamson and Wright[14] definition, eq. (4), is used to evaluate b_{12}^*, which can be expressed as

$$b_{12}^* = (b_{11} + b_{22})/2 \qquad (4)$$

According to Krigbaum and Wall,[12] information on the interaction between polymer molecules 1 and 2 should be obtainable from comparison of experimental b_{12} and theoretical b_{12}^* values. Here, the compatibility of the polymer mixture is characterized by a parameter Δb, which is expressed as

$$\Delta b = b_{12} - b_{12}^* \qquad (5)$$

where b_{12}^* is calculated from eqs. (3) or (4). Negative values of Δb are found for solutions of incompatible polymer systems, whereas positive values of Δb refer to attractive interactions. Observed intrinsic viscosity values are higher than the calculated values for compatible systems.[15]

In the study by Chee,[16] the compatibility of polymer blends can be identified by μ parameter. In the case of $[\eta_1]$ and $[\eta_2]$ values being different from each other, w_1 and w_2 values (which are weight fractions of polymer components 1 and 2, respectively) are defined in terms of $[\eta]$'s. For this purpose, the mean viscosity is given as

$$[\eta] = w_1[\eta_1] + w_2[\eta_2] \qquad (6)$$

As a result, another miscibility parameter μ is defined as

$$\mu = \Delta b/([\eta_2] - [\eta_1])^2 \qquad (7)$$

Table I   Viscometric Data for 4.8SPS/PDBrPO System in 1,4-dioxane at 25°C

Wt % 4.8SPS	$[\eta]$ (dL g^{-1})	b (dL^2 g^{-2})	Δb	μ	α
0.00	0.0927	0.029	—	—	—
0.15	0.0527	0.011	-0.500	-3.460	2.640
0.30	0.1150	0.009	-0.294	-2.030	-0.090
0.50	0.2340	-0.096	-0.165	-1.140	-2.170
0.70	0.3800	-0.207	-0.033	-0.228	-1.710
0.85	0.5105	0.058	0.226	1.570	0.012
1.00	0.4730	0.038	—	—	—

Again, for miscible systems, μ is positive and has a negative value, indicating immiscibility. According to Sun et al.,[17] for a ternary system of components, polymer A, polymer B, and the solvent, the Huggins coefficient K_m contains three interaction parameters.

1. Hydrodynamic interactions between polymer pairs

$$K_{m1} = \frac{K_1[\eta_1]^2 w_1^2 + K_2[\eta_2]^2 w_2^2 + 2(K_1 K_2)^{1/2}[\eta_1][\eta_2]w_1 w_2}{([\eta_1]w_1 + [\eta_2]w_2)^2} \quad (8)$$
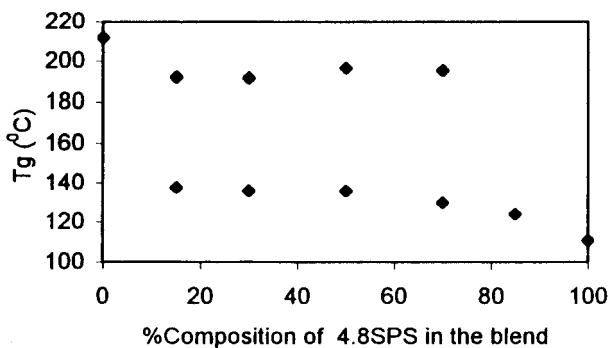
2. Formation of double molecules which presupposes actual contact

$$K_{m2} = \frac{K'}{[\eta]}([\eta]_2 - [\eta]_1) \quad (9)$$

K' is constant and can be neglected for nonpolar solvents. $[\eta]_1$ and $[\eta]_2$ are intrinsic viscosities for single and double molecules.

3. Intermolecular attraction or repulsion $K_{m3} = \alpha$. Then,

$$K_m = K_{m1} + K_{m2} + K_{m3} \cong K_{m1} + \alpha \quad (10)$$

K_{m2} is neglected in the absence of strong specific forces of attraction between molecules that would encourage aggregation, and at sufficiently low concentrations, then α becomes

$$\alpha = K_m$$
$$- \frac{K_1[\eta_1]^2 w_1^2 + K_2[\eta_2]^2 w_2^2 + 2(K_1 K_2)^{1/2}[\eta_1][\eta_2]w_1 w_2}{([\eta_1]w_1 + [\eta_2]w_2)^2}$$
$$(11)$$

$\alpha > 0$ shows miscibility and $\alpha < 0$ shows immiscibility.

EXPERIMENTAL

Sulfonated polystyrene and metal neutralized sulfonated polystyrene ionomers are prepared according to Tomita and Register[7] Na1.7SPS is obtained from Exxon Chemical Co. (USA).

Polystyrene (PS) is a Dow Chemical Inc. (USA) product with a viscosity-averaged molecular weight

Figure 2   Summary of the DSC results for 4.8SPS/PDBrPO system.
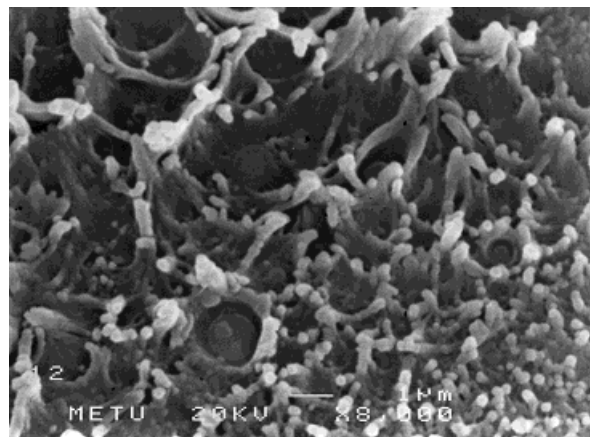
Figure 3   SEM photograph of 85%4.8SPS/15%PDBrPO blend.
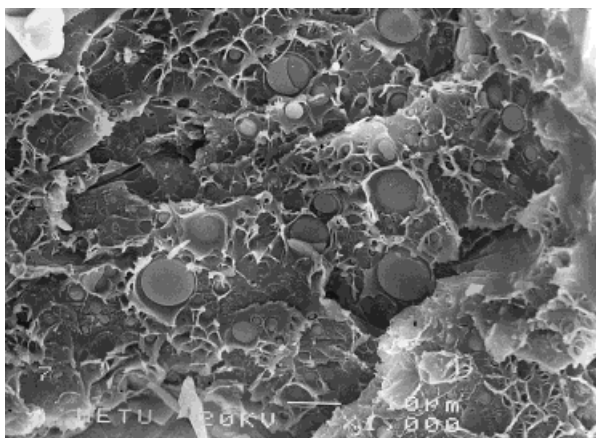
Figure 4 SEM photograph of 50%4.8SPS/50%PD-BrPO blend.

(M_v) of 225.000 g/mol. Sulfonated polystyrene (SPS) was obtained by sulfonation of PS with acetyl sulfate in 1,2-dichloro ethane, following the method described in the literature.[7] Functionality of the SPS is determined by titration with standard methanolic NaOH solution.

Na1.7SPS was purchased from Exxon Laboratories with appropriate weight-averaged molecular weight (M_w) of 300.000 g/mol. Mn- and Zn-neutralized ionomers were prepared by dissolving 3.8SPS and proper amounts of $Mn(CH_3COO)_2$ or $Zn(CH_3COO)_2$ in THF in separate beakers. The solutions were then mixed for 1 h at room temperature to achieve complete neutralization of sulfonic acid groups by the corresponding metal cation. The ionomers were then back titrated to confirm complete neutralization.

Synthesis of the phenoxo–copper complex and PDBrPO (fully brominated) and their characterization was carried out according to Kısakürek et al.[18]

Preparation of Polymer Blends

PDBrPO was blended with

1–4.8 mol % sulfonated polystyrene (4.8SPS)
2–1.7 mol % Na-neutralized sulfonated polystyrene (Na1.7SPS)
3–3.8 mol % Mn-neutralized sulfonated polystyrene (Mn3.8SPS)
4–3.8 mol % Zn-neutralized sulfonated polystyrene (Zn3.8SPS)

by solution-casting method at room temperature having compositions of 15, 30, 50, 70, and 85% by weight. 1,4-Dioxane was used as a solvent for the first two blends and THF was used as a solvent for the last two blends during both blending and viscosity measurements.

The blends were dried under vacuum at about room temperature for 2 weeks until constant weight. Viscosity measurements were carried out with a Ubbelohde viscometer in a constant-temperature water bath at 25°C. Differential scanning calorimetry thermograms were obtained with a TA instrument of DSC 910S by using a heating rate of 10°C min^{-1}. For SEM analysis, a JSM 6400 scanning electron microscope of Noran Instruments Inc. was used.
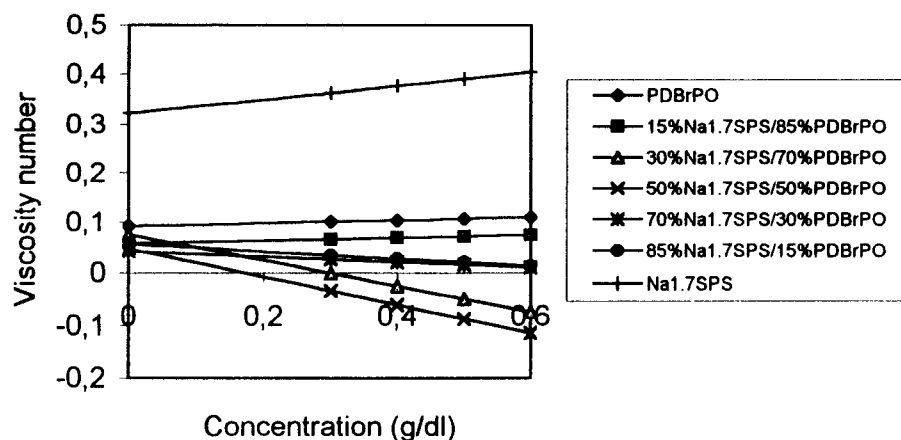
Figure 5 Viscosity number versus concentration relationship for Na1.7SPS/PDBrPO system.

Table II   Viscometric Data for Na1.7SPS/PDBrPO System in Dioxane at 25°C

| Wt % Na1.7SPS	$[\eta]$ (dL g^{-1})	b (dL^2 g^{-2})	Δb	μ	α
0.00	0.0927	0.029	—	—	—
0.15	0.0571	0.029	-0.432	-8.212	6.32
0.30	0.0734	-0.246	-0.336	-6.391	-4.771×10
0.50	0.0468	-0.270	-0.467	-8.873	-1.250×10^2
0.70	0.0414	-0.051	-0.732	-1.391×10	-3.122×10
0.85	0.0562	-0.072	-1.360	-2.584×10	-2.424×10
1.00	0.3220	0.136	—	—	—

RESULTS AND DISCUSSION

4.8SPS/PDBrPO System

Viscosity number versus concentration plots for 4.8SPS blended with PDBrPO in various compositions are given in Figure 1. As seen from Figure 1, all blends fall between the two virgin ones except a 15/85 blend, which shows the lowest viscosity number value, a condition which is close to immiscibility. On the other hand, the miscibility parameters determined the conclusion that 70/30, 50/50, 30/70, and 15/85 compositions are immiscible as well and the only miscible system is 85/15. Table I tabulates the Δb, μ, and α values, the b and $[\eta]$ values of which are the slopes and intercepts of the lines, respectively, in Figure 1.

The information given by Table I can be summarized as follows: the miscibility parameters Δb and μ are negative for all compositions except for the 85%4.8SPS/15%PDBrPO blend. The lowest numbers for Δb and μ are for the 15%4.8SPS/85%PDBrPO blend. As the percentage of 4.8SPS increases, the negative Δb and μ values decrease and reach a positive value for 85%4.8SPS/15%PDBrPO. However, α values do not obey this trend and α shows a positive value for both 15%4.8SPS/85%PDBrPO

and 85%4.8SPS/15%PDBrPO blends. Remembering that the positive miscibility parameters imply miscibility, the blend with 85%4.8SPS content is the only miscible composition for this system when Δb and μ are considered. The main reason for the miscibility of this composition may be the appropriate amounts of two components and H-bonding between SPS and oxygen of the PDBrPO. The same conclusion is reflected by DSC measurements as well.

The T_g versus %composition plots for 4.8SPS/PDBrPO blends are given in Figure 2. The two T_g values for specified blend compositions confirm the incompatibility and phase separation, whereas single T_g shows compatibility and single phase. Accordingly, Figure 2 also supports the fact that the only blend with a single phase in this system is with 85%4.8SPS composition. The lower T_g in Figure 2 corresponds to that found in the 85%4.8SPS/15%PDBrPO blend, whereas the upper T_g is PDBrPO saturated with 4.8SPS. The saturation is expected by the same upper T_g values for several PDBrPO–4.8SPS compositions. The decrease of
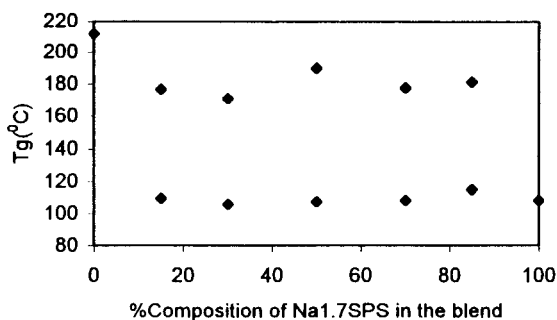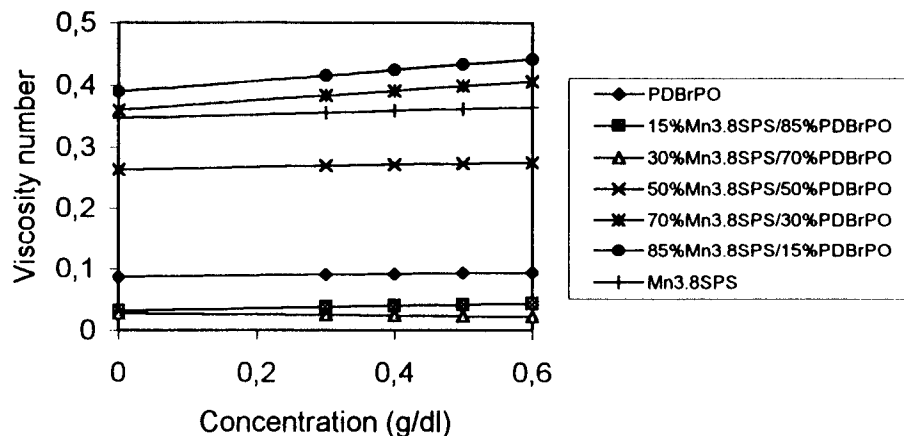

Figure 6   Summary of DSC results for Na1.7SPS/PDBrPO system.
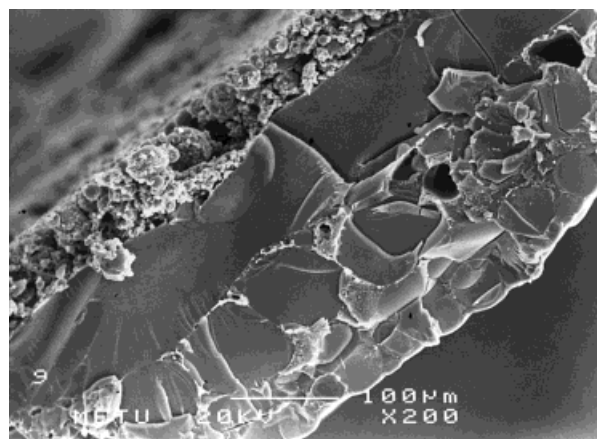
Figure 7   SEM photograph for 50%Na1.7SPS/50%PDBrPO system.

Figure 8 Viscosity number versus composition relationships for Mn3.8SPS/PDBrPO blends.

PDBrPO T_g in the blend is greater than the increase of 4.8SPS, implying that more 4.8SPS is dissolved in PDBrPO than the reverse. These results indicate that 4.8SPS/PDBrPO blends containing more than 15 wt % PDBrPO are phase separated with one phase being some (<15%) 4.8SPS dissolved in PDBrPO and the other is PDBrPO saturated in 4.8SPS. This behavior was observed in all the blends we examined, although PDBrPO content dividing the one- and two-phase regions depends on the bound cation.

Phase separations, except for 85%4.8SPS, are apparent from the SEM photographs also in agreement with the previous data. Figure 3 is the SEM photograph for the only miscible blend which is 85%4.8SPS/15%PDBrPO by weight; when this photograph is compared with Figure 4, which is the SEM photograph of 50% 4.8SPS blend, two phases are apparent.

4.8SPS/PDBrPO system consisting of blends with nonneutralized ionomer is expected to show enhanced miscibility due to H-bonding interactions. However, dibromo-substituted phenyl rings adjacent to the ether groups certainly may reduce the access of the sulfonate group to the PDBrPO ether groups. Even if the acid group in principle has access to the ether oxygen from a steric point of view, local chain conformation may reduce the interactions between PS and PDBrPO segments, thereby rendering the acid–ether interactions unfavorable. Another factor may be that the ether oxygen donates excess electron density to the neighboring phenyl groups, thereby reducing the ability of the ether to interact with the acid.[6] In any case, when favorable interactions do not take place, the introduction of the counits into PS may induce miscibility. Thus, these counits effectively act to reduce the interactions between PS and PDBrPO.

Na1.7SPS/PDBrPO System

Viscosity number versus concentration plots for Na1.7SPS/PDBrPO blend with various compositions are given in Figure 5. In Table II, the miscibility parameters for Na1.7SPS/PDBrPO sys-

Table III Viscometric Data for Mn3.8SPS/PDBrPO System in THF at 25°C

Wt % Mn-SPS	$[\eta]$ (dL g^{-1})	b (dL^2 g^{-2})	Δb	μ	α
0.00	0.086	0.0119	—	—	—
0.15	0.032	0.0183	−0.420	−6.140	1.690×10
0.30	0.027	−0.0091	−0.365	−5.350	-1.300×10
0.50	0.264	0.0193	0.055	0.805	−0.135
0.70	0.360	0.0785	0.162	2.370	0.289
0.85	0.390	0.0875	0.234	3.420	0.259
1.00	0.348	0.0287	—	—	—
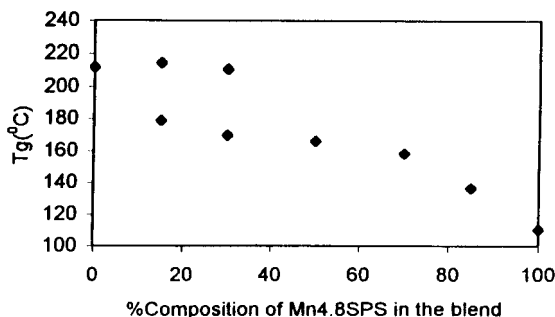
Figure 9 Summary of DSC results for Mn3.8SPS/PDBrPO system.

tem having various compositions are given (*b*, [η], Δ*b*, μ, and α).

As seen from Table II, all miscibility parameters, including α, for all compositions have negative values, indicate phase separation in all the blends. The most interesting feature of this table is the strong influence by the choice of neutralizing cation, which is the Na^+ ion.

T_g versus %composition for Na1.7SPS/PDBrPO blends are given in Figure 6. Table II and Figure 6 are in agreement, because all miscibility parameters have negative signs for all compositions which are confirmed by the two T_g values for each blend. Examining Figure 6 more closely, the lower T_g values correspond to that of pure Na1.7SPS and the upper T_g values are slightly lower than the T_g of the pure PDBrPO, which implies that a small degree (<15%) of miscibility of PDBrPO in Na1.7SPS is taking place. A slight deviation for 50% blend may be due to some experimental error.

SEM photograph of 50%Na1.7SPS/50%PDBrPO system is given in Figure 7. Phase separation is apparent from the photograph, which is also in agreement with the data in Table II.

Because Na is an alkali metal, Na^+ ion has small size and high strength for ionic association; the ion pairs tend to aggregate into groups of ion pairs via dipole–dipole interactions to form multiplets. These aggregates restrict the mobility of the nearest parts of the backbone chains to which they are covalently bound. The existence of a sufficient number of multiplets that are close enough to one another gives rise to regions of reduced chain mobility; these regions are called clusters. The experimental results show that ionic clusters do not accommodate a second phase in its matrix and no compatibility is detected by Na1.7SPS/PDBrPO system. This is usually the result of most of the miscibility studies in literature.[6]
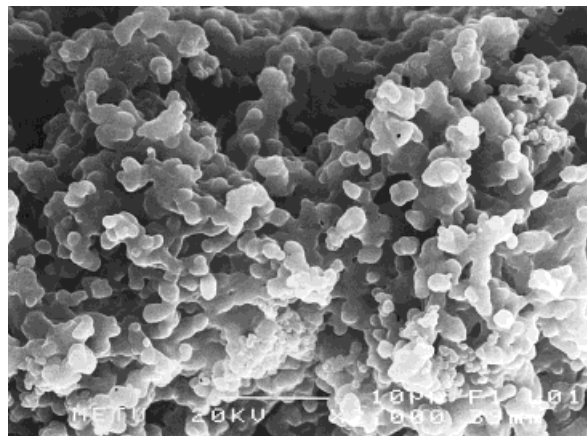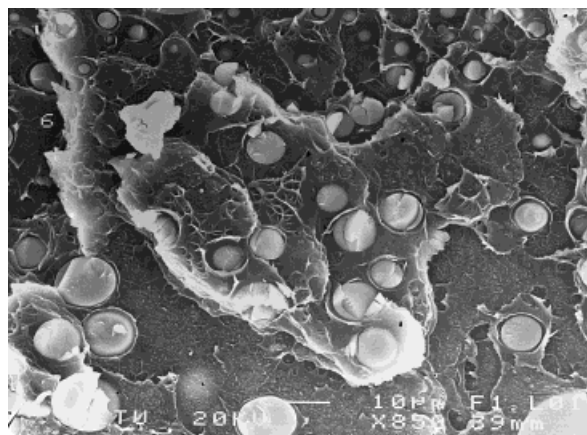

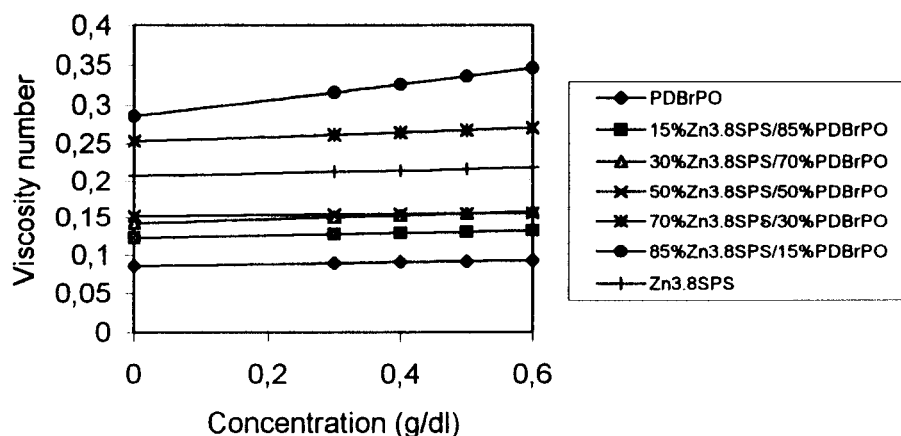**Figure 10** SEM photograph of 70%Mn3.8SPS/30%PDBrPO blend.

Mn3.8SPS/PDBrPO System

In Figure 8, viscosity number versus %composition relations for Mn3.8SPS/PDBrPO blends are given. Table III shows the miscibility parameters for these blends.

As seen from Table III, a part from α, Δ*b*, and μ parameters shows compatibility for 50, 70, and 85% Mn3.8SPS blends. However, α, as in the case of 4.8SPS/PDBrPO system, shows inconsistency for 15 and 50% Mn3.8SPS blends. The system shows saturation at 50% composition and increasing PDBrPO composition acts as a second phase in the blend. This fact is reflected in Figure 9, where T_g versus %compositions for Mn3.8SPS/PDBrPO blends are given. The phase separations for 15 and 30% Mn3.8SPS/PDBrPO blends are observable from the two T_g values which confirm

Figure 11 SEM photograph of 15%Mn3.8SPS/85%PDBrPO blend.

Figure 12   Viscosity number versus concentration relationship for Zn3.8SPS/PDBrPO system.

the results reflected in Table III. The upper T_g's correspond to the pure PDBrPO in the blends, whereas the lower T_g values correspond to 15 and 30% Mn3.8SPS/PDBrPO blends. The decrease in the T_g values as the percentage of Mn3.8SPS is increased in the blend shows a larger amount of PDBrPO solubility in Mn3.8SPS.

SEM photographs for 70%Mn3.8SPS/30%PD-BrPO and 15%Mn3.8SPS/85%PDBrPO blends are given in Figures 10 and 11, respectively. Small domains are observed in Figure 11 and this structure is considered the microphase structure in which domains are formed by ion aggregated in the homogeneous polymer matrix. In Figure 10, such phase separation is not observable.

The two-phase behavior of 15 and 30% Mn3.8SPS/PDBrPO blends also agree with their miscibility parameters in Table III. Single T_g values for 50, 70, and 85%Mn3.8SPS/PDBrPO blends and their miscibility parameters confirm the miscibility of these blends. The decrease in T_g values for single-phase blends reflects the fact that the miscibility of PDBrPO is increased with increasing Mn3.8SPS amount in the blend.

Mn is a transition metal, has +2 charge on its ion, and is larger in radius when compared to Na. As a result, binding chemistry of the Mn^{2+} ion is quite different from that of the Na^+ ion. Ion associations in Mn^{2+} ionomer are weaker, make smaller aggregates or disperse more ionic groups into the polymer matrix and are expected to accommodate more PDBrPO in its matrix.
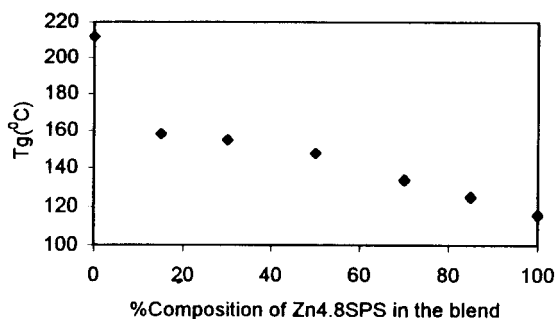
Zn3.8SPS/PDBrPO System

Viscosity number versus %composition relations for Zn3.8SPS/PDBrPO blends are given in Figure 12; the miscibility parameters for Zn3.8SPS/PD-BrPO blends with varying compositions are tabulated in Table IV. As seen from Δb and μ values again, all compositions for this system are miscible, but α values show inconsistency with this conclusion.

T_g versus %composition of Zn3.8SPS blends are shown in Figure 13. All the samples have single T_g values agreeing with the data in Table IV and confirm that Zn^{2+} ionomers of SPS are highly miscible with PPO in all proportions.[19-21]

Table IV   Viscometric Data for Zn3.8SPS/PDBrPO System in THF at 25°C

| Wt % Zn3.8SPS	$[\eta]$ (dL g^{-1})	b (dl^2 g^{-2})	Δb	μ	α
0.00	0.086	0.0119	—	—	—
0.15	0.122	0.0170	0.020	1.320	−0.037
0.30	0.142	0.0272	0.014	0.935	0.432
0.50	0.152	0.0078	0.020	1.350	−0.362
0.70	0.254	0.0270	0.158	1.070×10	−0.140
0.85	0.286	0.1000	0.311	2.100×10	0.734
1.00	0.208	0.0186	—	—	—

Figure 13 Summary of DSC results for Zn3.8SPS/PDBrPO system.

85%Zn3.8SPS/15%PDBrPO SEM showing single phase is given in Figure 14.

Single phase for Zn ionomer blends is expected by the more covalent bonding nature of Zn^{2+} ion when compared to Na^+ and Mn^{2+} ions.[21] The miscibility of the Zn3.8SPS ionomer with PDBrPO can be partly attributed to the dissolution of some of the Zn sulfonate groups into the PS matrix; this reduces the amount of cluster material in the ionomer and hence allows increased interactions between PS segments and the PDBrPO chains.[6] It was shown by many researchers that neutralization with Zn^{2+} consistently produces lower melt viscosity in ionomers when compared to neutralization with alkali metals. Ionomers having elastomeric matrices also exhibit greater creep when neutralized with Zn^{2+}. Finally, Zn^{2+} ionomers exhibit a notable decrease in phase separation at elevated temperatures.[19] These observations were explained by the more covalent bonding nature of Zn^{2+} relative to alkali metals, resulting in a lessened enthalpy of asso-
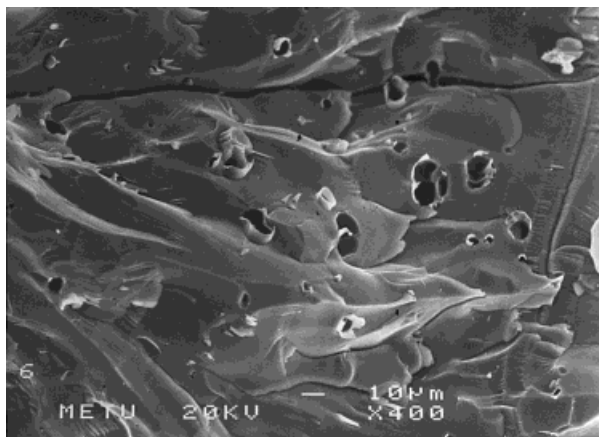
Figure 14 SEM photograph for 85%Zn3.8SPS/15%PDBrPO system.
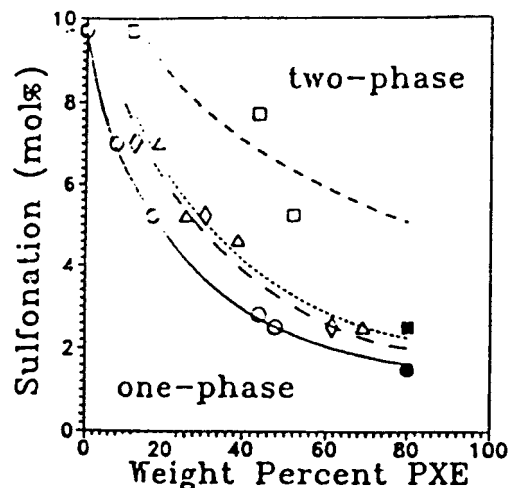
Figure 15 Phase diagram for SPS/PXE blends.

ciation between Zn^{2+} salts. As a result, the energy penalty involved in dispersing a Zn^{2+} group in the matrix is less than the comparable penalty for a Na^+ group, which accelerates the ion-hopping process by which ionomers flow. Consequently, if this energy penalty is larger for Na^+ than Zn^{2+}, miscibility is favored in the Zn^{2+} case and immiscibility is favored for the Na^+ case.

CONCLUSION

Several factors must be taken into account to analyze the miscibility behavior of PDBrPO with random polystyrene-based ionomers. Hydrogen bonding, dipole–dipole, and ion–dipole interactions are frequently observed to enhance miscibility. Sizes and strengths of the ion associations also affect the polymer ionomer miscibility. However, the most important factor is the binding chemistry of the cation.

In this work, it is experimentally shown that Zn3.8SPS is miscible with all compositions when blended with PDBrPO. Mn3.8SPS and 4.8SPS are intermediate and show miscibility to some extent, whereas Na1.7SPS is completely immiscible with PDBrPO. These results agree to a certain extent with Tomita and Register's results[7] shown in Figure 15. In their study, the miscibility of polystyrene-based ionomers with poly(2,6-dimethyl-1,4-phenylene oxide) is investigated. Even though the polymer of our work is PDBrPO and the methods of determination of miscibility are different, the results are consistent to a certain extent. In their work, NaSPS shows one phase below the sulfon-

ation percentage of 1.8. However, we could not detect miscibility with Na1.7SPS, which may be due to large bromine atoms on 2,6 positions of the polyphenylene oxide. MnSPS shows miscibility for 15, 30, and 50% poly(phenylene oxide) blends being in the one-phase region and immiscibility for 70 and 85% PPO, which fall to the two-phase region. Zn3.8SPS is in the one-phase region for all compositions. Unfortunately, they have no data for acid SPS to compare with the results of this work.

REFERENCES

1. Vukovic, R.; Zvanic, M.; Bogdanic, G.; Karasz, F. E.; MacKnight, W. J. Polymer 1993, 34, 1449.
2. Hseish, D. T.; Peiffer, D. G. Polymer 1992, 33, 1210.
3. Brinke, G.; Karasz, F. E.; MacKnight, W. J. Macromolecules 1983, 16, 1827.
4. Vukovic, R.; Bogdanic, G.; Kurusevic, V.; Srica, V.; Karasz, F. E.; MacKnight, W. J. J Appl Polym Sci 1994, 52, 1499.
5. Vukovic, R.; Bogdanic, G.; Kurusevic, V.; Segudovic, N.; Karasz, F. E.; MacKnight, W. J. Polymer 1994, 35, 3055.
6. Bazuin, C. G.; Rancourt, L.; Villeneuve, S.; Soldera, A. J Polym Sci, Part B: Polym Phys 1993, 31, 1431.
7. Tomita, H.; Register, R. A. Macromolecules 1993, 26, 2796.
8. Goh, S. H.; Lee, S. Y. Eur Polym J 1989, 25, 571.
9. Kambour, R. P.; Bendler, J. T.; Bopp, R. C. Macromolecules 1983, 16, 753.
10. Eisenberg, A.; Hara, M. Polym Eng Sci 1984, 24, 1306; Hara M, Eisenberg, A. Macromolecules 1987, 20, 2160.
11. Natansohn, A.; Murali, R.; Eisenberg, A. Macromol Chem Macromol Symp 1988, 16, 175.
12. Krigbaum, W. R.; Wall, F. J. J Polym Sci 1950, 5, 505.
13. Huggins, M. L. J Am Chem Soc 1942, 64, 2716.
14. Williamson, G. R.; Wright, B. J Polym Sci 1965, A3, 3885.
15. Lizymol, P. P.; Thomas, J. J Appl Polym Sci 1994, 51, 635.
16. Chee, K. K. Eur Polym J 1990, 4, 423.
17. Sun, Z.; Wang, W.; Feng, Z. Eur Polym J 1992, 28, 1259.
18. Kısakürek, D. Polym Mat Encycl 1996, 8, 5731.
19. Register, R. A.; Bell, T. R. J Polym Sci, Part B: Polym Phys 1992, 30, 569.
20. Kambour, R. P.; Gundlach, P. E.; Wang, C. W.; White, D. M.; Yeager, G. W. Polymer Commun 1988, 29, 170.
21. Bagrodia, S.; Wikes, G. C.; Kennedy, J. P. Polym Eng Sci 1986, 26, 662.