Miscibility of Polyamide-6 with Lithium or Sodium Sulfonated Polystyrene Ionomers

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ABSTRACT: Blends [50:50 (w/w)] of polyamide-6 (PA-6) with sulfonated polystyrene ionomers (containing 9.8 mol % of functional groups) show considerable miscibility enhancement (single glass transition at some compositions) when the counterion is Li but are immiscible when the counterion is Na. Dynamic mechanical measurements show that there is an optimum composition of the blends of the lithium sulfonated ionomers (LiSPS) with PA-6 at which the simultaneous disruptions of the stiffening effects of crystallinity and of the "cluster phase" in the blends are at a maximum. This is manifested as a maximum in the tan δ peak height and a minimum in the width at this composition. At 240–250 °C, the blends with LiSPS are either one- or two-phase (on the 50–100-Å scale), depending on the lithium sulfonate content of the ionomer and on the blend composition. This phase behavior can be described by considering the thermodynamics of blending to be dominated by two opposing interaction enthalpies: the specific interaction of the lithium styrenesulfonate units with the amide units of the PA-6 and the random, unfavorable interaction of the styrene with the amide units.

Introduction

While high polymers are generally immiscible due to the very low entropy of mixing, miscibility enhancement can be achieved when one or both of the polymers are functionalized with specific interacting groups. Specific intermolecular interactions lower the heat of mixing so that the thermodynamics of blending can lead to miscibility enhancement of the blend components. The functionalization of polymers with <15 mol % ionic groups, which produces polymers generally termed "ionomers", is particularly attractive in this respect since the ionic groups introduce the possibility of strong ion–ion, ion pair–ion pair, or ion–dipole interactions with other polymers. The miscibility enhancing effect of ionic groups has been clearly demonstrated for blends of polystyrene ionomers with various polar polymers such as poly(ethylene oxide),[1] poly(propylene oxide),[1,2] polycaprolactone, poly(vinyl chloride), poly(ethylene terephthalate), poly(epichlorohydrin),[3] and polyurethanes.[4] Since polyamides are also polar, due to the presence of amide groups along their backbone, ionomers are usually found to interact favorably with polyamides.

Polyamides constitute an important class of commercial polymers with a wide variety of applications, from engineering thermoplastics to fibers. Hence, the improvement of some of the properties of polyamides (e.g., impact, dyeability, vapor permeation, antistatic) through blending is of considerable interest. The use of ionomers containing ionic carboxylate groups to compatibilize various polymers with polyamides has been the subject of several studies and many patents.[5–10] There are a few patents to suggest that ionomers containing ionic sulfonate groups may also be compatible with polyamides.[11,12] However, it is only recently that some studies have demonstrated, by using differential scanning calorimetry (DSC), that there is significant miscibility enhancement between polyamide-6 (PA-6) and polystyrene ionomers when the ionomer contains lithium,[13–15] zinc,[15] or manganese[15,16] sulfonate groups. Blends of unneutralized sulfonated polystyrene and PA-6 are also compatibilized, although the PA-6 in these blends is susceptible to hydrolysis due to the catalytic activity of the sulfonic acid groups in these blends.[14,17] Degradation of the PA-6 is not evident when the sulfonated polystyrene is neutralized.[14]

In this paper it will be shown that the choice of counterion (Li vs Na) is critical in achieving enhanced miscibility (single glass transition) of sulfonated polystyrene with PA-6. The previous studies on blends of sulfonated polystyrene ionomers with PA-6 employ DSC to determine the miscibility. However, dynamic mechanical thermal analysis (DMTA) is often more sensitive than DSC in detecting the presence of different phases in polymer blends.[18] Therefore, in addition to DSC data, the phase behavior of the blends of PA-6 with lithium sulfonated polystyrene ionomer (LiSPS) as determined by DMTA is also presented here. The one or two phase behavior of these blends, as seen by DMTA, is described by considering the thermodynamics of mixing at 240–250 °C to be dominated by two factors: the specific interaction of the lithium sulfonate groups with the polyamide units, and the random unfavorable interaction of the styrene with the polyamide units. The effect of PA-6 on the "cluster phase" of the LiSPS ionomer will also be discussed and it will be shown that an optimum amide to lithium sulfonate ratio exists at which the tan δ of the blend becomes sharp and narrow.

Since DMTA can only resolved phases of at least 50–100 Å in size, the term "miscibility", as used in this paper, implies a single phase (single glass transition) on the 50–100-Å level. Thus miscibility, as used here, does not necessarily imply miscibility on the molecular level. This aspect is the subject of continuing study.

Experimental Section

Materials Used. PA-6 was obtained from Aldrich and was purified by dissolving in formic acid and precipitating in water. The polystyrene was also obtained from Aldrich and was sulfonated using the method of Makowski et al.[19] The sulfonation level of the sulfonated polystyrene was determined by titration with methanolic NaOH to a phenolphthalein end point. The sulfonated polystyrene was dissolved in benzene/methanol (90:10), neutralized with either LiOH or NaOH, and subsequently freeze-dried to produce the ionomers designated as LiSPS and NaSPS, respectively. All materials were dried under vacuum for 2 days at 80 °C prior to use. No further drying was done at

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Table I
Characteristics of the Blend Components

material	$\bar{M}_w$[a]	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	functional group content mol %	functional group content mequiv/g
PA-6	33	14	2.4	100	8.85
PS	225	105	2.1	0	0.00
LiSPS5	235	110	2.1	5.4	0.50
LiSPS10	243	114	2.1	9.8	0.87
NaSPS10	246	115	2.1	9.8	0.86

[a] The molecular weights for the PA-6 and PS were determined by size exclusion chromatography, while those of the ionomers were calculated from the values for the PS.

this stage, since a much more thorough drying procedure was used during the preparation of the blends. In order to ensure a fair comparison between the blend properties and the pure component properties, the pure components were dissolved, precipitated, and dried following the procedure described below for blend preparation. Table I lists the sample designations and characteristics of the polymers used in this study.

Blend Preparation. The blends of ionomers with PA-6 were prepared by dissolving the individual components in a solvent mixture of *m*-cresol/methanol (80:20) to produce 5% (w/v) solutions. The NaSPS10 ionomer is slightly hazy in this solvent and was clarified by the addition of 10 μL of distilled water/mL of solution. To ensure a uniform solvent mixture, the same level of water was added to all the solutions. Various blend ratios were prepared by mixing different volumes of the solutions under constant agitation. The solutions were then precipitated into an excess of hexanes. The precipitated product was thoroughly washed with fresh hexanes to remove residual *m*-cresol. Final drying of the precipitated polymer blends was accomplished by keeping the samples under vacuum at 140 °C for 1 week. Solid-state nuclear magnetic resonance showed no evidence of residual solvent after this drying procedure. Loss of material during precipitation was less than 5%, as determined by the difference in weight between the polymers before blending and after precipitation and drying. Blends of PA-6 with polystyrene were prepared in a similar fashion to the ionomer/PA-6 blends, except that a *m*-cresol/toluene (50:50) solvent mixture was used as the solvent. Some of these PS/PA-6 solution blends had to be clarified by the addition of some toluene. All of the blend materials were stabilized with 0.1% (w/w) Irganox 1098 (kindly supplied by Ciba-Geigy Corp.) by sprinkling the ground polymer blends with a 1% (w/v) solution of the stabilizer in either methanol (for PS and LiSPS5 blends) or acetone (for Li and Na SPS10 blends). The samples were dried under vacuum for a further 2 days at 140 °C prior to use.

Differential Scanning Calorimetry. A Perkin-Elmer DSC-7 scanning calorimeter was used for the DSC measurements. All scans were run under a nitrogen purge to minimize oxidative degradation. To ensure a uniform thermal history, the samples were first heated to 250 °C and held at this temperature for 5 min before cooling to −10 °C at 40 °C/min. The samples were then scanned from −10 to +250 °C at 20 °C/min to record the T_g and T_m. The glass transition temperatures were taken as the midpoint of the heat capacity changes while the melting temperatures (T_m) and crystallization temperatures (T_c) were taken at the maximum of the enthalpy endo/exotherm peaks. The T_c values were recorded during the cooling run. The percent crystallinity of the samples was estimated by assuming an enthalpy of melting of 160 J/g for 100% crystalline PA-6.[20]

Dynamic Mechanical Thermal Analysis (DMTA). The blend samples were prepared by compression moulding at 240–250 °C under low pressure. The samples were cooled using forced-air convective cooling. The average cooling rate was estimated at 5 °C/min, with inital cooling rates as high as 10 °C/min. A Polymer Laboratories DMTA instrument was used to record the dynamic mechanical properties of the samples at 1 Hz. The dual cantilever mode was used with an 8-mm free length. The samples were between 2 and 3 mm thick and approximately 11 mm wide. The samples were scanned at 1 °C/min from 0 °C up to the flow or melting temperature of the blends (usually about 220 °C). The tan δ peaks were deconvoluted using PeakFit (Jandel Scientific) software and the best fits to the data were obtained by assuming an exponential baseline and an exponentially modified Gaussian distribution for the peaks. From these the characteristics (positions, widths, areas, heights) of the constituent peaks could be obtained.

Table II
DSC Data for the Polymers and Their Blends

polymer	amt of polymer (%)[a]	T_g (°C)	ΔH_m (J/g)	T_c (°C)	T_m (°C)	crst (%)
PA-6	100	54	69.9	174.4	220.2	44
NaSPS10	10	58/132	58.0	171.0	220.5	36
	30	66/130	44.9	168.3	220.2	28
	50	66/129	39.2	166.4	220.7	24
	70	66/132	15.9	155.7	218.0	10
	90	–/131	4.2	169.1	218.3	3
	100	133				
LiSPS10	10	62	61.0	170.7	220.7	38
	40	91	32.1	141.8	212.5	20
	50	92	1.2		207.4	<1
	70	125				
	90	145				
	100	133				
LiSPS5	10	58/96	63.3	172.2	221.5	40
	30	68/105	44.6	167.4	220.5	28
	50	110	29.5	149.5	217.4	18
	70	112				
	90	120				
	100	122				

[a] Percent by weight of polymer in the blend with PA-6.

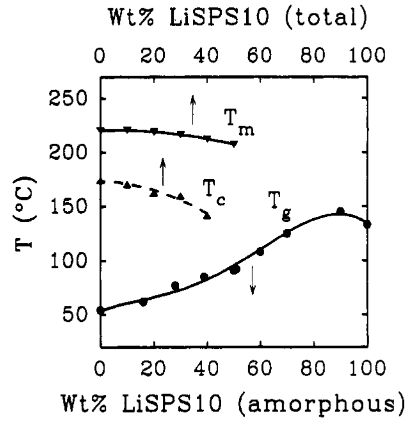

Figure 1. Transitions for LiSPS10 blends with PA-6 as determined by DSC.

Results

Differential Scanning Calorimetry. Table II lists the data obtained by DSC for the various ionomer blends with PA-6. The NaSPS10 ionomer blends are clearly immiscible, as evidenced by the presence of two glass transition temperatures (T_g) and by the negligible effect on the crystalline melting temperature (T_m) of PA-6. The LiSPS10 blends, on the other hand, show a single composition-dependent T_g and a T_m depression which varies with composition, which suggests the presence of strong interactions between this ionomer and PA-6. Figure 1 shows the variation of T_m, T_c, and T_g with composition for the LiSPS10 blend. T_m and T_c are plotted against the absolute ionomer content in the blend. Since T_g is only relevant to the amorphous phase, it is plotted as a function of the amorphous phase composition, which was calculated from the percent crystallinity in the blends. For compositions greater than 50%, the LiSPS10 blends are amorphous and the T_g increases until, at 90% ionomer composition, it reaches a maximum. This maximum is a reproducible feature of these blends and is also seen by DMTA.

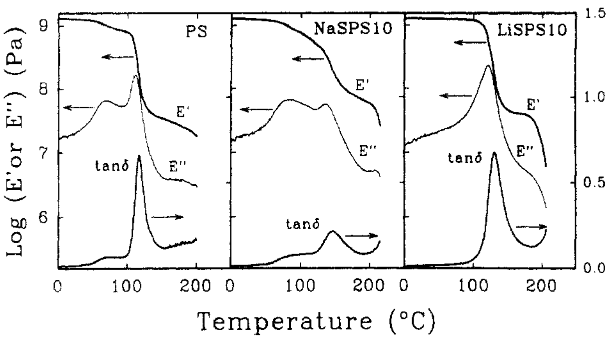

Figure 2. Dynamic mechanical results (1 Hz) for 50:50 blends of PA-6 with PS (left), NaSPS10 (middle), and LiSPS10 (right).

The DSC data in Table II for the LiSPS5 ionomer blends show that there are two glass transition temperatures at low ionomer contents, while at high ionomer contents there appears to be a single composition-dependent T_g. Considerable additional insight into the phase behavior of this blend can be gained from dynamic mechanical measurements, to be discussed later.

The progressive lowering of the crystallization temperature (T_c) of PA-6 with increasing ionomer content, shown in Table II, is an indication of the extent to which the PA-6 crystallization process is hindered. This, in turn, provides some insight into the level of interaction between the blend components. For the blends of PS with PA-6, T_c remains at about 174 °C throughout the composition range. The order in which the polymers hinder the crystallization process is as follows: LiSPS10 > LiSPS5 > NaSPS10 > PS.

Dynamic Mechanical Thermal Analysis (DMTA). DMTA is often more sensitive in detecting T_g in blends than DSC.[18] It is therefore used here for the detailed analysis of the phase behavior of the ionomer blends. Since all the DMTA samples were molded at ca. 240 °C, the DMTA data can be assumed to reflect closely the phase behavior of these blends at this temperature. Figure 2 shows the storage modulus (E'), loss modulus (E''), and tan δ profiles for the 50:50 blends and confirms the immiscibility of NaSPS10 and PS (two distinct transitions) and the miscibility (single distinct transition) of LiSPS10 with PA-6 on the 50–100-Å level, characteristic of the DMTA measurement. The storage modulus (E') drop at about 220 °C is due to the melting of the crystalline phase of PA-6. It is worth noting that the 50:50 LiSPS10 blend sample prepared for the DMTA has a higher crystallinity (about 14%) than that shown in Table II. This is a result of the slower cooling rate during the DMTA sample preparation than the 40 °C/min used to obtain the data in Table II. At other blend ratios (10, 30, 70, 90% ionomer or PS) the NaSPS10 and PS blends show two tan δ peaks, confirming the DSC results that these blends are phase separated throughout the composition range. In contrast, the LiSPS10 and LiSPS5 ionomer blends with PA-6 are either one-phase or two-phase, depending on the blend composition.

Figure 3 shows a series of tan δ profiles for the LiSPS5 and LiSPS10 blends, respectively. Figure 3 (left) shows the gradual merging of the LiSPS5 and PA-6 tan δ peaks with increasing LiSPS5 content in the blend until, at 70% ionomer content, a single peak is seen. Compositions having more than 70% ionomer show evidence of an ionomer cluster peak at higher temperatures, which is a characteristic feature of the unblended ionomers. Figure 3 (right) shows a similar trend for LiSPS10, except that a single (but broad) peak is already seen at a much lower ionomer content (30% ionomer).

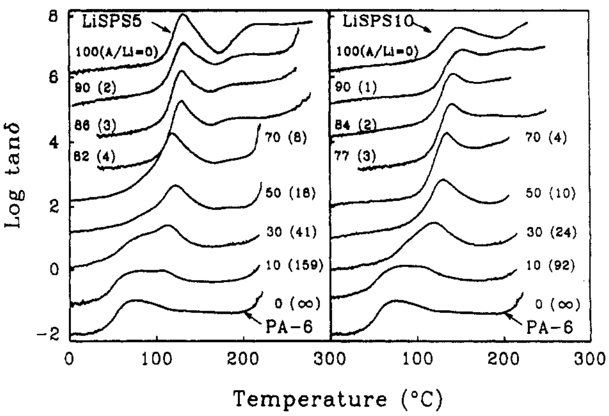

Figure 3. log tan δ (1 Hz) for various blends of PA-6 with LiSPS5 (left) and LiSPS10 (right). The vertical axis refers to the bottom curve only. Subsequent curves are separated by one log tan δ unit for clarity.

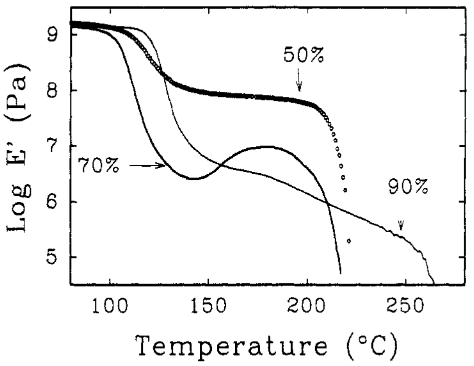

Figure 4. Storage modulus (E') for blends of PA-6 with LiSPS5 recorded during the 1 °C/min heating run of the DMTA experiment (1 Hz). The wt % LiSPS5 ionomer content in the blend is indicated. The experimental points are only shown for the 50% LiSPS5 blend.

Note that the blends containing 10% LiSPS10 and 50% LiSPS5 show two transitions by DMTA, but only a single transition by DSC (Table II). It may be argued that this is a consequence of possible phase separation during the slower cooling of the DMTA sample (vs faster cooling of the DSC samples). To test this, blend samples containing 10, 30, and 50% LiSPS10 were cooled at 2 °C/min from 250 °C and scanned by DSC as before. Single transitions were noted in all cases. Furthermore, the probable presence of a lower critical solution temperature (LCST) in these blends would also favor one-phase, rather than two-phase, behavior during a slow-cooling process. From these considerations, DMTA can be considered to be more sensitive than DSC in detecting phase domains in these blends, with cooling rate differences being less significant.

Figure 4 shows the log of the storage modulus (E') for blends containing 50, 70, and 90% LiSPS5 ionomer. For the 70% ionomer blend, PA-6 crystallizes during the slow heating run (1 °C/min) of the DMTA experiment. This, however, is not seen in the blends containing either 50% or 90% ionomer, the 50% ionomer blend is already crystalline, and the 90% ionomer blend is, and remains, amorphous. This behavior confirms the DSC results that the lithium sulfonate groups of the ionomer strongly hinder the crystallization of PA-6 in the blend. Again, the rapid drop in E' at about 220 °C for the 50 and 70% ionomer blends is due to the melting of the PA-6 crystalline phase. The much more gradual drop of E' for the 90% ionomer blend from 150 to 260 °C is a reflection of the presence of a cluster phase in this blend.[21]

Analysis by tan δ Peak Deconvolution. Even a casual inspection of the tan δ profiles of the blends containing

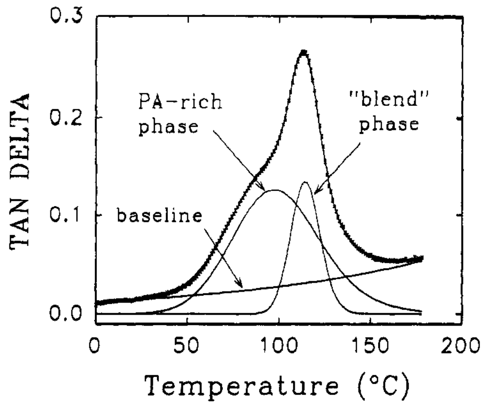

Figure 5. Deconvolution of the tan δ curve (1 Hz) of the blend containing 30% LiSPS5 ionomer. The experimental points are shown by an "x", while the solid lines represent the results of the deconvolution.

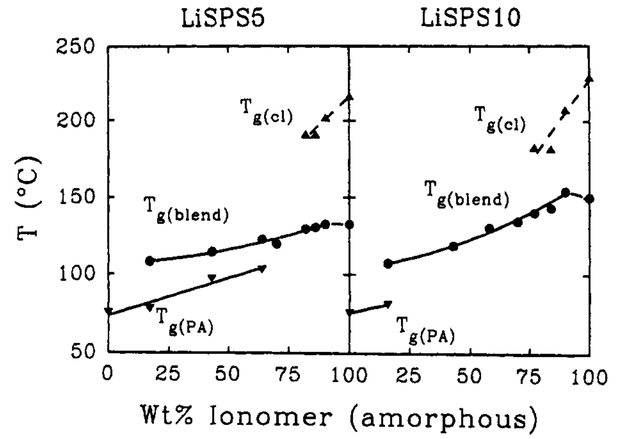

Figure 6. Transition temperatures of the phases, as determined by DMTA, for the blends of PA-6 with LiSPS5 (left) and LiSPS10 (right).

10 and 30% LiSPS5 suggests that two overlapping tan δ peaks are involved which reflects the presence of two separate phases. With modern deconvolution techniques, it is possible to deconvolute such peaks to obtain semiquantitative values for the peak positions, heights, etc. This procedure, while clearly not absolutely precise, gives a useful measure of the relative tan δ peak positions (T_g), peak heights, and peak widths (purity of the phases). An example of a typical deconvolution of a tan δ profile (plotted linearly) is shown in Figure 5.

In general, the tan δ peaks can be related to three different phases: the PA-rich phase, the blend phase, and the cluster phase of the ionomer. The phase with the lowest T_g is a mixture of PA-6 and ionomer and will be referred to as the PA-rich phase. The phase at intermediate T_g results from the mixture of PA-6 with much more of the unclustered ionomer and will be referred to as the blend phase. At high ionomer contents, some of the blends show the presence of a high-temperature transition, and this due to a cluster phase. It is worth recalling that the polystyrene ionomers studied here show two tan δ peaks in their pure, unblended form. The one occurring at lower temperature is attributed to the unclustered phase, while the other is due to a cluster phase.[21,22] The two tan δ peaks shown in Figure 5 for the blend containing 30% LiSPS5 ionomer are thus due to a PA-rich and a blend phase.

Figure 6 shows the variation with temperature of the three tan δ peaks in the blends of LiSPS10 and LiSPS5 with PA-6. The positions of these peaks along the composition axis have been adjusted for crystallinity to represent only the amorphous phase composition. Figure 6 clearly shows that the cluster phases of the ionomers are plasticized by the presence of PA-6 in the blends, which is seen as a decrease in the cluster-phase peak temperatures with decreasing ionomer content in the blend. Figure 6 also highlights the immiscible/miscible threshold of these two ionomers, the threshold being taken between the highest composition showing two glass transition temperatures, and the lowest composition showing only one T_g. Thus, the threshold is between 17 and 43% ionomer content in the amorphous phase for the LiSPS10 (10 and 30% total LiSPS10 content) and between 64 and 70% amorphous phase composition for the LiSPS5 blends (50 and 70% total LiSPS5 content). A maximum is seen in the T_g of the blend phase at 90% LiSPS10 ionomer content; this was also seen by DSC.

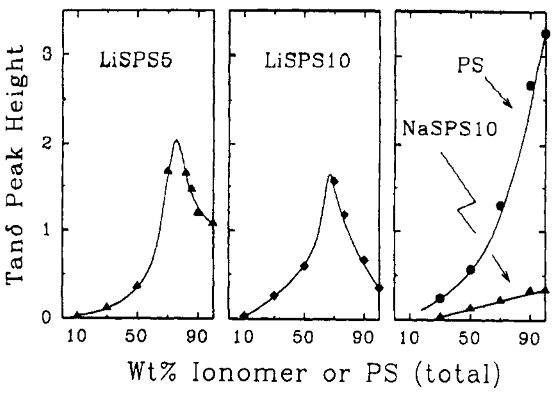

Figure 7. The tan δ peak heights, as obtained from deconvolution, for blends of PA-6 with LiSPS5 (left), LiSPS10 (middle), and NaSPS10 and PS (right).

The peak heights of the tan δ peaks, which were identified as $T_{g(blend)}$ in Figure 6, are plotted in Figure 7. For the PS and NaSPS10 blends, only the upper transition peak heights are shown, reflecting the PS- or NaSPS10-rich phases. In the immiscible blends, the tan δ peak heights of the PA-rich phase (not shown) decrease from a maximum of about 0.1 with decreasing PA-6 content in the blends. The cluster-phase peak heights (also not shown) usually remain constant at about 0.3. Figure 7 clearly shows that the variation of the peak heights with composition for the miscible blends is very different from that of the immiscible blends. In the immiscible (PS or NaSPS10) blends the peak heights increase continuously with PS or ionomer content. The miscible blends of LiSPS5 and LiSPS10, on the other hand, both show distinct maxima of the blend peak heights at compositions containing about 75% LiSPS5 and 70% LiSPS10. The tan δ peaks are also considerably narrowed at these compositions. For instance, the peak width at half-height is only 19 °C for the 70% LiSPS10 blend, while this value is 50 and 39 °C for the pure PA-6 and LiSPS10, respectively. This suggests that the blends are relatively homogeneous at these compositions. It is worth noting that the areas under the tan δ peaks parallel the trend shown by the tan δ peak heights.

Finally, it should be mentioned that the DSC results for the blends of LiSPS10 with PA-6, shown in Figure 1, differ from those reported recently for similar blends with a comparable lithium sulfonate content of LiSPS (10.1 mol%).[15] This can most probably be ascribed to differences in sample preparation and conditioning before scanning by DSC: in the present study, the blends were precipitated from solution, dried, and then conditioned in the DSC apparatus at 250 °C before recording T_g and T_m; in the study of Lu and Weiss,[15] blend films were cast from solution at 140 °C and dried at 90 °C before the DSC experiment. It was also reported that the blend containing 50% LiSPS10 phase separates after heating to 250 °C. This was not observed in this study, either by DSC or by DMTA (Figure 2).

Discussion

Polymer–Polymer Interactions. While PS and NaSPS10 are clearly immiscible with PA-6, throughout the entire composition range, the blends of LiSPS show strong interactions with PA-6, which results in the miscibility of both LiSPS10 and LiSPS5 at certain composition ranges. The decrease in interaction strength when going from a Li to a Na counterion is not entirely unexpected: in studies of the interaction between salts and model aliphatic amides, it has been found that Li ions interact most strongly among the alkali-metal cations;[23] cloud point curve measurements in blends of polystyrene ionomers with polypropylene oxide also show the decrease in interaction strength in the order Li > Na > K.[2] The counterion size and the charge density is, therefore, important in determining the interaction strength of the counterion. However, the result of going from a clearly immiscible blend to a miscible blend (on the 50–100-Å level) when the counterion is switched from Na to Li, as shown by Figure 2, could not have been predicted from these considerations alone.

Considerable insight into the interaction of LiSPS ionomers with PA-6 can be gained from studies on the interaction of LiCl with various amides. Earlier studies have shown that LiCl can interact strongly with amide solutions, and in some cases, a stable complex is formed.[24–27] For example, LiCl and *N*-methylacetamide (NMA) has been found to form a stable crystalline adduct. Crystallographic,[24] NMR, and infrared analysis[25] has shown that the Li ion is coordinated to four molecules of NMA at the carbonyl oxygen and that the Cl anion is hydrogen bonded with the amide hydrogen. This mode of interaction is generally supported by many studies on the interaction of LiCl with various aromatic as well as aliphatic polyamides.[28–31] Since it is improbable that lithium sulfonate and LiCl behave differently in their modes of interaction with PA-6, it is reasonable to expect that the Li ion of LiSPS also interacts at the carbonyl oxygen of the amide, with the sulfonate anion hydrogen bonded with the amide hydrogen. However, it should be pointed out that another interaction mechanism has been suggested, i.e. ion–dipole interaction between the Li cation and the amide nitrogen.[15] Further research in order to confirm the exact nature of the interaction is needed.

Blend Morphology. As shown by Figure 7, the tan δ peak height of the blend phase for the LiSPS10 ionomer blend reaches a maximum at around 70% ionomer content, which corresponds to a A/Li ratio of 4. It has been suggested that Li may coordinate to four amides in mixtures of LiCl salts with PA-6.[31] Although this may be possible in these blends too, the source of this maximum is most likely due to an optimization of two superimposable effects. Starting with pure PA-6 (0% ionomer), the addition of LiSPS10 ionomer decreases the total crystallinity of the blend because of the dilution of the crystalline PA-6 component, as well as the interaction of the LiSPS10 with the amides of the PA-6. This causes the E' to decrease and the tan δ (blend) peak height to increase with LiSPS10 addition (since tan $\delta = E''/E'$). At the other end of the composition scale, 100% ionomer has two phases: an unclustered phase and a cluster phase. The cluster phase of the ionomer increases E' due to the physical cross-linking by the lithium sulfonate groups, and this suppresses the measured tan δ peak height of the unclustered phase. The addition of PA-6 to the LiSPS10 ionomer disrupts the physical cross-linking effect of the cluster phase by interacting with some of the lithium sulfonate groups and thereby reduces E' and increases the measured height of the tan δ (blend) peak.

Since both these effects result in an increase of tan δ, starting with the respective pure materials, a maximum of tan δ is reached at some intermediate composition. The 70% ionomer blend represents a composition at which the combined disruption of the stiffening effects of the PA-6 crystalline and the ionomer cluster phases are at a maximum. Measurements of E'' and E', taken at the temperature of the tan δ (blend) peak positions, confirms that E' reaches a minimum at about 70% ionomer content (28 MPa vs 650 and 158 MPa for the pure PA-6 and LiSPS10, respectively), while E'' remains much less affected throughout the composition range (40–130-MPa range). Also, having eliminated the crystalline phase through the addition of LiSPS and having disrupted the cluster phase by the addition of PA-6, the 70% blend is now a one-phase material (within the experimental limits) with optimum phase purity. This is supported by the narrowing of the transition width at this composition (19 °C width at half-height of the tan δ peak as compared to 50 and 39 °C for pure PA-6 and LiSPS10, respectively). A similar though less distinct effect can be seen for the LiSPS5 ionomer blends where the tan δ peak heights reach a maximum for a blend containing about 75% LiSPS5.

A similar though less distinct effect can be seen for the LiSPS5 ionomer blends where the tan δ peak heights reach a maximum for a blend containing about 75% LiSPS5. It is worth noting that at this composition A/Li is about 6, which further suggests that the maximum in the tan δ peak heights is not directly related to the coordination number of the lithium and is rather due to the effects described above.

At this point it is instructive to compare the effects of PA-6 with low molecular weight diluents on the two transitions of the ionomer. It has been shown that polar and nonpolar diluents affect these transitions very differently: the addition of a nonpolar diluent, such as diethylbenzene, to a polystyrene ionomer is found to decrease the transition temperatures of both the unclustered and the cluster phases of the ionomer; on the other hand, a polar diluent, such as glycerol, has been found to decrease rapidly the cluster-phase tan δ peak height and to be much less effective in decreasing the unclustered-phase transition temperature.[32] Polar diluents also increase significantly the unclustered-phase transition tan δ peak height, as opposed to a decrease caused by nonpolar diluents. Figure 6 shows that the addition of PA-6 to both LiSPS5 and LiSPS10 causes the rapid decrease of the cluster-phase transition temperature ($T_{g(cl)}$) and a much more gradual decrease of the unclustered-phase transition temperature of the ionomer ($T_{g(blend)}$). This, together with the sharp increase of the tan δ (blend) peak height (Figure 7) with small additions of PA-6 to these ionomers, indicates that PA-6 acts in a way similar to a polar diluent. The addition of glycerol to polystyrene ionomers, as well as the addition of ethylene glycol to polyelectrolytes, increases the tan δ peak height at a rate of ca. 0.01/wt % diluent.[32,33] PA-6 increases the tan δ peak height at a rate of ca. 0.03- and 0.04/wt % PA-6 for the LiSPS5 and LiSPS10 ionomers, respectively. Polar diluents for ionomers and polyelectrolytes tend to narrow the transition width of the blend phase, while nonpolar diluents tend to broaden it.[32,34,35] As mentioned earlier, PA-6 addition to the LiSPS ionomers (up to 25 wt % PA-6) results in the considerable narrowing of the transition width. It can therefore be concluded that PA-6 acts as an effective polymeric polar diluent for the LiSPS ionomers. In contrast, PA-6 acts as neither a polar nor a nonpolar diluent for the NaSPS ionomer, being phase separated at all compositions.

Thermodynamics of Blending. As was pointed out in the Results, the dynamic mechanical measurements of the lithium ionomer blends show that miscibility thresholds exist, separating one- and two-phase regions. When the ionomer contains 9.8 mol % lithium sulfonate groups (LiSPS10), this miscibility threshold is between 10 and 30% ionomer content, while when the ionomer contains 5.4 mol % functional groups (LiSPS5), this miscibility threshold is found to be between 50 and 70% ionomer content. The compositions here refer to the amorphous blend compositions at 240–250 °C (total blend compositions). It must be kept in mind that these miscibility thresholds are based upon the DMTA measurements and therefore reflect the phase behavior on the 50–100-Å level. This phase behavior, together with the observed maximum in the T_g at 90% LiSPS10 content, can be given a theoretical interpretation. The thermodynamic treatment presented here is an approximate treatment; the limitations of DMTA and DSC in determining thermodynamic miscibility do not warrant a more fundamental approach. The derivations are merely presented to show that a simple unified treatment, even if based upon a few simplifying assumptions, can indeed correlate the miscibility thresholds and maximum in the T_g of the 90% LiSPS10 blend and, furthermore, allow some predictions to be made about the behavior of the ionomers with other ion contents.

The Gibbs free energy of mixing, ΔG_m, can be expressed in terms of the total heat of mixing, ΔH_m, and the total entropy of mixing, ΔS_m, as

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (1)$$

where T is the absolute temperature of the blend at which the miscibility is determined. For this analysis, the entropic term $-T\Delta S_m$ will be ignored due to the very low entropy of mixing for these high molecular weight polymers, relative to ΔH_m, as a result of which ΔG_m is expected to be dominated by ΔH_m. Thus, $\Delta G_m \approx \Delta H_m$. In the ensuing discussion, a negative free energy of mixing, ΔG_m, will be considered as a sufficient criterion for miscibility (see later for limitations of the analysis).

(A) Random Mixing. First, it will be shown that a random-mixing approach cannot predict a composition-dependent miscibility. Let PA-6 be polymer 1 and the ionomer be polymer 2. ξ is defined as the fraction of lithium-functionalized styrene units (LiS) of the ionomer, B_c as the interaction energy density associated with the complexing of a LiS unit with a PA-6 unit (PA), and B_s as the interaction energy density characteristic of a styrene unit–PA unit pair. It should be remembered that the PA and LiS units exist as associated species in the amorphous phase of pure PA-6 and LiSPS, respectively, and therefore B_c represents the interaction energy density of a LiS–PA complex relative to these associated species. Uninteracted LiS groups are assumed to remain self-associated in the blend, and therefore their contribution to the heat of mixing upon blending is zero. The random-mixing enthalpy ΔH_m for polymers 1 and 2 can now be written as a sum of two van Laar type expressions:[36]

$$\Delta G_m \approx \Delta H_m = B_c\phi_1\phi_2\xi + B_s\phi_1\phi_2(1 - \xi) \qquad (2)$$

Here ϕ_1 and ϕ_2 represent the volume fractions of segment units of polymers 1 and 2 in the blend and thus $\phi_1 = 1 - \phi_2$. The first term on the right reflects the contribution to ΔH_m due to the random contacts of lithium styrenesulfonate units with PA units, and the second term on the right represents the contribution due to the random interaction of styrene units (of the ionomer) with the PA units of PA-6. The $\phi_1\phi_2$ can be factored out and an effective interaction energy density, defined by $B = [B_c\xi + B_s(1 - \xi)]$, used to give $\Delta H_m = B\phi_1\phi_2$. The blend is immiscible when $\Delta G_m > 0$, and can only be miscible if $\Delta G_m < 0$. A composition-dependent miscibility therefore requires $\Delta G_m > 0$ for some values of ϕ_2 and $\Delta G_m < 0$ for others. Since B is independent of blend composition and $\phi_1\phi_2$ is always positive, the equation shows that the sign of ΔH_m, and hence ΔG_m cannot be determined by changes in the relative amounts of 1 and 2. Thus, in the absence of entropic effects, a random mixing approach cannot predict a composition-dependent miscibility of polymers 1 and 2.

The expression for ΔH_m given by eq 2 is similar to the equations developed to describe the miscibility of binary blands of random copolymers,[37–39] with the exception that the random intramolecular interactions of LiS with styrene units are not represented. As mentioned earlier, the LiS units are strongly self associated, both in the pure ionomer and in the blend (if uninteracted), and hence the incorporation of a random intramolecular interaction term in eq 2 would be unrealistic. However, even if such a term were included, the expression would still reduce to $\Delta H_m = B\phi_1\phi_2$, leading to the same conclusions as before.

(B) Nonrandom Mixing. Several theories have been recently developed to describe the miscibility of polymer blends where specific interactions take place.[40–45] The equation derived here has been specifically tailored to described the blend system under study but is similar to theories employing an equilibrium or quasichemical approach.[43–45] With the assumption that the interaction between the LiS units and the PA-6 units (PA) to be specific, and one to one, the equilibrium constant for the association of these two units to form an interacting LiS–PA complex is given by

$$\text{LiS} + \text{PA} \rightarrow \text{LiS–PA} \qquad (3)$$

$$K = \frac{[\text{LiS–PA}]}{[\text{LiS}][\text{PA}]} = \frac{(1/2)\phi_c V_r}{\{\phi_2\xi - (1/2)\phi_c\}\{\phi_1 - (1/2)\phi_c\}} \qquad (4)$$

where [LiS], [PA], and [LiS–PA] are the equilibrium molar concentrations of LiS, PA, and LiS–PA, respectively, while ϕ_c is the equilibrium volume fraction of the complex formed. $\phi_2\xi$ and ϕ_1 are the initial volume fractions of LiS and PA units, respectively. V_r is a reference volume and usually chosen so as to represent the molar volume of the smallest repeat unit, ca. 100 cm^3/mol, for polymeric blends.[46] V_r remains constant for the blend system and therefore $K_r = K/V_r$ will be used for convenience. The factor (1/2) arises in eq 4 because the molar volume of the complex is approximately twice that of the reference volume. Equation 4 can be solved for ϕ_c, and for any given set of K_r and ξ, ϕ_c is only a function of ϕ_2 (or ϕ_1). The equation for nonrandom mixing can now be written as

$$\Delta G_m \approx \Delta H_m = B_c(1/2)\phi_c + B_s\phi_2(1 - \xi)\{1 - \phi_2 - (1/2)\phi_c\} \qquad (5)$$

The first term on the right is the contribution to ΔH_m due

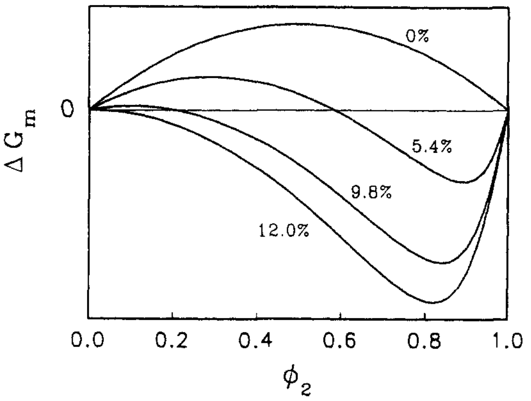

Figure 8. Predicted profile of ΔG_m using eqs 4 and 5 with $\beta = -7.5$ and $K_r = 25$ for blends of PA-6 with LiSPS ionomers having various mol % of functionalized units (as indicated).

to the formation of the LiS–PA complex upon mixing, while the second term reflects the contribution due to the random interaction of the styrene units of the ionomer with the uncomplexed PA units of the polyamide. For any given set of values for K_r, ξ, B_c, and B_s, the sign of ΔG_m, and hence miscibility of the blend are now found to be a function of ϕ_2. The miscible/immiscible threshold occurs at a composition $\phi_2 = \phi_2'$ where $\Delta G_m = 0$ ($\phi_2' \neq 0$; $\phi_2' \neq 1$). Thus ϕ_2' at the miscibility threshold must satisfy

$$0 = \beta(1/2)\phi_c + \phi_2'(1-\xi)\{1-\phi_2'-(1/2)\phi_c\} \qquad (6)$$

where $\beta = B_c/B_s$. For the LiSPS ionomer blends with PA-6, the lithium styrenesulfonate content of the ionomer, ξ, is known and the miscibility threshold composition, ϕ_2', can be reasonably well estimated from the results of the DMTA data. This leaves eq 6 as a function of β and K_r (since ϕ_c is determined by the value of K_r).

The two ionomer blends (LiSPS5 and LiSPS10) provide two sets of conditions for eq 6 ($\xi = 0.054$, $\phi_2' = 0.6$ and $\xi = 0.098$, $\phi_2' = 0.2$, respectively), and thus the two unknowns, β and K_r, can be estimated. Using an iterative calculating procedure, values of $\beta = -7.5$ and $K_r = 25$ fit the threshold miscibility ranges quite well. Note that ϕ_2 and the weight fraction w_2 of the ionomer in the blend are equivalent since the amorphous densities of the two polymers are about the same. It is also worth recalling that the miscibility thresholds used here are based upon the total blend compositions at 240–250 °C, i.e. between 10 and 30 wt % for LiSPS10 blends and between 50 and 70 wt % for the LiSPS5 blends.

The profiles of ΔG_m as a function of composition are shown in Figure 8 for various lithium sulfonate group contents of the LiSPS ionomer. As expected, ΔG_m is positive throughout the composition range for the unfunctionalized PS blends (0% in Figure 8), supporting the observed immiscibility of this blend at all compositions. On the other hand, the results of the analysis show that ΔG_m is negative throughout the composition range for an LiSPS ionomer having about 12 mol % lithium sulfonate groups, suggesting that this polymer may be miscible with PA-6 (on the DMTA scale) at all compositions. The LiSPS5 (5.4% curve) and the LiSPS10 (9.8% curve) ionomer blends are immiscible at compositions where $\Delta G_m > 0$, and as can be seen from the profile of the $\Delta G_m - \phi_2$ curves, these blends should phase separate into an essentially pure PA-6 phase and a blend phase. The composition of the blend phase can be expected to be close to the compositions at which ΔG_m is a minimum.

It is also worth noting that the assumed one-to-one association of the LiS with PA units does not imply that all the LiS are associated with amide units when there is a stoichiometric quantity of these groups in the blend. For instance, the LiSPS10 blend containing 90% ionomer has approximately stoichiometric quantities of the interacting groups, but by using the obtained $K_r = 25$ (and $\xi = 0.098$) and solving for ϕ_c, the fraction of interacted LiS ($0.5\phi_c/\phi_2\xi$) is only 0.56. The remaining uninteracted LiS units are self-associated in the blend, and this is also supported by the observed presence of a cluster phase at this composition by DMTA (Figure 6). At 70% ionomer content, the calculated fraction of interacted LiS increases to 0.86, leaving very few uninteracted LiS units available for the formation of a cluster phase, and consequently results in the inability of DMTA to detect such a phase at this composition.

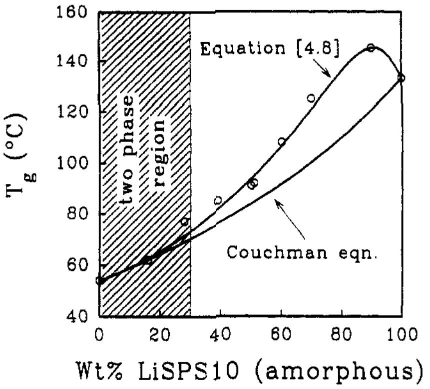

Figure 9. T_g of blends of PA-6 with LiSPS10 as determined experimentally by DSC (hollow circles), compared to that predicted by using eq 8 and the Couchman equation (solid lines).

(C) T_g Calculation. The blends of LiSPS10 ionomer with PA-6 show that there is a positive deviation of the blend T_g with composition, which reaches a maximum at 90% ionomer content (Figure 1). Several equations have been proposed to describe the variation of T_g with composition for miscible blends.[16,47–53] Some of these equations are capable of predicting a positive deviation of the T_g–composition curve from the rule of mixtures,[16,51–53] but only one of these is capable of directly relating this positive deviation of T_g to a thermodynamic parameter:[16]

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} - \frac{\chi R (T_{g2} - T_{g1}) b w_1 w_2}{\Delta C_{p1}(w_1 + k w_2)(w_1 + b w_2)^2} \qquad (7)$$

where χ is the Flory–Huggins interaction parameter, ΔC_{pi} is the heat capacity change at T_{gi} for polymer i, b is the ratio of the amorphous densities of the two polymers and $k = \Delta C_{p2}/\Delta C_{p1}$. This equation has been successfully applied to ionomer blends with PA-6,[16] and is used here because it can be easily modified to replace the implied random-mixing term $\chi R(T_{g2} - T_{g1}) b w_1 w_2$ with a nonrandom-mixing term based upon the equations from the previous sections. As mentioned earlier, the amorphous densities of the two polymers are about the same, so b can be taken as unity, which in turn reduces the $(w_1 + b w_2)$ term to unity. Furthermore, since $\Delta H_m = \chi R T w_1 w_2$, the expression for T_g can be rewritten as

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} - \frac{\Delta H_m (T_{g2} - T_{g1})}{\Delta C_{p1}(w_1 + k w_2) T} \qquad (8)$$

where T is the temperature at which miscibility is determined. This equation can now be used to predict the T_g for the LiSPS10 blends with PA-6 by using eq 5 for ΔH_m with $B_c = -7.5 B_s$ ($\beta = -7.5$), $T = 513$ K (240 °C), $K_r = 25$, $T_{g1} = 327$ K (54 °C), $T_{g2} = 407$ K (134 °C), $\Delta C_{p1} = 0.37$ J/(g K),[16] and $\Delta C_{p2} = 0.25$ J/(g K) (obtained from the DSC scans of pure LiSPS10). Figure 9 shows that a good fit to the DSC T_g data is obtained for the essentially amorphous blends (LiSPS10 contents ≥50 wt %) when $B_s = 120$ J/g ($B_c = -900$ J/g). The maximum at 90% ionomer content can thus be related to the blend interaction thermodynamics. Equations which do not take into account specific interactions, e.g. the frequently used Couchman equation,[47] do not predict this type of T_g behavior.

(D) Limitations of the Thermodynamic Treatment. The values for B_c and B_s appear quite large, and these numbers should only be taken as approximations of these interaction energy densities. While the ratio of these two values, β, can be expected to be reasonable, the magnitude of B_c and B_s is essentially determined by the fit of eq 8 to the experimental DSC data. The experimental limitations of DMTA and DSC and also the assumptions of the thermodynamic treatment are bound to introduce some errors in the values obtained.

While DMTA is limited to the resolution of phases which are at least 50–100 Å in size, the thermodynamic treatment ignores the second condition for a thermodynamically stable miscible blend: that the second derivative of the free energy with respect to composition be greater than zero ($\partial^2\Delta G_m/\partial\phi_2^2 > 0$). As can be seen from Figure 8, at $\phi_2 = 0.2$, for instance, the 12% curve is concave down (i.e. $\partial^2\Delta G_m/\partial\phi_2^2 < 0$), even though ΔG_m is negative, and therefore the blend, if miscible, is thermodynamically unstable. It must be remembered that the thermodynamic treatment does not take the connectivity of the polymer units into account (except by ignoring the entropic effects, of course), and this connectivity may only allow microphase separation to take place for blends where the thermodynamic driving force for phase separation is small, i.e. blends where $\partial^2\Delta_{Gm}/\partial\phi_2^2 < 0$ but close to $\partial^2\Delta G_m/\partial\phi_2^2 = 0$. Thus, while mathematically more complex, the location of the spinodal (compositions where $\partial^2\Delta G_m/\partial\phi_2^2 = 0$) would only really be useful if miscibility could be determined on the molecular level. It is worth noting that the limitations of DMTA and the exclusion of the strict miscibility condition of $\partial^2\Delta G_m/\partial\phi_2^2 > 0$ have the effect of balancing each other out, so that the simplified thermodynamic treatment may be closer to the true picture than one might expect.

The incorporation of the entropic term $-T\Delta S_m$ may also influence the profile of the $\Delta G_m - \phi_2$ curve, especially at the composition limits, but as mentioned earlier, the influence of this term is expected to be minimal for these polymer blends where strong interactions appear to dominate the miscibility behavior.

In the equation for the prediction of T_g (eq 8), ΔH_m is assumed to vary linearly with temperature, since its true temperature dependence is unknown. Although this may be a source of some error, it is not believed to be large. The ΔC_p values in eq 8 may also be a source of some inaccuracy, especially in blends with semicrystalline polymers, since the ΔC_p at T_g of some semicrystalline polymers is not always proportional to the fraction of amorphous phase present.[54] The ΔC_p of ionomers is also significantly reduced by the presence of ionic aggregation, and this is especially important at high ion contents.[55] These factors may have a substantial effect on the ratio k in eq 8 and may influence the T_g predicted for the semicrystalline, ion-containing blends studied here.

In the development of the equilibrium constant, the interaction between the LiS and the PA units is taken as one to one. Other A/Li ratios may also be possible, for example four to one, but the maximum in the T_g for the 90% LiSPS10 blend (A/Li = 1), suggests that a one to one interaction dominates the blend, at least at low PA-6 contents. The use of an equilibrium constant assumes an equilibrium state in the blend. Although the samples were held at 240–250 °C in the melt for 5–10 min and cooled relatively quickly, this may not have been adequate to establish an equilibrium state of the blends and to "freeze-in" the morphology. Since crystallization took place during the cooling of some of the blends, some rearrangement does obviously take place. However, the driving force and kinetics for crystallization can be expected to be much higher than for phase separation (or mixing) in the amorphous phase, and therefore the experiments most probably reflect closely the amorphous-phase morphology of these blends at 240–250 °C.

Despite these limitations, the trends shown by the very simple thermodynamic analysis are expected to remain valid. It demonstrates that the composition-dependent miscibility and the maximum in the T_g for the 90% LiSPS10 ionomer blend can be predicted by considering the interaction of the lithium sulfonate groups with the amide units in the blend to be specific and the interaction of the styrene with the amide units to be random.

Conclusions

The DSC and DMTA results clearly show that the choice of counterion (Li vs Na) is critical in determining the miscibility of polyamide-6 (PA-6) with sulfonated polystyrene ionomer. The lithium sulfonate group shows strong interaction with amide units of PA-6, most probably with the carbonyl oxygen of the amide, and this results in strong miscibility enhancement of the lithium sulfonated polystyrene (LiSPS) ionomer with PA-6. The sodium-neutralized ionomer, on the other hand, is immiscible with PA-6 at the same level of functionalization.

PA-6 shows the characteristics of an effective polymeric polar diluent for the LiSPS ionomer, which is seen as the progressive disruption of the cluster phase of the ionomer and the increase of the tan δ (blend) peak height with PA-6 content. At singular blend compositions, where the amide to lithium ratios are between 3 and 8, the tan δ (blend) peak height reaches a maximum and the transition width is also considerably narrowed. This composition represents a relatively homogeneous, single-phase blend at which the disruptions of the crystallinity and the cluster phase are at a maximum.

The miscibility of the LiSPS ionomer with PA-6 depends on both the lithium sulfonate content of the ionomer as well as the relative quantity of the blend components. A simple nonrandom-mixing approach is used to demonstrate that the miscibility behavior of these blends can be described by assuming a specific, nonrandom interaction of the lithium sulfonate groups with the amides and a random, unfavorable interaction of the styrene units with the amide units of PA-6. This simple thermodynamic treatment is incorporated into a recently proposed equation for the prediction of the T_g of blends, and it is shown that in this way the observed maximum in the T_g for the blend containing 90% LiSPS10 can be related to the specific interactions in the blend.

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Nomenclature

B	effective interaction energy density (J/g)
B_c	interaction energy density for the LiS–PA complex formation (J/g)
B_s	interaction energy density for a styrene unit–PA-6 unit pair (J/g)
b	ratio of the amorphous densities of the two polymers in the blend
ΔC_{pi}	heat capacity change at T_{gi} for polymer i (J/g K)
ΔG_m	Gibbs free energy of mixing (J/g)
ΔH_m	heat of mixing (J/g)
K	equilibrium constant (cm^3)
K_r	equilibrium constant normalized to V_r
k	$\Delta C_{p2}/\Delta C_{p1}$
LiS	lithium sulfonated styrene unit
LiSPS	lithium sulfonated polystyrene
NaSPS	sodium sulfonated polystyrene
PA	PA-6 unit
PA-6	polyamide-6
ΔS_m	entropy of mixing [J/(g K)]
T	temperature at which miscibility is determined (°C or K, as indicated)
T_c	crystallization temperature (°C)
T_g	glass transition temperature of blend (°C or K, as indicated)
T_{gi}	glass transition temperature of polymer i (°C or K, as indicated)
T_m	melting temperature (°C)
V_r	reference volume (100 cm^3)
w_i	weight fraction of polymer i in the blend
β	B_c/B_s
χ	Florry–Huggins interaction parameter
ϕ_i	volume fraction of polymer i in the blend
ϕ_c	volume fraction of LiS–PA complex in the blend
ϕ_2'	value of ϕ_2, between 0 and 1, where $\Delta G_m = 0$
ξ	fraction of ionomer units functionalized with lithium sulfonate groups

Supplementary Material Available: Table giving the analysis of the DMTA data (1 page). Ordering information is given on any current masthead page.

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