Solid-State NMR Analysis of Blends of Nylon 6 and Zinc Salts of Sulfonated Polystyrene Ionomers

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ABSTRACT: Solid-state NMR was used to establish the specific intermolecular interactions responsible for the miscibility of blends of nylon 6 (PA6) and the zinc salt of lightly sulfonated polystyrene (Zn-SPS) and to characterize the scale of molecular mixing. ^{13}C CP/MAS spectroscopy identified the interpolymer interaction as a complex between the Zn^{2+} cation of the ionomer and the amide nitrogen. Measurements of the ^1H spin–lattice relaxation times, T_1^H and $T_{1\rho}^H$, indicated that mixing of the two polymers in the amorphous phase occurred at least down to a size scale of 2 nm. $T_{1\rho}^H$ measurements also revealed a microphase of >2.5–3.5 nm in the neat ionomer, which is consistent with the size of ionic domains inferred from previous small-angle X-ray (SAXS) measurements. Adding PA6 to Zn-SPS reduced the microheterogeneity in the ionomer as measured by $T_{1\rho}$.

Introduction

The use of ionomers in polymer blends to promote mixing or compatibilization has been demonstrated in recent years to be very effective.[1,2] In particular, lightly sulfonated polystyrene ionomers (SPS) have been used effectively in a variety of blends, and specific interactions between the metal sulfonate groups and polar functional groups on another polymer have resulted in miscible blends of SPS with polyamines,[3] polyethers,[4] polycarbonates,[5] polypeptides,[6] and polyamides[7,8] as well as with a variety of copolymers containing a suitable functionalized monomer.[9]

A number of papers concerning blends of SPS and flexible polyamides, specifically nylon 6, have recently been published. The interest in this system is due in part to the fact that polystyrene and nylon 6 (PA6) are important commercial polymers but also because of the richness of specific physical interactions that arise in that particular blend. Previous work has shown that interactions between the metal sulfonate groups of SPS salts and the amide groups of the polyamide are sufficiently strong to promote miscibility. In an earlier paper,[11] we showed that the intensity of the specific interactions in M-SPS/PA6 blends, where M denotes the metal cation of the SPS salt, can be moderated by the choice of the cation, as well as the degree of sulfonation of the M-SPS.

Of the cations thus far studied by us and by others,[7,8,10,11] it appears that the strongest intermolecular interactions occur in M-SPS/PA6 blends when M = Li^+, Zn^{2+}, or a transition metal such as Mn^{2+}. For Li-SPS, FTIR spectroscopy showed that a specific ion–dipole interaction occurs between the Li^+ ion and the carbonyl oxygen of the amide group. This was expected since Li–amide complexes are well documented in the polyamide literature, especially for polyaramides. FTIR analysis, however, also suggested that for Mn–SPS and Zn-SPS, a stronger interaction occurred between the cation and the amide nitrogen.[7,10,11]

The purpose of the present paper is twofold: first, to report solid-state ^{13}C NMR confirmation of the assignment of a Zn–N interaction in Zn-SPS/PA6 blends and second, to report proton spin–lattice measurements, $T_{1\rho}^H$, that demonstrate molecular mixing of the blend components, at least on a scale of a few nanometers. With respect to the latter objective, several other recent solid-state NMR studies have probed the miscibility of poly(vinylpyridine) and zinc neutralized poly(ethylene-*co*-methacrylic acid),[12] hydrogen-bonded polymer complexes,[13] and charge-transfer complexes.[14] Also, of particular relevance to our investigation is a report of an NMR study by Gao et al.[15] for Li-SPS/PA6 blends that indicated when a sufficiently high sulfonation level was used, the blends were miscible down to a scale of at least 2 nm.

Experimental Section

Materials. Atactic polystyrene was obtained from the Dow Chemical Co., Styron 666, and had the following molecular weight averages as determined by gel permeation chromatography: M_n = 100000; M_w = 280000. Sulfonated polystyrenes (SPS) and their zinc salts (Zn-SPS) were prepared by the procedure described by Makowski et al.[16] The sulfonation reaction was carried out in dichloroethane at ca. 50 °C using acetyl sulfate as the sulfonating reagent. This particular reaction provides random substitution along the chain and predominantly at the para position on the phenyl ring. The sulfonation level (mole percent of styrene rings sulfonated) was determined by titration of the free acid derivative (H-SPS) in a toluene/methanol (90/10, v/v) mixed solvent with methanolic sodium hydroxide. Three sulfonation levels were prepared: 11.5, 22, and 60 mol %. Fully neutralized ionomers were prepared by titrating H-SPS with a 20% excess of zinc acetate dihydrate in a toluene/methanol mixed solvent. The neutralized polymers were precipitated in a large excess of ethanol, filtered, washed several times with ethanol, and dried under vacuum at 70 °C for 1 week. The nomenclature used for the ionomer salts is *x*.*y*Zn-SPS, where *x*.*y* denotes the sulfonation level.

Nylon 6 (PA6) with M_w = 24000 was obtained from Polysciences, Inc. Blends of PA6 and Zn-SPS were prepared by adding a solution of the polyamide in *m*-cresol dropwise to a stirred solution of Zn-SPS in *m*-cresol/dimethylformamide (60/40, v/v). The blend solution was then added dropwise to excess ethyl ether, and the precipitate was filtered and dried under vacuum for 1 week at 100 °C. The blends were melt pressed at 240 °C and quenched to room temperature to minimize the crystallinity of the samples.

A methylated polyamide oligomer (m-PA), poly(*N*,*N*′-dimethylenediamine sebacamide), was prepared by reacting a 4 wt %

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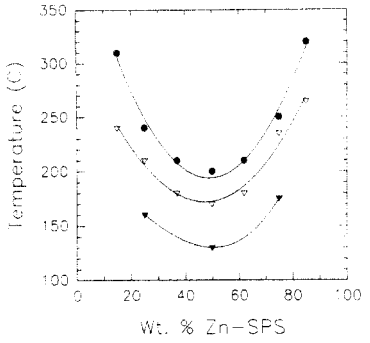

Figure 1. Liquid–liquid phase diagrams for *x.y*Zn-SPS and PA6 blends: *x.y* = (▼) 6.5; (▽) 8.1; (●) 9.0.

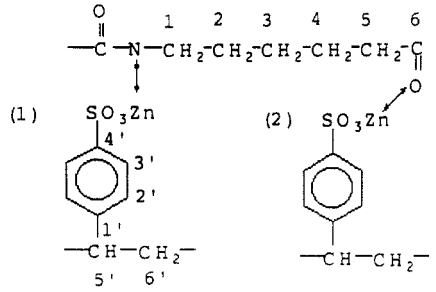

Figure 2. Two possible Zn^{2+}–amide complexes for intermolecular interactions between Zn-SPS and PA6. The numbers identify the specific carbon atoms referred to in the discussion of the NMR results in the text.

solution of *N,N'*-dimethylethylenediamine in tetrachloroethane containing 150% pyridine at ca. −15 °C with a 10% molar excess of sebacoyl chloride. The details of the synthesis were described elsewhere.[17] The degree of polymerization was estimated from elemental analysis to be ca. 14. Blends of m-PA and 11.5Zn-SPS were prepared by mixing solutions of each polymer in dimethyl sulfoxide, adding the blend solution dropwise to excess ethyl ether, filtering the precipitate, and drying the blend under vacuum. Although the m-PA was crystallizable, the crystallization kinetics were very slow, and for the thermal histories used to prepare samples in this study, no crystallinity was detected by differential scanning calorimetry for the pure m-PA or the blends.

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{13}C CP/MAS NMR measurements were made with a GN 300 spectrometer equipped with a Chemagnetics solid probe. Resonance frequencies for ^{1}H and ^{13}C were 300 and 75 MHz, respectively. The radio-frequency field strength was 42.7 kHz. ^{13}C NMR spectra at room temperature were used to characterize the nature of the intermolecular interactions between PA6 and Zn-SPS. Proton spin–lattice relaxation times in the rotating frame and laboratory frame, $T_{1\rho}$ and T_1, were measured with spin lock and inversion–recovery pulse sequences, respectively.

Results and Discussion

^{13}C CP/MAS Spectra and Specific Interactions. Zn-SPS and PA6 blends exhibit lower critical solution temperature (LCST) behavior as shown in Figure 1. Those curves were constructed from DSC data obtained on samples quenched from different annealing temperatures. The points in Figure 1 correspond to the temperature below which a single T_g (i.e., one phase) was observed and above which two T_gs (i.e., two phases) were observed. The temperature of the coexistence curve was a strong function of the sulfonation level, and miscibility in this system is believed to be due to the formation of a complex between the zinc cation and the amide group. Two different complexation sites are plausible: (1) Zn^{2+} with the amide nitrogen and (2) Zn^{2+} with the carbonyl oxygen (Figure 2). Infrared spectroscopy analyses[11] suggested that the first mechanism is the dominant one, but the results were not entirely conclusive.

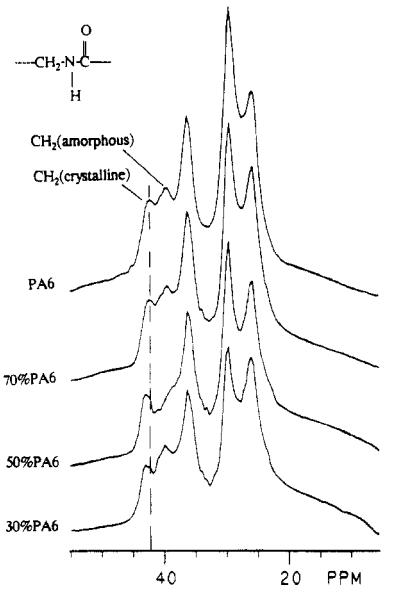

Figure 3. ^{13}C NMR difference spectra ($[NMR]_{blend} - [NMR]_{11.5Zn\text{-}SPS}$) for 11.5Zn-SPS/PA6 blends.

Table I. Assignments of the Chemical Shifts for ^{13}C NMR Spectra of Zn-SPS/PA6 Blends

	chemical shift (ppm)							
	172	145	127	42	39	36	29	26
PA6	C6			C1		C5	C2,3	C4
Zn-SPS		C1′	C2′,3′		C5′			

^{13}C NMR provides an unambiguous resolution of the nature of the Zn^{2+}–amide complex. On the one hand, if the zinc cation complexes with the nitrogen atom, the C=O and CH_2 next to the nitrogen (C1 in Figure 2) should exhibit downfield chemical shifts; on the other hand, only the carbonyl carbon should be affected if the zinc cation complexes with the carbonyl oxygen. The assignments of the chemical shifts for PA6 and 11.5Zn-SPS are given in Table I; the assignments were based on ^{13}C spectra of the blends (not shown) and published data from other laboratories.[18,19] Figure 3 shows the ^{13}C NMR difference spectra $[NMR]_{blend} - [NMR]_{11.5Zn\text{-}SPS}$ for blends of PA6 and 11.5Zn-SPS as a function of the composition. The difference spectra were used because the chemical shifts of the CH_2 carbons for the polyamide overlapped with those of the backbone carbons for the ionomer. The spectra in Figure 3 show only the chemical shifts for the polyamide carbons and any changes that occurred in the resonances for the two polymers that result from intermolecular interactions.

The key features of interest in Figure 3 are the peaks at 39.9 and 42 ppm in the neat PA6 that correspond to the C1 carbon in the amorphous and crystalline phases, respectively. A subtle, though significant change in that region of the NMR spectrum occurred when 11.5Zn-SPS was added to the PA6. The 39.9 ppm chemical shift was unperturbed, but the 42 ppm peak moved to ca. 42.8 ppm in the blend containing 70% Zn-SPS. Although the 42.8 ppm chemical shift was close to that for the C1 carbon in the crystalline phase of PA6, previous calorimetry studies[11] indicated that these blends were completely amorphous above a composition of ca. 40% Zn-SPS. As a result, the 42.8 ppm chemical shift in the blends cannot be due to a resonance in a crystalline phase. An alternative explanation is that peak represents ca. a 3 ppm downfield shift of the C1 resonance in the amorphous phase, which is

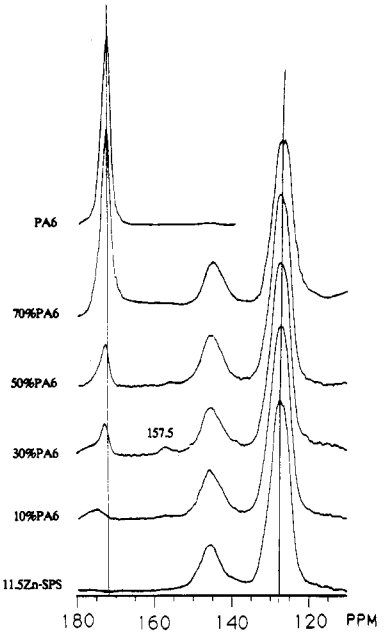

Figure 4. ^{13}C NMR spectra for 11.5Zn-SPS/PA6 blends.

consistent with the first complexation mechanism proposed above—that is, a Zn–N complex.

Figure 4 shows that the addition of 11.5Zn-SPS to PA6 also shifted the carbonyl carbon peak downfield from the 172 ppm resonance for the neat PA6; e.g., for the blend containing 90% Zn-SPS, this resonance shifted to 175 ppm. A downfield shift is expected for any interaction of the Zn ionomer with either the amide nitrogen or carbonyl oxygen, but FTIR results do not support the latter interaction. Taken together with the shift of the carbon in the CH_2 group next to the nitrogen, as discussed in the above paragraph, the downfield shift of the carbonyl carbon supports the assignment of the specific intermolecular interaction to a Zn–N complex.

NMR measurements for blends of 11.5Zn-SPS with a methylated polyamide, m-PA, were carried out to further substantiate the formation of a N–Zn complex. In this case, because of the strong deshielding effect of a N–Zn complex, interaction of the Zn-SPS with the amide nitrogen should affect the *three* carbon atoms attached to the nitrogen: (1) the carbonyl carbon, (2) the methylene carbon on the backbone, and (3) the methyl carbon (see Figure 5). If the Zn^{2+} complexes with the oxygen of the carbonyl, only the resonance of the carbonyl carbon is expected to be affected. Since the m-PA was amorphous, complications due to crystallinity in analyzing the PA6/ZnSPS blends were avoided. Figure 5 shows that the CH_3 peak at 44.0 ppm and the CH_2 peak at 35.4 ppm for the neat m-PA shift downfield ca. 3 and 4 ppm, respectively, for a blend containing 80% 11.5Zn-SPS. The CH_3 resonance was also noticeably broadened, which suggests a decrease in the mobility of the methyl group occurred as a result of the interpolymer complexation.

The effects of the formation of an ionomer–polyamide complex on the resonance of the phenylene carbons of the Zn-SPS are shown in Figures 6 and 7. Figure 6 shows the NMR spectra of the phenylene carbon region for ZnSPS ionomers with three different sulfonation levels: 11.5, 22, and 60 mol %. The resonances at 145 ppm due to the phenylene carbon attached to the polystyrene backbone, i.e., position C1′ (note that the prime denotes a carbon on the styrene ring; cf. Figure 2), and at 140 ppm due to the sulfonated carbon at the para position of the ring, position C4′, were resolved. The intensity of the latter resonance increased with increasing degree of sulfonation.

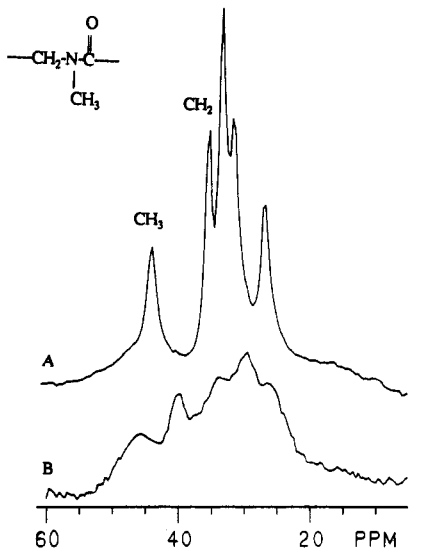

Figure 5. (A) ^{13}C NMR spectrum for m-PA and (B) difference spectrum for a blend of 80% (wt) 11.5Zn-SPS/20% m-PA minus the spectrum of 11.5Zn-SPS.

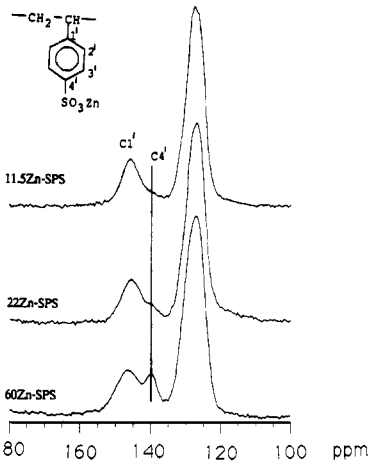

Figure 6. ^{13}C NMR spectra of the phenylene carbon region for Zn-SPS ionomers.

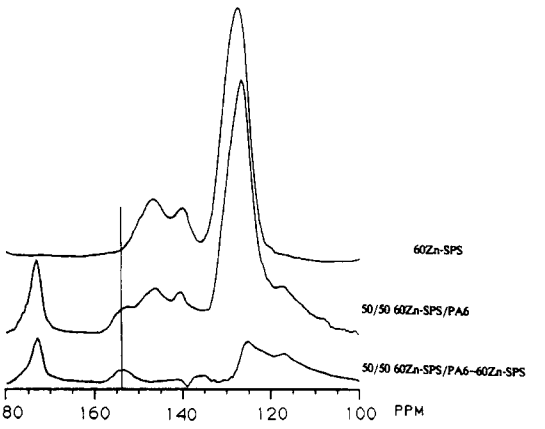

Figure 7. ^{13}C NMR spectra of 60Zn-SPS, a 50/50 blend of 60Zn-SPS and PA6, and the difference spectrum $[NMR]_{blend} - [NMR]_{60Zn\text{-}SPS}$.

Figure 7 shows the spectra of 60Zn-SPS, a 50/50 blend of 60Zn-SPS and PA6, and the difference spectrum $[NMR]_{blend} - [NMR]_{60Zn\text{-}SPS}$. Since PA6 exhibited no resonances in this region, the difference spectrum displays only changes in the resonances of the SPS phenylene carbons due to complexation. The results of forming the blend were a shift to higher field of the intense resonance at ca. 127 ppm for C2′ and C3′ of the Zn-SPS and the

development of two new resonances at 117 and 154 ppm. For this particular blend, the Zn:N ratio was 1.1:1—that is, there was an excess of Zn sulfonate groups, assuming a 1:1 complex. Accordingly, the difference NMR spectrum showed five different phenylene carbon peaks, corresponding to unsubstituted carbons on the styrene ring (C2′ and C3′ (~127 and 117 ppm)), the carbon attached to the polystyrene backbone (C1′ (145 ppm)), sulfonated carbon atoms (C4′) that participated in the interpolymer complex (154 ppm), and C4′ atoms that did not participate in the interpolymer complex (~137 ppm).

The new, weak resonance at 154 ppm resulting from the phenylene carbon bonded to the sulfonate groups that were complexed with the amide N emerged at the expense of the 140 ppm peak in the neat Zn-SPS. As shown in the difference spectrum in Figure 7, the latter resonance shifted to slightly lower field as a result of the complexation of the ionomer with PA6. That result may be explained by a deshielding of these carbon atoms due to breakup of the microphase-separated, ionic aggregate structure usually observed in ionomers. The disruption of the ionic aggregate structure was due to solvation of the sulfonate dipole interactions by the polyamide, which was evident from the disappearance of the small-angle X-ray scattering peak normally observed with ionomers.[11]

Although solution NMR spectra of Zn-SPS (not shown) resolved separate resonances for the ortho (i.e., C2′) and meta (C3′) phenylene carbons of Zn-SPS, these resonances were consolidated into a single peak at 127 ppm in the solid-state spectra; see Figures 6 and 7. For the blend, however, two peaks are resolved, which are most easily seen in the difference spectrum at ~126 and 117 ppm. The splitting may arise from preferential shielding of the meta carbons by the Zn–N interaction, which shifts the resonance to 117 ppm, according to the shielding–deshielding alternative rule for carbons on the ring.[20]

Changes in the solid-state spectra similar to those described above for the blends involving 60Zn-SPS were also observed for 11.5Zn-SPS/PA6 blends. A small peak was seen at 156 ppm for a 70/30 Zn-SPS/PA6 blend, and a very shallow peak was observed in the 90/10 blend spectrum; see Figure 4. The intensity changes with changing composition were in line with the cross-polarization of the protons and carbon atoms, since there are more protons in the environment of the styrene ring when the PA6 concentration was increased. This is moderated, however, by the concurrent decrease of Zn sulfonate groups as the PA6 content increases, and above 50 wt % PA6, no peak was observed, presumably because there were too few sulfonate groups to provide a resolvable resonance.

T_1^H and $T_{1\rho}^H$ Relaxation Times. As discussed above, ^{13}C CP/MAS spectra identified the nature of the specific interactions that occurred in the Zn-SPS/PA6 blends. Further information about the strength of the specific interactions and phase behaviors of the Zn-SPS/PA6 blends can be obtained by studying nuclear relaxation times, which are associated with the motion of the polymer chain and molecular proximity of the different polymers in the blends. The experimental values of T_1^H and $T_{1\rho}^H$ for the 11.5Zn-SPS/PA6 blends are summarized in Table II.

Although both component polymers are known to be two-phase systems, as a result of crystallization in the PA6 and ionic aggregation in the neat 11.5Zn-SPS, only a single T_1^H was observed for each; see Table II. This result indicates that the sizes of the dispersed phases, the PA6 crystallites in the PA6 and the ionic aggregate in 11.5Zn-SPS, were smaller than the size scale probed by T_1^H, ca. 20–30 nm, and the relaxation rate was averaged by the spin-diffusion coupling between two phases.[21] Similarly, a single T_1^H was obtained for each 11.5Zn-SPS/PA6 blend, though the value varied with composition.

Table II. T_1^H and $T_{1\rho}^H$ Values for 11.5Zn-SPS/PA6 Blends

samples		11.5Zn-SPS (127 ppm)		PA6 (172 ppm)	
% (wt) 11.5Zn-SPS	% (wt) PA6	T_1^H (s)	$T_{1\rho}^H$ (ms)	T_1^H (s)	$T_{1\rho}^H$ (ms)
100	0	1.14	5.57 (0.84)[a] 21.7 (0.16)[a]		
90	10	0.244	5.49		
70	30	0.423	5.38	0.437	5.41
50	50	0.568	5.32	0.634	5.37 (0.86)[a] 19.6 (0.14)
30	70	0.584	5.28	0.644	5.30 (0.79)[a] 20.9 (0.21)[a]
0	100			1.191	5.21 (0.65)[a] 20.5 (0.35)[a]

[a] Weight fraction of the corresponding $T_{1\rho}^H$ component.

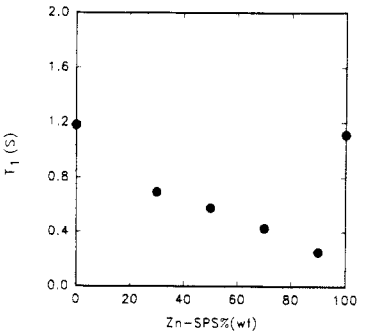

Figure 8. T_1^H vs composition for 11.5Zn-SPS/PA6 blends.

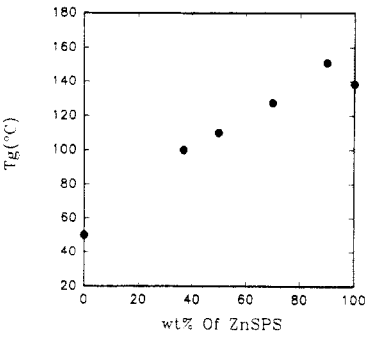

Figure 9. Glass transition temperature vs composition for 11.5Zn-SPS/PA6 blends.

T_1^H is plotted against the blend composition in Figure 8. The T_1^H values exhibited negative deviation from a weighted average of the two components and a minimum T_1^H occurred at a composition of 90% (wt) Zn-SPS. The negative deviation of the T_1^H reflects decreased mobility or decreased molecular separation of the two polymers as a result of the strong Zn–N complexation in the blends. Similar relaxation behavior was observed for other blends in the presence of strong specific interactions, i.e., hydrogen-bonding complexes[13] and charge-transfer complexes.[14] The minimum in T_1^H in Figure 8 corresponds to a molar stoichiometry of 1:1 for the Zn–N complex. The blend glass transition, T_g, also displayed a maximum at the same composition (see Figure 9), which further supports the conclusion of a 1:1 stoichiometry. A 1:1 Zn:N complex rather than 1:2 probably resulted because one coordination site of the cation was already occupied by the sulfonate group. A similar stoichiometry was observed by Peiffer et al.[22] for complexes involving zinc-neutralized sulfonated EPDM and poly(*r*-styrene-*co*-*r*-4-vinylpyridine).

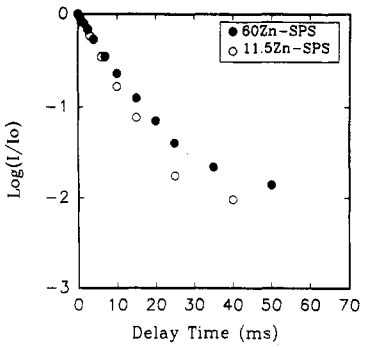

Figure 10. Logarithm of normalized resonance intensity at 127 ppm vs delay time for (●) 60Zn-SPS and (○) 11.5Zn-SPS.

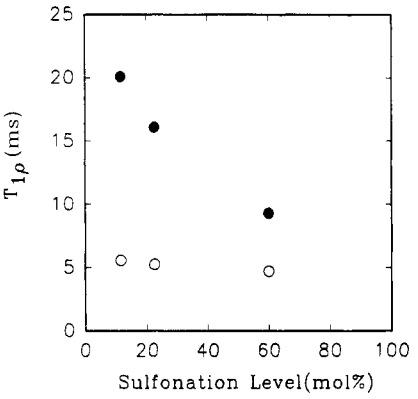

Figure 11. $T_{1\rho}^{H}$ vs sulfonation level for Zn-SPS.

The phase structure on a smaller scale, ca. 2–3 nm, can be characterized by measuring $T_{1\rho}^{H}$. An important characteristic of ionomers like Zn-SPS is microphase separation of ion-rich aggregates, as evident by a SAXS peak[23,24] corresponding to a characteristic dimension of ca. 2–5 nm. Figure 10 plots the intensity of the NMR resonance at 127 ppm versus CP contact time for the neat 60Zn-SPS ionomers. The relaxation data were best described by a double-exponential decay, and the calculated $T_{1\rho}^{H}$ values are tabulated in Table II. The double-exponential decay indicates a two-phase morphology. The shorter $T_{1\rho}^{H}$, 5.6 ms, was similar to the $T_{1\rho}^{H}$ value of PS, 5.4 ms and, therefore, was assigned to an ion-poor phase in the ionomer. The longer $T_{1\rho}^{H}$, 21.7 ms, was assigned to an ion-rich microphase, based on the current understanding of the structure of ionomers. Moreover, the double-exponential decay became more prevalant at higher sulfonation level, which suggests as one might expect, that the fraction of the ion-rich phase increased with increasing sulfonation level.

The variation of the $T_{1\rho}^{H}$ values with sulfonation level is shown in Figure 11. The $T_{1\rho}^{H}$ value for the ion-rich phase decreased as the sulfonation level increased, but the $T_{1\rho}^{H}$ value for the ion-poor phase was relatively insensitive to sulfonation level. The maximum diffusive path length L of a spin, corresponding to the minimum phase size that is detectable by $T_{1\rho}^{H}$, can be estimated from the formula[21]

$$L = (6DT_{1\rho}^{H})^{1/2} \quad (1)$$

where D is a spin diffusion coefficient, typically 10^{-12} cm^2/s. On the basis of the measured $T_{1\rho}^{H}$ values and eq 1, the size of the ionic domains is larger than 3.4 nm for 11.5Zn-SPS, 3.0 nm for 22Zn-SPS, and 2.5 nm for 60Zn-SPS. That size scale corresponds well with the dimension calculated from the SAXS peak, which for Zn-SPS is ca. 3–4 nm.

When 10% or more of PA6 was added to the 11.5Zn-SPS, the longer $T_{1\rho}^{H}$ component was no longer observed

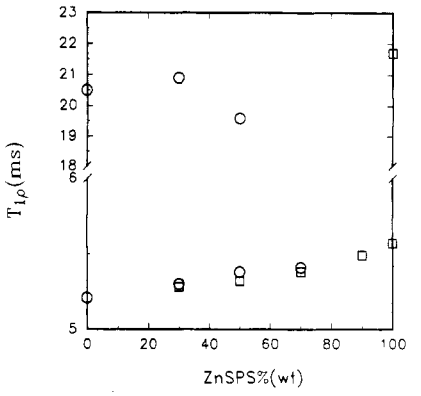

Figure 12. $T_{1\rho}^{H}$ vs composition for 11.5Zn-SPS/PA6 blends: (○) calculated from the 172 ppm peak for PA6; (□) calculated from the 127 ppm peak for Zn-SPS.

(see Figure 12), which indicates that the size of the ionic aggregates, if they still existed, in the blends was less than 1.75 nm. We reported in a previous paper[12] that addition of 10% (wt) PA6 to Zn-SPS reduced the intensity of the SAXS peak and shifted it to lower angle. Although the SAXS peak and the changes upon blending reflect the ionic microstructure, the interpretation of the SAXS is model dependent and is an unresolved issue in the field of ionomers. Two general classes of microstructural models, *intra*particle interference and *inter*particle interference models, have been proposed to explain the SAXS data of ionomers.[25] On the one hand, on the basis of the latter interpretation, the shift of the SAXS peak to lower angle when PA6 was added to Zn-SPS indicates an increased separation of the aggregates. On the other hand, the intraparticle model suggests an increased size of the aggregates swollen by the PA6. The $T_{1\rho}^{H}$ data, however, exclude the possibility of an increased aggregate size and seem to support the interparticle interference interpretation. An increased distance between ionic aggregates is consistent with a decrease in the concentration of aggregates, which may result from solvation of the zinc sulfonate dipole–dipole interactions by the polyamide.

When the PA6 content of the blends with 11.5Zn-SPS was increased to >50%, the PA6 component partially crystallized as determined by DSC. In that case, a second $T_{1\rho}^{H}$ ~20 ms resulted from the crystalline PA6 phase (Figure 12). The weighting factors for the two exponentials used in the fits of the relaxation data are also given in Table II. The decrease in the weight fraction of the long-time component for the PA6 in the blend with increasing ionomer concentration is consistent with the decrease of the crystallinity of the PA6 in the blend.[11] The shorter $T_{1\rho}^{H}$ exhibited a monotonic composition dependence, and the values calculated from the 127 ppm peak of the ionomer and the 172 ppm peak of PA6 were the same within experimental error. That result indicates that the Zn-SPS and the amorphous PA6 phase were miscible down to at least a molecular scale of 1.7 nm.

Conclusions

The nature of the specific interactions and the phase behavior of Zn-SPS/PA6 blends were investigated by solid-state NMR as functions of the sulfonation level and composition. The specific interactions responsible for enhancing the miscibility of PA6 and Zn-SPS were confirmed by ^{13}C CP/MAS spectroscopy analyses to occur between the amide nitrogen and the zinc cation. This was evident from the downfield changes in the chemical shifts of the two carbon atoms adjacent to the amide nitrogen and a new peak at ca. 154 ppm that was due to the

phenylene carbon attached to the sulfonate group participating in the Zn–N complex. Further evidence for the zinc–nitrogen complexation was obtained from the ^{13}C CP/MAS spectra of blends of an N-methylated polyamide and Zn-SPS. In that case, all three carbon atoms adjacent to the amide nitrogen were affected by the formation of the Zn-SPS–PA6 complex.

The microscopic structure of the 11.5Zn-SPS/PA6 blends was characterized by measuring the ^1H spin–lattice relaxation times in the laboratory frame, T_1^H, and in the rotating frame, $T_{1\rho}^H$. T_1^H for the blends showed a large negative deviation from the compositionally weighted average and exhibited a minimum at a composition corresponding to a molar stoichiometry of 1:1 Zn^{2+}:N. $T_{1\rho}^H$ indicated that a microphase-separated phase (presumably ionic aggregates) of >3.4 nm existed in the neat 11.5Zn-SPS, and the size of that phase diminished when PA6 was added. That result indicated that the ionic aggregates were effectively solvated by the PA6. With the addition of 10% (wt) PA6, the $T_{1\rho}^H$ component corresponding to the ionic microphase was no longer detected, which indicated that the ionic aggregate, if present, was no more than 1.7 nm in size. The $T_{1\rho}^H$ corresponding to the ion-poor phase in neat Zn-SPS varied monotonically with composition in the 11.5Zn-SPS/PA6 blends, which indicated that the amorphous phases of the two polymers were miscible, at least down to a size of ca. 1.7 nm.

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