Compatibilization of Polymer Blends by Complexation. 1. Spectroscopic Characterization of Ion−Amide Interactions in Ionomer/Polyamide Blends

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ABSTRACT: Electron paramagnetic resonance (EPR), Fourier transform infrared (FTIR), and solid-state ^{15}N nuclear magnetic resonance (^{15}N-NMR) spectroscopies were used to characterize the structure and relative strength of the interactions between metal sulfonate and amide groups in blends of lightly sulfonated polystyrene ionomers and an *N*-methylated polyamide, poly(*N*,*N*′-dimethylethylene sebacamide), and low molecular weight model complexes. The metal sulfonate groups, which aggregate in the neat ionomer, were dispersed by the polyamide in the blend as a consequence of a complexation that involved the sulfonate cation and both the carbonyl oxygen and the amide nitrogen of the polyamide. The FTIR and ^{15}N-NMR spectra were consistent with a $2p_z$ electron redistribution model for the complex, in which electrons migrate from the nitrogen to the metal ion through the carbonyl group. The sulfonate anion did not appear to particpate in the complex, but it remained in the vicinity of the metal cation. The strength of the ion−amide complex increased with increasing electron-withdrawing power of the cation in the order of $Zn^{2+} \approx Cu^{2+} > Mn^{2+} \geq Cd^{2+} > Li^{+}$.

Introduction

Compatibilization of polystyrene and polyamide blends by the introduction of a small amount of metal sulfonate groups into polystyrene has been studied in recent years by several laboratories.[1−9] The choice of the metal counterion significantly affects the phase behavior, presumably due to the difference in the relative strength of metal−amide interactions.[3,4] The strongest enhancement of miscibility occurs when a transition metal cation such as Mn^{2+} or Zn^{2+} is used. Among alkali-metal cations, lithium provides substantial improvement of miscibility, while sodium does not.[3−8]

Although it is accepted that enhancement of miscibility for blends of sulfonated polystyrene ionomers (SPS) with polyamides is due to interactions between the metal sulfonate and amide groups, the specific nature of those interactions and the differences between the various cations have not been well characterized. This paper describes the results of spectroscopic studies of the metal cation−amide interactions in blends of a number of metal salts of SPS with an *N*-methylated polyamide. Particular attention is directed at delineating the specific interactions that constitute the intermolecular complex and the effect of the metal cation on the relative strength of the complex.

Metal ion−amide complexation of low molecular weight compounds has been documented for a variety of metal salt adducts with secondary and tertiary amide compounds.[10] In most cases, the result of the complex was a red shift of the carbonyl absorption in the infrared (IR) spectrum, which was attributed to coordination of the metal with the carbonyl oxygen. In those studies, however, correlation between the type of metal and the strength of complexation was inconclusive, because the strength depends not only on the metal cation but also on the counteranion and the particular crystal structure of the complex.

Studies of metal ion−amide complexation of low molecular weight metal salts and polyamides have also been reported.[11−13] Dunn and Sansom[11] related stress cracking of nylon 6 treated with metal halides to structure changes of the polyamide that arose from its coordination with the metal salt. They classified the metals as "type I" and "type II" depending on the spectroscopic changes observed in salt−polyamide complexes and in low molecular weight model complexes. Type I metals were mainly transition metals, and type II were group 1A or 2A metals. Nylon 6 containing type I metal halides exhibited a characteristic new absorption band in the IR spectrum at about 1595 cm^{-1}, which was ascribed to a shift to lower frequency of the amide I absorption resulting from coordination of the metal ion with the carbonyl oxygen of the amide group. Although the new band at 1595 cm^{-1} was not observed in the spectra of nylon 6 containing type II metal halides, the amide I band did shift to slightly lower frequencies in those compounds.

FTIR and ^{13}C-NMR spectroscopies have been used to probe the specific interpolymer interactions between SPS ionomers and nylon 6.[1,2,4,8,14] Composition-dependent perturbations of the IR and NMR spectra were attributed to interactions of the metal sulfonate and amide groups. For a constant blend composition, the frequency shift of the amide II overtone IR vibration upon adding the ionomer to nylon 6 increased with varying cation in the order $H^{+} < Li^{+} < Zn^{2+}$, which indicates that the strength of the interaction also increased in the same order.[4] One question that has not been answered, however, is whether the interaction between SPS ionomers and polyamides involves a discrete structure or whether it simply represents a perturbation of the electronic environment of the two functional groups. That is, in the former case, one expects a characteristic frequency associated with a complex, while in the latter case, intermediate structures are possible which should produce a composition-dependent frequency for the interaction. Crystalline

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adducts of low molecular weight metal−amide complexes usually comprise a characteristic structure that depends on the specific compounds and crystal structure. One goal of the present study was to answer this question for SPS/polyamide blends by studying the IR absorbances associated with the metal sulfonate and amide groups. Another goal was to identify the specific nature of the interactions, i.e., at what site(s) do the metal ions complex with the amide group, and the relative strength of the complex for different cations.

When comparing the strengths of interaction for different metal ion−amide complexes, one needs to consider a couple of factors. First, low molecular weight metal−amide complexes usually form crystals, and the long-range structural regularity of a crystal requires every metal cation to form a fixed number of ligands coordinated to the amide groups. That may not be true for polymer−polymer complexes, because of steric hindrance due to the polymer chains and the lack of long-range order in the chain conformations. As a result, the electron density distributions in low molecular weight and high molecular weight complexes are likely to be very different, which diminishes the value of using low molecular weight model complexes for studying polymer blends.

Another factor to be considered in the SPS ionomer/polyamide blend is the complication that arises from hydrogen bonding between amide groups and between the amide hydrogen with the sulfonate group. For blends of nylon 6 and SPS ionomers, hydrogen bonding competes with complexation of the metal cation and the amide, and, therefore, the spectral changes that occur upon blending the two polymers cannot be unambiguously assigned to the metal ion−amide complex, especially when the strength of hydrogen bonding is comparable to that of the complex.

In the present investigation, hydrogen-bonding interactions were avoided by using an *N*-methylated nylon 2,10, i.e., poly(*N,N′*-dimethylethylene sebacamide), as a model polyamide. Substitution of the methyl group for the amide hydrogen prevents self-hydrogen bonding of the *N*-methylated polyamide, and as a result, the *N*-methylated nylon 2,10 had a relatively low melting point, $T_m = 75$ °C, and very slow crystallization kinetics.[15] Because there were no amide protons to form hydrogen bonds with the carbonyl groups of the nylon or with the sulfonate anion of the ionomer, the only possible interaction between the *N*-methylated nylon 2,10 and SPS was a metal−amide interaction. In addition, the low melting point and slow crystallization kinetics allowed the preparation of completely amorphous blends for FTIR spectroscopy, which avoided broadening of the absorption peaks due to a crystalline phase and allowed unambiguous analysis of the interaction strength.

In this paper, we present a spectroscopic characterization of the nature of the intermolecular complex formed between lightly sulfonated polystyrene ionomers and *N*-methylated nylon 2,10. We first discuss electron paramagnetic resonance (EPR) spectra that provide information on the local environment of the metal cation in the Cu^{2+} salt of the neat ionomer and the changes that occur upon blending the ionomer with the polyamide. We then discuss FTIR spectra that characterize the interactions of the sulfonate anion and the amide carbonyl group, and finally, we describe solid-state ^{15}N-NMR experiments that consider the effect of blending on the amide nitrogen.

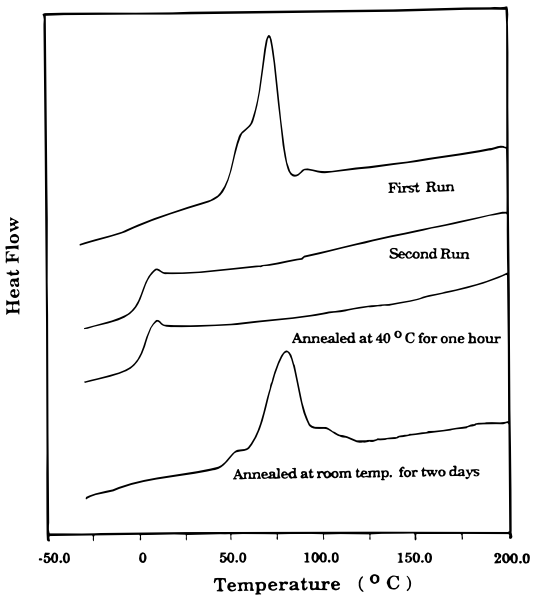


Figure 1. DSC heating thermograms for mPA following different thermal histories.

Experimental Details

Materials. Poly(*N,N′*-dimethylethylene sebacamide) was prepared by a nucleophilic acyl substitution reaction of sebacoyl chloride with *N,N′*-dimethylethylenediamine in a tetrachloroethane solution containing 150% pyridine.[15] The resulting polymer was washed first with water and then heptane. The number-average and weight-average molecular weights measured by gel permeation chromatography were 25 000 and 65 000, respectively, based on polystyrene standards. The *N*-methylated nylon 2,10 is hereafter referred to as mPA and has the following repeat structure:

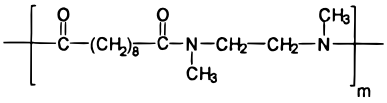


Figure 1 shows differential scanning calorimetry thermograms for the pure mPA following several thermal histories using a Perkin-Elmer DSC-7 at a heating rate of 20 °C/min. The first heating run of the as-prepared polymer shows a melting endotherm with a peak temperature of 70 °C. The second heating scan run immediately after cooling the sample from the first scan exhibits a glass transition at ca. 0 °C and no crystallization or melting. Even after this specimen was annealed at 40 °C for 1 h, no evidence of melting was observed in the subsequent DSC heating scan, which indicates that the mPA has very slow crystallization kinetics. Appreciable crystallinity did develop, however, when the polymer was annealed at room temperature for 2 days. This is evident from the reappearance of the melting endotherm at a slightly higher temperature, 75 °C, in the last DSC heating scan shown in Figure 1.

Lightly sulfonated polystyrene ionomers (SPS) were prepared by sulfonating a narrow molecular weight distribution polystyrene (Pressure Chemical Co.; $M_n = 4000$, $M_w/M_n = 1.06$) with acetyl sulfate in 1,2-dichloroethane (DCE) at 50 °C.[16] This particular reaction produces random substitution along the chain primarily at the *para* position on the phenyl ring. The sulfonation level was determined by titration of the free acid derivative, H-SPS, in a solvent mixture of 90% toluene/10% methanol. Lithium, zinc, copper, and cadmium salts were prepared by neutralizing the H-SPS in a toluene/methanol solution with a 20% excess of a methanol solution of the appropriate metal acetate. The ionomer salts were precipitated by steam stripping, filtered, washed with deionized water, and dried under vacuum. The ionomer nomenclature used in this paper is M-SPS, where M denotes the metal cation.

Salts of *p*-toluenesulfonic acid (*p*-TSA) were used as model compounds of the ionomers for studying amide−sulfonate interactions. The salts were prepared by neutralizing aqueous solutions of *p*-TSA with stoichiometric amounts of the appropriate metal acetate, followed by drying at 130 °C. The metal toluenesulfonates are designated as M-TS, where M represents the metal cation.

Blends of the M-SPS ionomers or the model compounds with the mPA were prepared by first dissolving the two components in a mixture of dichloroethane and methanol (90/10 v/v) and then casting a film onto a KBr window for FTIR measurements or onto a Teflon dish to prepare samples suitable for EPR or solid-state NMR measurements. All films were dried in a vacuum oven overnight at 130 °C.

Fourier Transform Infrared (FTIR) Spectroscopy. Infrared spectra were measured with a Nicolet 60SX FTIR spectrometer using 128 scans with a resolution of 2 cm^{-1}. To avoid crystallization of the mPA, all measurements were made at room temperature within several minutes after the film on a KBr window was removed from the vacuum oven. Special care was also taken to avoid absorption of moisture while transferring samples from the oven to the spectrometer.

Electron Paramagnetic Resonance (EPR). EPR measurements were carried out with a Varian E-3 spectrometer operating at an X-band frequency of 9.06 GHz with 100 kHz field modulation. Measurements were made at liquid nitrogen temperature (77 K), and 4 mm quartz tubes (Wilmad Glass Co.) were used to hold the samples.

Natural-Abundance ^{15}N Solid-State Nuclear Magnetic Resonance (^{15}N-NMR). ^{15}N-NMR spectra of the pure methylated nylon and of its blends, M-SPS/mPA, were obtained using cross polarization magic angle spinning (CPMAS) experiments on a Chemagnetics CMX300 three-channel spectrometer. The natural abundance of ^{15}N was suitable for these measurements, which eliminated the need to use isotope-enriched materials. A Chemagnetics double-resonance APEX probe with 7.5 mm (i.d.) zirconia pencil rotors was employed. The ^{15}N and ^{1}H frequencies were 30.4 and 300 MHz, respectively. The cross polarization period was 1 ms with Hartmann−Hahn match at a 50 kHz H_1 level and ^{1}H-decoupling power of 77 kHz; spinning speed was maintained at 5 kHz. Spectra for samples with weights ranging between 230 and 310 mg were accumulated over periods of 12−72 h (depending on the relative amide content in the sample) at a 2 s repetition time. The ^{15}N chemical shifts are referenced relative to an external ammonium oxalate standard.

Results and Discussion

Electron Paramagnetic Resonance. EPR is sensitive to the local environment of paramagnetic cations. For Cu^{2+}, different spectra are obtained depending upon whether the ions are isolated from each other or in close proximity.[17,18] In a dilute solution of a polar solvent, Cu^{2+} (nuclear quantum spin number = $^3/_2$) exhibits an EPR spectrum with four lines due to electron−nuclear spin−spin coupling.[19] In concentrated solution, however, dipole−dipole and exchange interactions between the electron spins of neighboring Cu^{2+} broaden the hyperfine structure, and in the limiting case of associated Cu^{2+} ions, the hyperfine structure may coalesce into a single broad-line spectrum.

Figure 2 compares the EPR spectra of a neat Cu-SPS (11.9 mol % sulfonate) and its two blends with mPA. The neat Cu-SPS spectrum exhibits a single, broad absorption, indicating that the Cu^{2+} cations in the neat ionomer are mainly associated, presumably in the form of microphase-separated ionic aggregates that are well-known for such ion-containing polymers.[20] With the addition of 20 wt % mPA, the hyperfine structure in the EPR spectrum begins to be observed, which demonstrates the strong solvation of the metal sulfonate aggregates by the polyamide. Although the EPR spectra do not identify the origin of the solvation effect, we will show below that it arises from specific interactions between the amide and the metal cation. When the amount of mPA is increased to 80 wt % of the blend, the four hyperfine lines characteristic of isolated Cu^{2+} ions[17,19] are well resolved in the EPR spectrum. This result indicates that the mPA has efficiently dispersed the Cu^{2+} ions, or the Cu sulfonate groups, and a comparison of the spectra of the two different blends in Figure 2 indicates that in the 80% Cu-SPS/20% mPA blend, a significant concentration of the ionic groups remained associated.

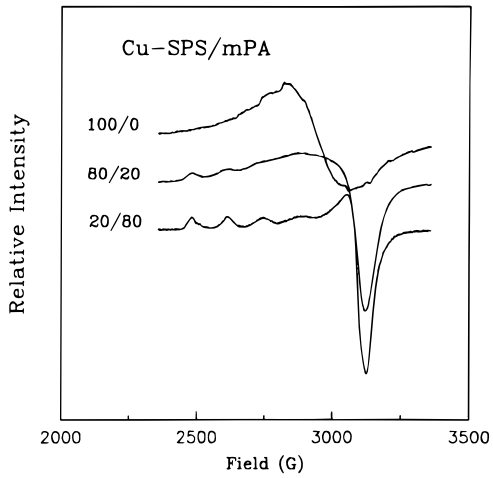


Figure 2. EPR spectra of Cu-SPS (11.9 mol %) and its two blends with mPA.

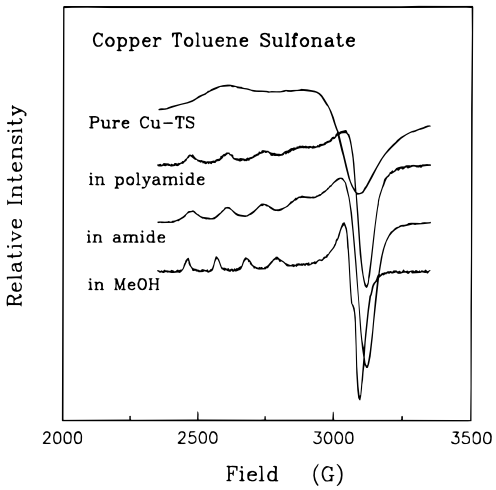
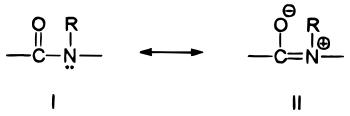


Figure 3. EPR spectra of Cu-TS and its mixtures with mPA, a model amide (*N*,*N*-dimethylacetamide), and methanol.

The EPR spectra of Cu-TS and model compound mixtures are given in Figure 3. The spectrum of neat Cu-TS shows a single broad line due to a high concentration of associated Cu^{2+}. When Cu-TS is mixed with polar compounds such as *N*,*N*-dimethylacetamide (a model compound for the polyamide), mPA, or methanol, the hyperfine structure of isolated Cu^{2+} is resolved in the EPR spectra. For each mixture, the concentration of Cu-TS was ca. 5 wt %. The methanol solution of Cu-TS was used as a reference for noncomplexed Cu^{2+}. The EPR spectra of the mixtures of Cu-TS with mPA and *N*,*N*-dimethylacetamide were similar to that of the 20 wt % Cu-SPS/80 wt % mPA (cf. Figure 2 and 3), which indicates that the dispersion of the Cu^{2+} ions at the molecular level was similar in each mixture. In contrast, the hyperfine structure is sharper in the Cu-TS/methanol solution and the peak positions differ from those in the other three spectra.

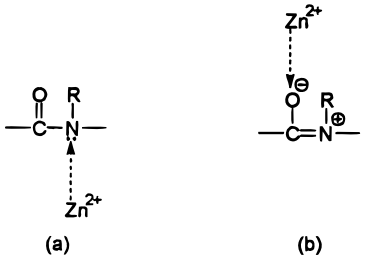
Characterization of g values from the EPR spectra provides additional information on the local environment of the transition metal cation or differences between different systems. Because the Cu^{2+} complex is anisotropic, different principal g-tensor values are obtained. The $g_\perp$ component is usually not particularly sensitive in the Cu^{2+} spectrum,[19] but the $g_\parallel$ component may be readily calculated from the positions of the singularities in hyperfine structure. All of the mixtures of either Cu-SPS or Cu-TS with mPA or *N*,*N*-dimethylacetamide had similar values of $g_\parallel = 2.42$ and a hyperfine splitting of $G_\parallel = 135$ G, whereas for the Cu^{2+} in the Cu-TS/MeOH solution, $g_\parallel = 2.47$ and $G_\parallel = 110$ G. That result confirms that the local environment of Cu^{2+} was the same for the mixtures of the ionomer or the model compound with either a low or high molecular weight methylated amide compound. In contrast, the local environment of the Cu^{2+} ions was significantly different when Cu-TS was dissolved in methanol. As will be discussed in the next section, the difference arises from the formation of a specific complex of Cu^{2+} with the amide group, while methanol simply changes the local environment of the Cu sulfonate group.

Fourier Transform Infrared Spectroscopy. FTIR was used to evaluate the changes in the local environment of the amide carbonyl group that occurred upon blending the mPA and the ionomer. The amide group may be described as a hybrid of two resonance structures as shown below:[21]



I II

This resonance hybrid structure has two possible electron-donating sites to which a positive metal ion may coordinate, the amide nitrogen or the carbonyl oxygen:[10−13]



(a) (b)

If the metal cation coordinates to the oxygen as in structure b, the resonance equilibrium shown above should shift to the right toward resonance structure II. That should decrease the stretching energy of the C−O bond and shift the infrared absorption for the carbonyl group to a lower frequency. However, if coordination is with the lone electron pair on the nitrogen atom as in structure a, the resonance structure I will be favored and the frequency of the carbonyl band should increase.

Figure 4 shows the carbonyl stretching region of the FTIR spectrum for mPA and its blends with Zn-SPS (13.7 mol % sulfonate). The spectrum of the pure Zn-SPS was subtracted from the spectra of the blends, so that the difference spectra in Figure 4 show the contributions from the infrared spectrum of the polyamide and any spectral changes associated with complexation of the two polymers. The subtraction was performed using the stretching vibration of the skeleton C−H groups of the benzene rings of the ionomer between 2985 and 3140 cm^{-1} as a reference. The pure mPA has a strong carbonyl stretching absorption at 1645 cm^{-1}, whereas the blends exhibit two absorptions in the carbonyl region, at 1645 cm^{-1} and 1577 cm^{-1}. The relative intensity of the latter band became more prominent as the Zn-SPS concentration increased. By analogy with the 1595 cm^{-1} absorption that was reported for metal halide/polyamide complexes,[11] we attribute the 1577 cm^{-1} absorption to carbonyl groups that are coordinated to Zn^{2+} ions, i.e., a Zn^{2+}−oxygen ligand. The larger shift of the carbonyl absorption observed here, 68 cm^{-1}, compared with that in ref 11, which indicates a stronger metal−oxygen complex, may be a consequence of the methylation of the amide nitrogen in the present study.

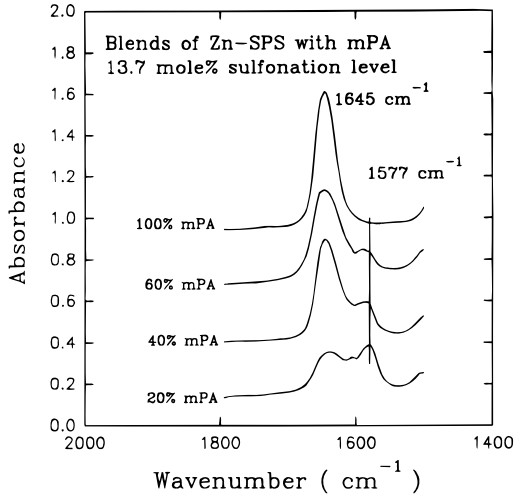


Figure 4. FTIR spectra of mPA and its blends with Zn-SPS-(13.7 mol %). The spectrum of Zn-SPS was subtracted from that of the blends so that the difference spectrum represents the spectral contributions of the polyamide and any changes that occur due to blending. The spectra were shifted vertically for clarity.

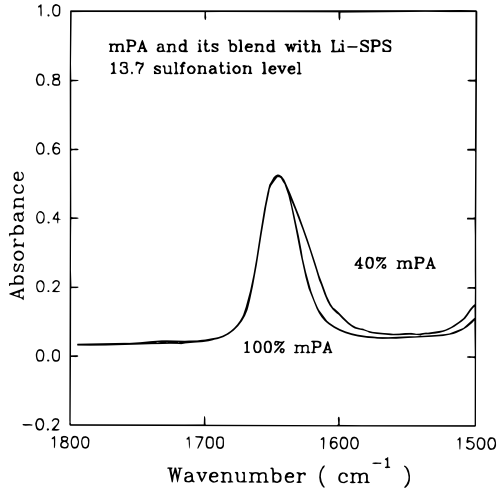


Figure 5. FTIR spectra of mPA and a blend with Li-SPS. The spectrum of Li-SPS was subtracted from the spectrum of the blend so that the difference spectrum represents the spectral contributions of the polyamide and any changes that occur due to blending. The spectra were shifted vertically for clarity.

Figure 5 compares the difference spectrum for a Li-SPS (13.7 mol %)/mPA blend with the spectrum of the pure polyamide. In this case, no distinctive shift of the carbonyl absorption was observed. The 1645 cm^{-1} peak only broadened slightly on the low-frequency side, which indicates that like Zn^{2+}, Li^+ coordinates with the carbonyl oxygen of the polyamide, but the Li^+−carbonyl

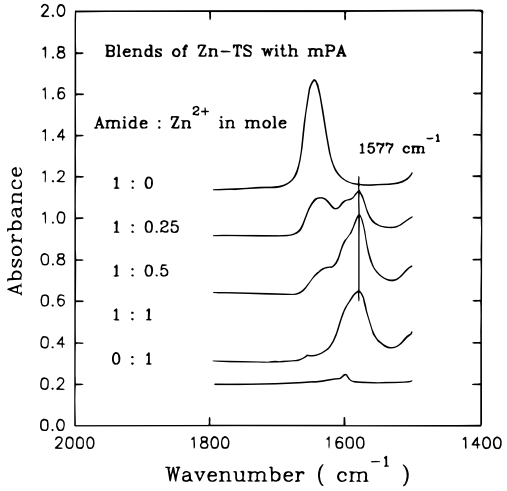


Figure 6. FTIR spectra of mPA and its mixtures with Zn-TS, a model salt for Zn-SPS. The spectra were shifted vertically for clarity.

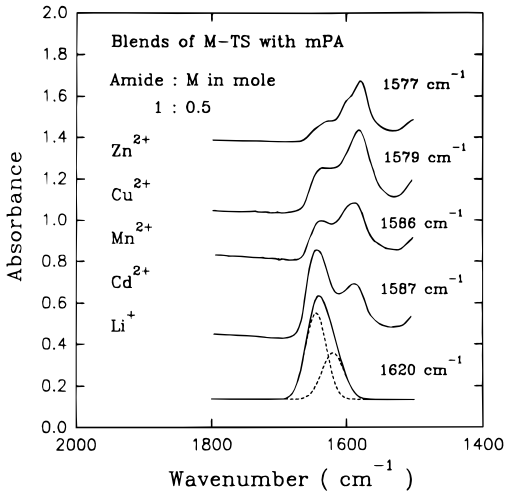


Figure 7. FTIR spectra of mPA/M-TS mixtures in the carbonyl stretching region, where M represents Zn^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, and Li^{+}. The spectra were shifted vertically for clarity.

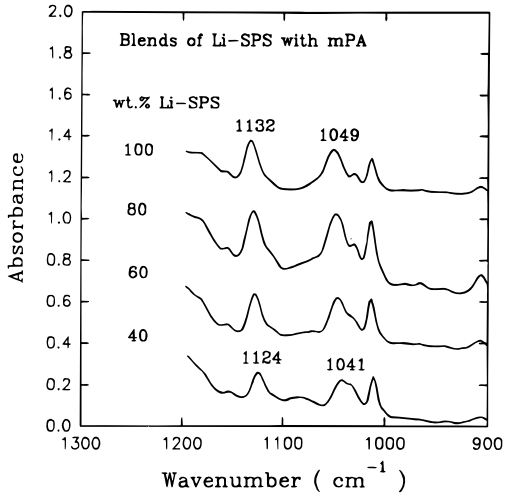


Figure 8. FTIR spectra of Li-SPS and its blends with mPA in the sulfonate stretching region. The spectrum of mPA was subtracted from the spectra of the blends so that the difference spectrum represents the spectral contributions of the ionomer and any changes that occur due to blending. The spectra were shifted vertically for clarity.

interaction is much weaker than the Zn^{2+}−carbonyl interaction.

FTIR studies of model compound mixtures were consistent with the conclusions made in the previous paragraphs for the ionomer/polyamide blends. Since the infrared absorption of the model compounds in the carbonyl stretching region are small, subtraction of spectra was not necessary in this case. Figure 6 compares the FTIR spectra of mPA/Zn-TS blends of several compositions with the spectra of the pure components. The FTIR spectra of the mPA/Zn-TS blends exhibited two bands in the carbonyl region, the usual 1645 cm^{-1} band characteristic of the neat polyamide and, similar to the mPA/Zn-SPS blends, a new band at 1577 cm^{-1} that we attribute to a metal ion−amide complex. The relative intensity of the 1645 cm^{-1} absorption decreases and the 1577 cm^{-1} peak increases as the zinc sulfonate concentration increases, which, like the spectra for the mPA/Zn-SPS blends, supports the assignment of the latter absorption to an interaction involving the metal ion. The distinct absorption band at 1577 cm^{-1}, independent of composition, for all the blend compositions shown in Figures 4 and 6 indicates that the complex involves a specific structure rather than a simple perturbation of the electronic environment of the carbonyl group. The latter phenomenon would be expected to produce a composition-dependent shift in the carbonyl band, i.e., many intermediate structures rather than a single coordination structure.

Because the metal−amide complex absorbs at a specific frequency, the position of the absorption provides a measure of the change in energy of the carbonyl relative to that in the neat polyamide, i.e., compared with the 1645 cm^{-1} absorption. Figure 7 shows the carbonyl stretching region of the FTIR spectra for blends of mPA and different metal salts of M-TS. It is clear from the magnitude of the shifts of the metal−carbonyl absorption from 1645 cm^{-1} that the relative strength of the metal−amide complex follows the order $Zn^{2+} \approx Cu^{2+} > Mn^{2+} \geq Cd^{2+} > Li^{+}$.

Evidence for interactions between the metal sulfonate groups of M-SPS and the polyamide may also be obtained from examination of the IR stretching vibrations of the sulfonate anion. The frequencies of the antisymmetric and symmetric stretching bands of the S−O bonds depend on the electrostatic influence of the metal cation on the sulfonate anion.[22] In the neat ionomer, the metal cation is closely associated with the sulfonate anion, and the strong polarization of the anion shifts the antisymmetric and symmetric stretching vibrations of the S−O bonds to higher frequencies relative to the absorption of an isolated sulfonate anion, which occurs at 1034 cm^{-1} for the bare anion in fully sulfonated polystyrene.[22] When the local electrostatic field of the cation is weakened, e.g., with a polar solvent that solvates the ion pair,[23] the force constant of the ion pair is weakened, which decreases the frequencies of both the symmetric and antisymmetric stretching vibrations toward 1034 cm^{-1}. A similar result is expected to occur in complexes of the polyamide with the metal cation, in which amide−metal interactions decrease the influence of the cation on the sulfonate anion.

FTIR spectra of the sulfonate stretching region for Li-SPS(13.7 mol %) and three blends with mPA are shown in Figure 8. The spectrum of mPA was subtracted from the blend spectra so that the difference spectra shown in Figure 8 reveal the features that arise from the sulfonate group and any spectral changes due to complex formation. The symmetric bending vibration of the

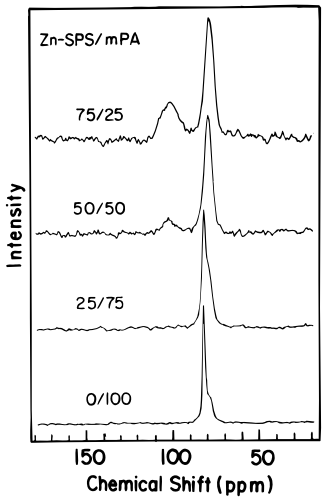


Figure 9. Solid-state ^{15}N-NMR spectra of mPA and its blends with Zn-SPS(13.7 mol %).

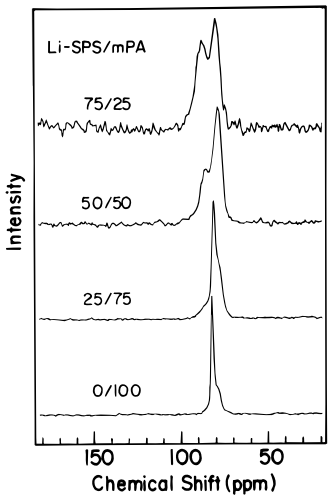


Figure 10. Solid-state ^{15}N-NMR spectra of mPA and blends with Zn-SPS(13.7 mol %).

methyl group at 1358 cm^{-1}, which was unaffected by blending the two polymers, was used as the reference band for the substraction. For the Li-SPS spectrum, the 1132 cm^{-1} absorption is one of the two antisymmetric S−O stretching vibrations and the band at 1049 cm^{-1} is due to the symmetric stretching vibration of the sulfonate anion. Both bands gradually shift to lower frequencies with the increasing addition of mPA. For a blend with a composition of 60 wt % mPA and 40 wt % Li-SPS, the two absorptions shifted to 1124 and 1041 cm^{-1}, respectively. Similar results were also observed in this IR absorbance region for Zn-SPS/mPA blends.

The shift of the sulfonate stretching vibrations to lower frequencies upon the addition of more and more mPA indicates that the amide group weakens the force field between the metal cation and sulfonate anion. That result is a consequence of the intermolecular complexation between the metal cation and the amide group that effectively solvates the ion pair. The fact that the frequencies of the stretching vibrations of the sulfonate anion gradually decrease as the concentration of mPA in the blend increases, as opposed to a step change in the frequencies independent of the blend composition, suggests that the sulfonate group does not directly participate in the complexation.

Natural-Abundance ^{15}N Solid-State Nuclear Magnetic Resonance (NMR). Recently, ^{13}C CPMAS NMR was used to characterize the miscibility of blends of M-SPS and nylon-6. Spectral evidence (^{13}C) for complex formation[14] and relaxation measurements (^{13}C and ^{1}H) to deduce domain sizes[7] provided molecular details of the origin of miscibility. For those blends, as well as for the M-SPS/mPA blends reported here, raw one-dimensional ^{13}C spectra are relatively insensitive to the formation of specific interactions in the blends. ^{15}N, however, is especially sensitive to its immediate environment. This fact has been exploited in the characterization of polyamides (crystalline and amorphous domains), both at its natural abundance (ca. 0.3%) and in isotopically enriched samples.[24−26] In the present study, since the amide group participates in the complex formation, ^{15}N-NMR should be an excellent probe of the nature of the complexes. Despite the low natural abundance and the low gyromagnetic ratio of this nucleus, it turned out to be highly informative.

Figure 9 compares the natural-abundance ^{15}N CP-MAS NMR spectra of the pure mPA (top) and three different blends of Zn-SPS/mPA. The mPA spectrum exhibits two partially resolved resonances—a sharp peak at ca. 81.5 ppm assigned to the amides in the crystalline phase, and a broader higher field shoulder at ca. 78.5 ppm due to the ^{15}N in the amorphous phase. Those assignments were confirmed by the spectrum of the pure mPA sample after it was first melted above 75 °C and then quenched to −20 °C, which exhibited only the amorphous peak (not shown). After annealing the samples at room temperature for several days, the crystalline peak at 81.5 ppm redeveloped. The spectra of the blends clearly show that as the Zn-SPS concentration in the blend increases, the intensity of the amorphous peak increases while the crystalline peak diminishes. These changes demonstrate the suppression of the mPA crystallization by the addition of the ionomer.

In addition, a new peak at ca. 102 ppm was observed when the Zn-SPS concentration exceeded 50 wt %. The growth of this peak with the increase of Zn-SPS content of the blend and its composition-independent chemical shift allow us to unambiguously assign this peak to the amides in a new chemical species, namely the complexes with the Zn^{2+} ions. Furthermore, the relative integrated intensity of this peak with respect to the total integrated intensity can provide a direct measure of the percentage of amides that are involved in the complex formation. In order to accurately quantify the intensity values, we need to fully account for the rotating-frame spin dynamics[27] (polarization transfer and rotating frame relaxation rates). Currently, based on preliminary experiments, the measured relative peak intensities are within 15% confidence limits. Experiments to measure these effects are planned and will be reported in a future publication.

Similar ^{15}N-NMR results were also obtained for M-SPS/mPA blends with other metal cations. For example, ^{15}N spectra of mPA and its blends with Li-SPS are shown in Figure 10. As for the Zn-SPS/mPA blends, two effects result from blending: (1) inhibition of the mPA crystallinity as indicated by the dominant amorphous peak and (2) the formation of complexed amides evidenced by the new peak. For the Li-SPS/mPA blends, the new peak is also shifted to low field, but to a smaller extent, ca. 85 ppm, than for the Zn-SPS/mPA blends. The smaller shift indicates that the amide−Li^+ complex is weaker than the amide−Zn^{2+} complex.

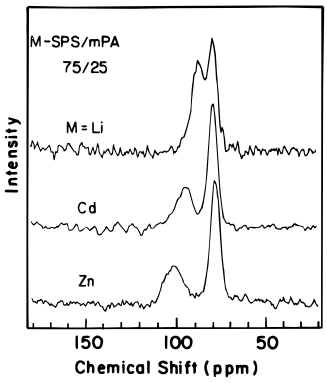


Figure 11. Solid-state ^{15}N-NMR spectra of 75 wt % M-SPS/25 wt % mPA blends, where M represents Zn^{2+}, Cd^{2+}, or Li^{+}.

The ^{15}N-NMR spectra for three different cations of M-SPS/mPA blends with a 75/25 wt % composition are compared in Figure 11. Each blend displays a major amorphous peak and a new downfield peak due to the formation of a metal ion−amide complex. The position of the downfield peak indicates that the relative strength of the complex follows the order $Zn^{2+} > Cd^{2+} > Li^{+}$, which agrees with the FTIR analysis discussed earlier in this paper. For blends with paramagnetic ions, e.g., Cu^{2+} and Mn^{2+}, spectra were severely broadened by the paramagnetic centers, thus obscuring spectra details.

Structure of the Metal−Amide Complex. The literature contains conflicting explanations of the chemistry of metal ion−amide complexes. Although some studies have concluded that metal ions coordinate to amides via the carbonyl oxygen,[10−13] others attribute the spectral results to the formation of a metal−nitrogen ligand.[1,14,28,29]

The EPR, FTIR, and solid-state ^{15}N-NMR results discussed herein indicate that for the mPA/M-SPS blends, both the carbonyl oxygen and amide nitrogen are directly involved in the structure of the complex. The sulfonate anion, though perturbed by the close proximity of the amide group, is not part of the structure of the intermolecular complex. The correspondence of the FTIR and ^{15}N-NMR results for blends containing the Zn^{2+}, Cd^{2+}, or Li^{+} salts of the ionomer strongly suggests that the chemistry of the complex for those three metal ions is identical, though the strength of the complex is dependent on the particular metal ion. The qualitative similarity of the FTIR results for blends prepared from ionomers with those ions and ones prepared from the Cu^{2+} and Mn^{2+} salts also suggests that the complexation chemistries of the latter are the same as for Zn^{2+}, Cd^{2+}, or Li^{+}.

In a study of hydrogen bonding and metal-complex formation of formamide and *N*-methylacetamide, Saitô et al.[27] proposed an electron redistribution model of $2p_z$ electrons at the nitrogen atom upon metal-complex formation. This electron redistribution model appears to also be applicable to our experimental observations. Figure 12 provides a schematic representation of the model; the arrows indicate the migration of electrons associated with complexation.

According to this model, the complex involves the metal cation, the carbonyl group, and the amide nitrogen. Coordination of the metal cation with the carbonyl oxygen induces a charge transfer at the carbonyl group that lowers the order of the C=O bond, which results in a shift to a lower frequency of the IR absorption from carbonyl stretching. Charge transfer at the carbonyl group also induces a $2p_z$ electron redistribution from the

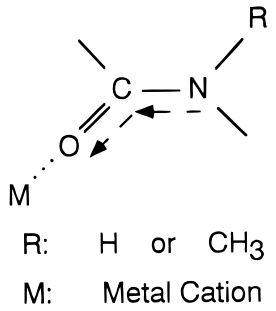


Figure 12. Schematic representation of the electron redistribution model for the metal ion−amide complex.[24] The arrows indicate the migration of electrons associated with complexation.

nitrogen to the carbonyl group, which results in electron deshielding at the nitrogen and a downfield shift of the nitrogen resonance in the ^{15}N-NMR spectrum. The electron redistribution model implies that the extent of nitrogen $2p_z$ electron migration toward the carbonyl group depends mainly on the extent of charge transfer at the carbonyl group, which is determined by the electron-withdrawing power of the metal cation. The locations of the new absorbance and resonance observed in the different blends by FTIR and ^{15}N-NMR spectroscopies were consistent with this model and indicate that the strength of the complex decreases with decreasing electron-withdrawing power of the cation in the order $Zn^{2+} > Cd^{2+} > Li^{+}$.

The electron redistribution model pictured in Figure 12 also implies a stoichiometric equivalence of complexed carbonyl and amide nitrogen groups. Strictly speaking, the relative intensities of the carbonyl IR absorbances in the blends may not provide a quantitative measure for the amounts of complexed and uncomplexed carbonyl groups, because the extinction coefficients of the two bands may be different. Nevertheless, we have made that assumption in order to estimate the relative populations of complexed carbonyl and nitrogen in the blend; the latter can be obtained directly from the ^{15}N-NMR.

Suppose we assume that the ionic aggregates are dispersed into individual metal sulfonates in a Zn-SPS/mPA blend and each metal cation forms a complex with *n* amide groups of the mPA (e.g., with a ligand number *n*). Then for the Zn-SPS/mPA blend with a given composition and a given sulfonation level of the Zn-SPS, the percentage of carbonyl groups (or nitrogen) that are involved in the complex may be calculated.

Figure 13 shows the calculated percentages of carbonyl (or nitrogen) groups that are complexed for three different values of *n* (i.e., three different ligand numbers) as a function of the Zn-SPS (13.7 mol % sulfonation) concentration in the blend. The open circles in Figure 13 represent the actual fraction of carbonyl groups that are complexed as estimated by deconvoluting the carbonyl stretching region of the FTIR spectra in Figure 4 into two Gaussian peaks at 1645 cm^{-1} and 1577 cm^{-1} and integrating each peak. The fraction of the carbonyl group in the complex is the area of the 1577 cm^{-1} absorption divided by the total area of both bands. The filled circles in Figure 13 represent the fraction of amide nitrogen groups that are complexed with the ionomer as obtained by integrating the ^{15}N-NMR resonances at 102 and 78.5 ppm in Figure 9. The fraction of complexed nitrogen is the ratio of the area of the 102 ppm resonance to the total area of both resonances. The data for the blends with compositions between 0.4 and

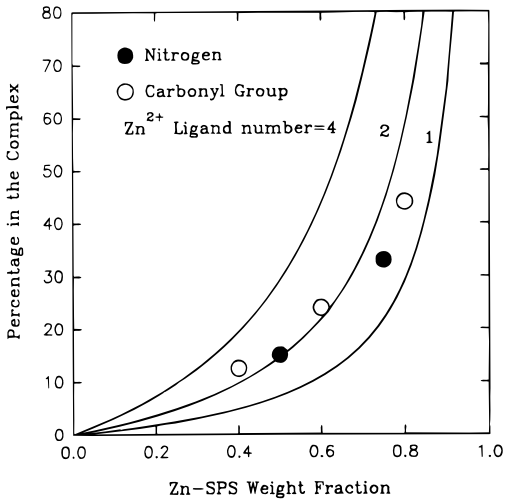


Figure 13. Percentage of the carbonyl groups and nitrogen that participate in the ionomer−amide complex versus blend composition in weight fraction of the Zn-SPS with a sulfonation level of 13.7 mol %. The three lines were calculated by assuming that all the metal ions were coordinated with the polyamide and the number of ligands to Zn^{2+} were 4, 2, or 1. The values of the open circles (carbonyl groups) and filled circles (nitrogen atoms) were calculated from FTIR and ^{15}N-NMR spectroscopy, respectively. The details are described in the text.

0.6 weight fraction of Zn-SPS fell on the same curve for $n = 2$. That result confirms that equivalent amounts of nitrogen and carbonyl participated in the complex, which is consistent with the electron redistribution model, and that each Zn^{2+} coordinated with two amide groups. The data for the higher concentration of Zn-SPS deviated from the $n = 2$ line toward a lower percentage of complexed species. This deviation can probably be explained by the EPR results in Figure 2 which indicated that at high ionomer weight fraction a significant degree of self-association of the ionic species persisted in the blend. As a result, not all sulfonate groups were available for complexation with the polyamide, which effectively lowers the percentage measured in Figure 13. If one accounts for the self-association of ionic groups at the higher Zn-SPS concentrations, the data for the higher Zn-SPS weight fractions may be reconciled with the data for the lower Zn-SPS concentrations and are most consistent with a ligand number = 2 for the complex.

Previous authors who proposed a metal ion−nitrogen ligand[1,28,29] studied secondary amides, i.e., where R is hydrogen in Figure 12, and based their conclusions on a shift of the IR N−H stretching absorption to lower frequency upon addition of a metal salt. A decrease of the N−H stretching vibration frequency could indicate a decrease in the force constant of N−H stretching as a result of coordination of the metal cation to the lone pair of electrons on the nitrogen atom. That experimental observation may also be explained, however, by the electron redistribution model, which does not assume ion−nitrogen coordination. Still, one must be cautious in extrapolating the results for ion complexation with a methylated polyamide to complexation with a polyamide containing amide protons. The difference in the electronic structure of the nitrogen in the two cases and the occurrence of hydrogen bonding for the latter may change the nature of the ion−amide complex. While the present study offers some new insight into the development of miscible or compatibilized blends by ion−amide complexation and the ramifications of changing the ion, these data may not resolve the question of the nature of the complex in SPS/nylon 6 blends.

Comparison of Ion Effect with Electrostatic Field Theory. Although the specific ion−dipole interactions discussed in this paper are limited, it is, nevertheless, instructive to compare those results with the electrostatic field theory[30] predictions for the coordination behavior of low molecular weight systems. For ion−dipole interactions, the strongest bonds with a specific dipolar ligand should form with ions that have the strongest peripheral electric fields, which is favored by small ionic radius and large charge. If one defines an *ionic potential* as the ratio of the ionic charge and the radius, q/r, ions with the largest ionic potentials are expected to form the strongest ion−dipole complexes. Then, the comparatively small, but more highly charged ions of the 3d transition metals are expected to produce stronger complexes with a specific ionic or dipolar ligand than monovalent alkali metal ions. The ionic potentials for the particular cations that were evaluated in this study are given below.

ion	q	r (nm)	q/r
Li^+	1	0.071	14.08
Cd^{2+}	2	0.096	20.83
Mn^{2+}	2	0.078	25.64
Cu^{2+}	2	0.072	27.78
Zn^{2+}	2	0.072	27.78

Based on these ionic potentials, one would expect the relative strength of an ion−amide complex to decrease in the order of ion as $Zn^{2+} \approx Cu^{2+} > Mn^{2+} \geq Cd^{2+} > Li^+$, which is exactly what was observed in this investigation. This suggests that electrostatic field theory might be useful for predicting the behavior of ionomer/polyamide complexes for additional cations.

Conclusions

The metal ion−amide complexation in M-SPS ionomer/polyamide blends was characterized by EPR, FTIR, and ^{15}N-NMR spectroscopies. The competing interaction from hydrogen bonding usually observed with polyamides was eliminated by using an *N*-methylated polyamide. This investigation produced the following conclusions:

(1) The ionic aggregates that are usually observed in ionomers due to association of the ionic groups are solvated by the polyamide. This solvation is directly linked to the formation of an intermolecular complex involving the metal cation of the ionomer and the amide group.

(2) The ionomer−polyamide complex involves coordination of the oxygen of the amide carbonyl group with the metal cation. Evidence for this complex is provided by the development of a new IR absorption at lower frequency than the unperturbed carbonyl stretching vibration, the position of which is independent of the blend composition. The position of the new absorption does, however, depend on the cation used, and the strength of the complex decreases with decreasing electron-withdrawing power of the cation in the order $Zn^{2+} \approx Cu^{2+} > Mn^{2+} \geq Cd^{2+} > Li^+$, which is consistent with electrostatic field theory. To the best of our knowledge, this represents the first report of the characterization of such a metal ion−amide complex in a binary polymer blend.

(3) Solid-state ^{15}N-NMR indicates that although the ion−amide coordination occurs through the carbonyl

oxygen, the amide nitrogen also participates in the complex. This may be explained in terms of a $2p_z$ electron redistribution mechanism in which electrons move from the nitrogen to the metal ion through the carbonyl group.

(4) Zn^{2+} appears to coordinate with two amide groups, and the numbers of oxygen and nitrogen atoms involved in the complex are equal, which supports the electron redistribution model shown in Figure 12. The sulfonate anion is not directly involved in the complex, but remains in the vicinity of the metal cation.

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