Blends of Polyamide-6 and Sulfonated Polystyrene. A Solid-State NMR Study

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ABSTRACT: Polymer blends of polyamide-6 (PA6) with polystyrene at 5.4% and 9.7% sulfonation levels (SPS5 and SPS10) were investigated by means of solid-state NMR techniques. In the measurement of proton spin–lattice relaxation of PA6 in the rotating frame, a double-exponential decay curve, corresponding to the relaxations of PA6 in the crystalline and the amorphous phases, was observed. When the blend was miscible with separated phases smaller than ca. 20 Å, the PA6 carbon magnetization displayed a single-exponential decay during the spin-lock time; the relaxation time was equal to that of polystyrene in the blend. It was found that the unfunctionalized polystyrene and the sodium salt of the sulfonated polystyrene were immiscible with PA6, but the lithium salt of the sulfonated polystyrene could be highly miscible with PA6 to such an extent that either the blend was completely homogeneous or the separated phases, if present, were smaller than ca. 20 Å. It is of particular interest that the miscibility of the blends of lithium sulfonated polystyrene and PA6 is dependent on the polymer ratio and the sulfonation level. Among the LiSPS5/PA6 and LiSPS10/PA6 blends at ratios of 70:30, 50:50, and 30:70, only the blends at 70:30 are highly miscible with separated phases smaller than ca. 20 Å. However, the blends at other polymer ratios are all miscible on the scale of ca. 200 Å, based on the measurements of proton spin–lattice relaxation in the laboratory frame. In combination with DMTA data, we conclude that the dimensions of the separated amorphous phases are between 50 and 200 Å for the LiSPS5/PA6 50:50 and 30:70 blends, while for the LiSPS10/PA5 50:50 and 30:70 blends they are between 20 and 100 Å. Annealing at 140 °C induced the formation of a PA6 crystalline phase in the LiSPS5/PA6 70:30 blend, while it had a minimum effect on the LiSPS10/PA6 70:30 blend.

Introduction

Polyamide (nylon) and polystyrene are both very important commercial polymers which have been used in a variety of products. It thus seems reasonable that the blends of polyamide and polystyrene may be of potential importance in many applications. The miscibility enhancement of polyamide-6 and polystyrene has been achieved recently in this laboratory[1-3] and in others,[4,5] by functionalizing 5–10% of the polystyrene repeat units with sulfonic acid groups. It has also been found that at certain blend compositions, when the sulfonic acids were converted into lithium salts, the sulfonated polystyrene became miscible with polyamide-6 to such an extent that only a single glass transition temperature was observed in a dynamic mechanical thermal analysis (DMTA) experiment.[1,3] This is generally considered to be an indication either that the material is homogeneous or, if it is phase-separated, that the sizes of the separated phases in the blend are smaller than ca. 100 Å. It is clear that additional information based on other experimental techniques which characterize miscibility on scales lower or higher than that of DMTA is needed in order to understand the polymer blends more completely. Once the conditions for miscibility on different scales are known, one can control the extent of mixing of the polymers for different purposes.

In recent years, solid-state NMR spectroscopy has played an important role in characterizing polymer blends,[6-10] following the pioneering work by McBrierty et al.[11] and by Stejskal et al.[12] The proton spin–lattice relaxation times in the rotating frame ($T_{1\rho}^{H}$) and in the laboratory frame (T_1^{H}) are related to the spin-diffusion process, with maximum path lengths of ca. 20 and ca. 200, respectively. Thus, if the two polymers share a common $T_{1\rho}^{H}$, which is usually on the order of a few milliseconds, the blend is miscible or the separated phases, if present, are smaller than approximately 20 Å. On the other hand, if a common T_1^{H}, which normally has a value of a few hundred milliseconds, is observed along with two $T_{1\rho}^{H}$ values for the two polymers, one can conclude that the blends, while miscible on a scale of 200 Å, are phase-separated on a scale of ca. 20 Å. Note that these interpretations are valid only when the two polymers have different $T_{1\rho}^{H}$ and T_1^{H} values before blending. It is thus obvious that solid-state NMR techniques, in combination with DMTA and DSC, can improve our understanding of polymer blends.

The situation becomes a little more complicated when one of the polymers is partially crystalline. The structure of solid polyamide-6 has been investigated by a variety of techniques, including X-ray diffraction[13,14] and solid-state NMR (^{1}H, ^{13}C, ^{15}N, and ^{2}H).[15-20] Two kinds of crystal structures, a thermodynamically stable α form and a less stable γ form, are normally observed. The α and γ forms are generally considered to be planar zigzag and helical structures, respectively.[18] The ^{13}C CP/MAS spectrum of polyamide-6 is dominated by the crystalline fraction due to its narrower line widths.[16] In the present study, two $T_{1\rho}^{H}$ values have been obtained from the proton relaxation decay curve of polyamide-6 in the rotating frame, corresponding to the spin–lattice relaxations in the crystalline phase and in the amorphous phase.

Miscibility enhancement has been observed in many polymer blends when ionic groups are introduced to one or to both components.[21,22] As a typical example given by Smith and Eisenberg, incorporation of small amounts of styrenesulfonic acid (ca. 5%) and 4-vinylpyridine (ca. 5%) onto a polystyrene and a poly(ethyl acrylate), respectively, can compatibilize the otherwise incompatible polystyrene and poly(ethyl acrylate).[23] In a polymer blend containing an ionomer and a polar polymer such as poly(ethylene oxide), ion–dipole interaction is generally responsible for the miscibility enhancement.[24,25] Copolymers of ethylene and methacrylic acid[26-28] were found to be miscible with polyamide-6, as a result of the interaction between the

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Table I
Characteristics of Polymers Used[1,3]

polymer	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	functional group content (mol %)
PA6	33	14	2.4	100
PS	225	105	2.1	0
LiSPS5	235	110	2.1	5.4
LiSPS10	243	114	2.1	9.8
NaSPS10	246	115	2.1	9.8

carboxylic groups and the amide groups. Miscible blends of poly(styrene-*co*-acrylic acid) and polyamide-6 were also reported very recently.[29] In these cases, the observation of a single glass transition temperature was taken as an indication of a miscible blend.

In the last few years, the miscibility of sulfonated polystyrene with polyamide-6 has been the subject of investigation for Molnár and Eisenberg in this laboratory[1-3] and for Lu and Weiss at the University of Connecticut.[4,5] It has been demonstrated, based on DMTA and DSC, that the miscibility of the lithium salts of sulfonated polystyrene with polyamide-6 is dependent on the composition of the blend and the level of sulfonation.[1,3] A single glass transition temperature was observed for lithium sulfonated polystyrene at 5.4% sulfonation when its fraction in the blend with polyamide-6 is higher than ca. 60% (w/w), while for lithium sulfonated polystyrene at 9.7% sulfonation, a single glass transition temperature was observed when its fraction in the blend is higher than ca. 30% (w/w).[1,3] This interesting phenomenon prompts us to explore the miscibility in blends of sulfonated polystyrene and polyamide-6 further by means of solid-state NMR.

Specifically in this paper, we present a solid-state NMR study of the polymer blends of lithium salts of sulfonated polystyrene (5.4% and 9.7% sulfonation) and polyamide-6 at different ratios. Blends of unfunctionalized polystyrene with polyamide-6 and the sodium salt of sulfonated polystyrene with polyamide-6 were also examined for comparison. The effects of annealing on the miscibility were investigated by means of NMR relaxation measurements. The NMR results were then compared with the DMTA results reported previously.[1,3] Proton spin–lattice relaxation times in the rotating frame ($T_{1\rho}^H$) and in the laboratory frame (T_1^H) were determined indirectly from high-resolution ^{13}C CP/MAS experiments.[12]

Experimental Section

Polystyrene (PS; Aldrich) and polyamide-6 (PA6; Aldrich) were purified by precipitation respectively from toluene into methanol and from formic acid into water. Sulfonated polystyrene samples were prepared using the method of Makowski et al.[30] The sulfonic acid contents were determined to be 5.4 and 9.7 mol % from titration, and the polymers were denoted as SPS5 and SPS10, respectively. Sodium and lithium salts of the sulfonated polystyrene were prepared by quantitatively neutralizing the sulfonic acid in solutions of 80:20 benzene/methanol with methanol solutions of sodium hydroxide and lithium hydroxide, respectively. The characteristics of the polymers used in this study are given in Table I.

The functionalized polystyrenes and PA6 were blended by dissolving 5% (w/v) of individual components into 80:20 *m*-cresol/methanol mixtures and then mixing them together under constant agitation. The polymer blends were obtained by precipitating these clear solutions, dropwise, into excess hexanes, and then transferring the precipitates to fresh hexanes and agitating for 1 day to extract residual solvents. The samples were filtered and dried under vacuum for 1 week at 140 °C. Irganox (Ciba-Geigy) in a 1% (w/w) methanol or acetone solution was added to the ground polymers as a stabilizer; its final content in the polymers was approximately 0.1% (w/w). The samples were further dried under vacuum for 2 days at 140 °C. The same procedure was also applied to the pure polymers in order to minimize the effect of sample preparation. The polystyrene/PA6 blend was prepared by the same procedure except that a *m*-cresol/toluene mixture was used as solvent. All the polymer samples used in the present study were subjected to a dynamic mechanical measurement on a Rheometrics dynamic analyzer RDA-II operating at 0.1–500 rad/s at 250 °C under nitrogen. After the measurements, the samples were cooled with air at room temperature. Rheological properties of these blends will be published in a separate paper.[31] Differential scanning calorimetry results, recorded on a Perkin-Elmer DSC II, indicate that after the rheology measurements the crystallinity of PA6 was ca. 40%, similar to that quenched at the maximum cooling rate setting of the DSC instrument (320 °C min^{-1}), while the crystallinity of PA6 obtained directly from solution precipitation is as high as ca. 70%.

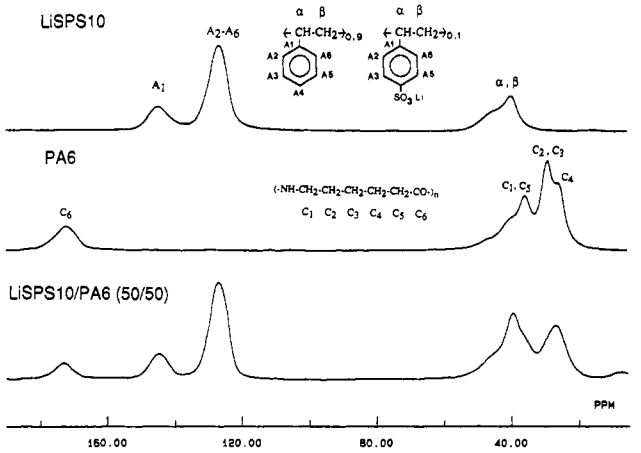

Figure 1. ^{13}C CP/MAS NMR spectra (25 MHz) of LiSPS10 (top), PA6 (middle), and LiSPS10/PA6 (50:50) (bottom).

NMR experiments were performed on Chemagnetics M-100 and CMX-300 spectrometers operating at field strengths of 2.35 and 7.05 T, respectively. The operational frequencies for ^{13}C and ^1H were 25.1 and 99.9 MHz, respectively, on the Chemagnetics M-100 spectrometer and 75.3 and 299.6 MHz, respectively, on the Chemagnetics CMX-300 spectrometer. Proton relaxation times, $T_{1\rho}^H$ and T_1^H, were determined from resolved ^{13}C resonances by means of cross-polarization transfer experiments.[11] For the measurements of $T_{1\rho}^H$, a variable delay was used before the fixed contact time while the protons were spin-locked. The proton spin-lock field strengths used were 50 and 55 kHz on the Chemagnetics M-100 and CMX-300 spectrometers, respectively. The dependencies of measured ^{13}C signal intensities on the delay times were fitted to a single- or double-exponential function. T_1^H values were measured by use of an inversion–recovery pulse sequence and calculated from a three-parameter fitting procedure. Typical pulse sequences used a 5-μs 90° pulse, a 1-ms contact time, 10–14 variable delays, and a pulse delay of at least $5T_1$. In these measurements, phase cycling was also used to minimize artifacts and samples were spun at the magic angle at 4–5 kHz. All the experiments were carried out at room temperature (20 ± 2 °C).

Results and Discussion

NMR Relaxation and Spin Diffusion. ^{13}C CP/MAS spectra of LiSPS10, PA6, and the LiSPS10/PA6 (50:50) blend are shown in Figure 1. The assignments of the spectra were made by comparison with solution spectra and were consistent with previous reports.[10,16] The ^{13}C signals of the aromatic carbons of polystyrene and the C_2–C_4 of PA6 were well separated from the others, which allows for the determination of the spin–lattice relaxation times of the individual polymers in the blends.

It is well-known that, in the solid state, spin energy can propagate between neighboring nuclei by an energy-conserving "flip-flop" process termed spin diffusion. As a result of the spin-diffusion process, a single spin–lattice

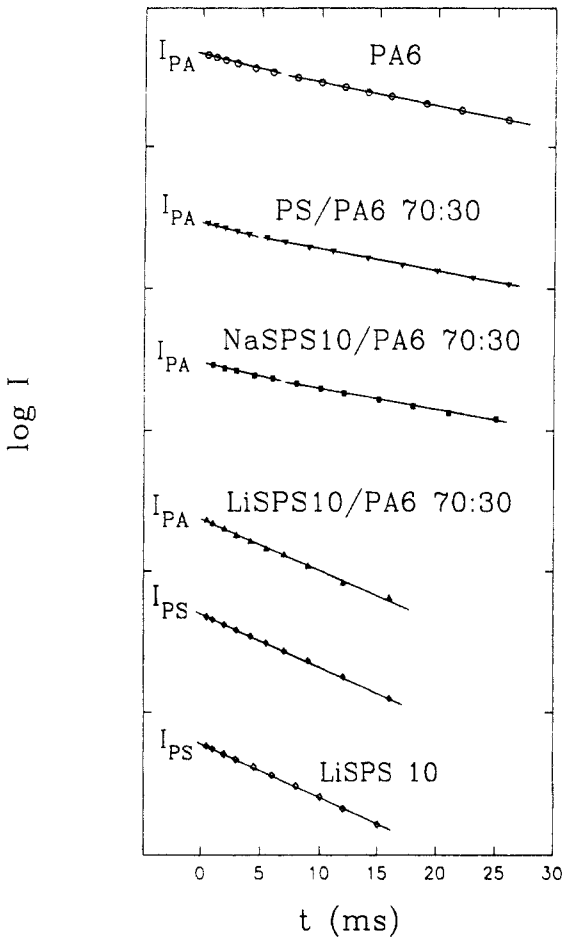

Figure 2. Plots of PA6 (C_2–C_4) and/or PS (A_2–A_6) carbon magnetization vs proton spin-lock time for PA6 (○), PS/PA6 70:30 (▼), NaSPS10/PA6 70:30 (■), LiSPS10/PA6 10:30 (▲ C_2–C_4 of PA6 and ♦ for A_2–A_6 of PS), and LiSPS10 (◇).

relaxation time is observed for strongly coupled nuclei which may be even located in different morphological regions. The maximum diffusion path length is related to the diffusion coefficient and the time over which the diffusion takes place. It can be estimated from the following equation:[11,21]

$$\langle L^2 \rangle = (t/T_2)\langle l_0^2 \rangle \quad (1)$$

where $\langle L^2 \rangle$ is the mean-square length over which the spin-diffusion process is effective, t is the time over which spin diffusion takes place, which is in the range of a few milliseconds for relaxation in the rotating frame or a few hundred milliseconds for relaxation in the laboratory frame, $\langle l_0 \rangle$ is the mean-square jump length which is taken to be the distance between neighboring protons, typically 0.1 nm. T_2 is the proton spin–spin relaxation time, which is normally around 10^{-5} s for polymers below their glass transition temperatures.[7] Therefore, the maximum diffusion path lengths for spin–lattice relaxations in the rotating frame (5 ms) and in the laboratory frame (0.5 s) are approximately 20 and 200 Å, respectively.

The decay curves of ^{13}C signal intensity on a logarithmic scale vs proton spin-lock time are given in Figure 2 for PA6, PS/PA6 70:30, NaSPS10/PA6 70:30, LiSPS10/PA6 70:30, and LiSPS10. A double-exponential decay is observed for the C_2–C_4 signals of pure PA6, which is attributed to the different proton relaxation rates in the amorphous and the crystalline regions. In the 70:30 LiSPS10/PA6 blend, the aromatic carbons of LiSPS10 and the C_2–C_4 of PA6 show an identical single-exponential decay, indicating that the separated phases, if present, are smaller than ca. 20 Å. In this blend, there is no evidence of crystallinity in the PA6, which is in agreement with DSC results. The slopes of the decay curves of the aromatic carbons of LiSPS10 in the pure polymer are higher than those of the C_2–C_4 of pure PA6 in the amorphous phase but lower than those of the C_2–C_4 of PA6 in the crystalline phase. In the LiSPS10/PA6 70:30 blend, the slopes of the decay curves for the aromatic carbons of LiSPS10 and the C_2–C_4 of PA6 are equal to those of the aromatic carbons of the pure LiSPS10. In general, the slopes of the decay curves, or the $T_{1\rho}^H$s, of both polymers in the miscible blends should appear as the proton weighted average of the slopes of the decay curves, or the $T_{1\rho}^H$s, of individual polymers before blending if the motions of both polymers in the blends remain the same as those in the pure form.[10,11] However, substantial deviations from this ideal model have been observed for most of the polymer blends since the motions and the orientations of individual polymers were perturbed due to the interactions between the two polymers.[9,10] Chu et al.[10] reported in a recent paper on polystyrene/poly(vinyl methyl ether) blends that at −5 °C the relaxation times in the rotating frame for both polymers are insensitive to blend composition between 60% < PS < 90% and equal to that of PS in pure polymer. It has also been observed recently that for the poly(vinylphenol)/poly(methyl acrylate) system, the relaxation times in the rotating frame of the polymer blends are longer than those of both components before blending.[32]

PS, NaSPS, and LiSPS in Polymer Blends with PA6. Also shown in Figure 2 are the decay curves of the C_2–C_4 signals of PA6 in the PS/PA6 70:30 blend. It is obvious that the double-exponential feature of PA6 remains in this blend. The $T_{1\rho}^H$ values of both components in the blend are exactly the same as those of LiSPS and PA6 in the pure forms, as shown in Table II. Moreover, in this blend, the T_1^H values of PS and PA6 are not equal, indicating that the microphases of PS and PA6 are greater than 200 Å. It is of interest that similar observations were also obtained for the 70:30 NaSPS10/PA6 blend. At the same polymer ratio, LiSPS10 and PA6 are miscible on a molecular scale, or the microdomain sizes are smaller than ca. 20 Å, while the blends of NaSPS10 or PS and PA6 are phase-separated, with domain sizes larger than ca. 200 Å. These results are in agreement with DMTA and DSC experiments which show two glass transition temperatures for both the NaSPS10/PA6 and the PS/PA6 blends. It has been suggested that the difference between LiSPS10 and NaSPS10 in blending with PA6 is due to the stronger interactions between lithium ions and PA6.[1,3] It has been reported that the addition of LiCl or LiBr to PA6 led to a depression of the melting temperature.[33,34] Among the alkali cations, Li^+ was found to interact most strongly with model aliphatic amides.[35]

Effect of the Polymer Ratio on Blend Miscibility. In the present study of the partially sulfonated polystyrene/PA6 blends, ion–dipole interactions were involved in the miscibility enhancement. The ionic content of the sulfonated polystyrene and the polymer ratio thus become important parameters which affect the miscibility of the polymer blend significantly. We have examined these effects by measuring $T_{1\rho}^H$ and T_1^H of the LiSPS10/PA6 and LiSPS5/PA6 blends at ratios of 70:30, 50:50, and 30:70. The relaxation decay curves of the C_2–C_4 signal intensities of PA6 in the rotating frame for LiSPS10/PA6 and LiSPS6/PA6 are given in Figure 3. It is of interest to find from Figure 3 that while the LiSPS10/PA6 70:30 blend shows a characteristic single-exponential decay of the miscible phase, a double-exponential decay curve

Table II
$T_{1\rho}^H$ and T_1^H Values of Sulfonated Polystyrene and Polyamide-6 (PA6) Blends

	$T_{1\rho}^H$ (ms)		T_1^H (s)	
	PA6	PS	PA6	PS
PA6	3.19 (22%),[a] 13.2 (78%)		0.50	
PS/PA6 70:30	3.30 (18%), 14.2 (82%)	5.76	0.67	1.53
NaSPS10		5.88		0.45
NaSPS10/PA6 70:30	3.67 (19%), 14.9 (81%)	5.96	0.46	0.86
LiSPS10		5.88		0.32
LiSPS10/PA6 70:30	5.62	5.89	0.58	0.59
LiSPS10/PA6 50:50	double-exponential	6.05	0.41	0.41
LiSPS10/PA6 30:70	triple-exponential	5.31	0.47	0.47
LiSPS5/PA6 70:30	5.86	5.85	0.58	0.57
LiSPS5/PA6 50:50	triple-eponential	5.66	0.50	0.50
LiSPS5/PA6 30:70	3.34 (23%), 12.8 (77%)	5.75	0.48	0.49
PA6[b]	4.74 (24%), 19.6 (76%)			
LiSPS10/PA6[b] 70:30, after 4 days annealing at 140 °C	9.04	7.46		
LiSPS5/PA6[b] 70:30, after 4 days annealing at 140 °C	20.2	7.02		

[a] The weight fraction obtained from the double-exponential fitting procedure, which does not necessarily indicate the fraction of PA6 in the crystalline or amorphous phase. [b] Measured at a proton spin-lock field strength of 55 kHz (CMX-300); all the others were measured at a proton spin-lock field strength of 50 kHz (M-100).

is observed for the LiSPS10/PA6 50:50 blend. This double-exponential decay very likely corresponds to the relaxations of the unmixed PA6 protons in the amorphous phase and in the phase mixed with LiSPS10, indicating that at this blend ratio these two polymers are not completely miscible, with separated phase dimensions larger than ca. 20 Å. The separation of these two polymers becomes more obvious when their ratio reaches 30:70, as indicated in Figure 3. Another exponential function appears in the decay curve, in addition to the two mentioned previously. This third exponential function corresponds to the PA6 in the crystalline phase. It may be easier to visualize the third component by comparing the slope with that of the pure PA6 in the crystalline phase. DSC and DMTA measurements also clearly indicated that the crystalline phases exist in the LiSPS10/PA6 30:70 blend but not in the LiSPS10/PA6 70:30 and 50:50 blends.[1,3]

Going from LiSPS10 to LiSPS5, the reduction in the ion content results in a substantial decrease in the miscibility of these two polymers. While the LiSPS5/PA6 70:30 blend in Figure 3 displays a single-exponential decay, a triple-exponential decay is observed for the LiSPS5/PA6 50:50 blend, corresponding to the PA6 in the amorphous and crystalline phases, as well as in the mixed phase with LiSPS5. The decay curve for PA6 in the LiSPS/PA6 30:70 blend is double-exponential, similar to that of pure PA6, which is due to the presence of a higher percentage of PA6 in the crystalline phase. The presence of crystalline domains in these two blends is consistent with the DSC and DMTA results.[1,3]

The spin–lattice relaxation times in the laboratory frame for these polymer blends are also given in Table II. It is clear that all these LiSPS/PA6 blend samples with

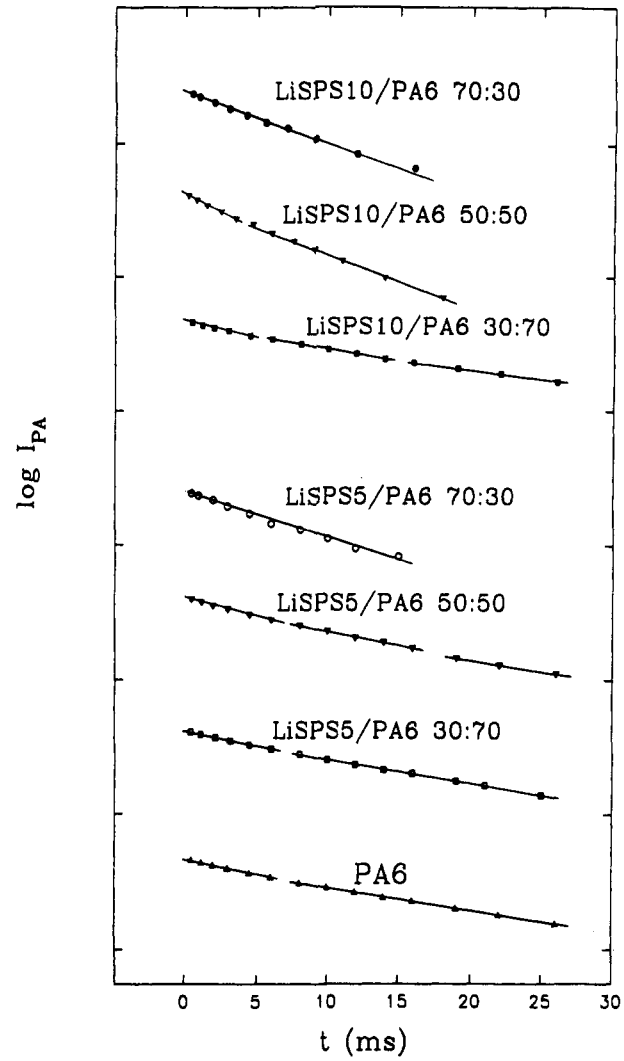

Figure 3. Plots of PA6 (C_2–C_4) carbon magnetization vs proton spin-lock time for the LiSPS10/PA6 70:30 (●), LiSPS10/PA6 50:50 (▼), LiSPS10/PA6 30:70 (■), LiSPS5/PA6 (○), LiSPS5/PA6 50:50 (▽), and LiSPS5/PA6 30:70 (□) blends and PA6 (▲).

different ionic contents and different ratios are miscibile on a scale of 200 Å, even when some PA6 is present in the crystalline domains.

Comparison with DMTA Results.[1,3] The combination of the NMR $T_{1\rho}^H$, T_1^H, and DMTA results allows us to characterize the miscibility of polymer blends on three different scales. Generally, DMTA is considered to be sensitive to separated phases with sizes in the range of 50–100 Å. On the other hand, NMR relaxation measurements in the rotating frame and in the laboratory frame are informative about the phase domains of ca. 20 and ca. 200 Å, respectively. For LiSPS10/PA6 at ratios equal to or higher than 30:70, only one tan δ peak was observed in DMTA, while in the present NMR study the 30:70 and 50:50 blends exhibit triple- and double-exponential decays, respectively, in the $T_{1\rho}^H$ measurements. These results imply that the sizes of separated domains in the 30:70 and 50:50 LiSPS10/PA6 blends fall into the range of 20–100 Å. For the LiSPS5/PA6 blends with ratios equal to or less than 50:50, two tan δ peaks can be identified in DMTA. In the NMR measurements of these blends, the T_1^H values of LiSPS5 and PA6 are equal within experimental error, indicating that the dimensions of the separated phases are smaller than 200 Å. It is clear, based on the DMTA and NMR data, that the sizes of the separated phases in these blends are between 50 and 200 Å. Miscibility diagrams of LiSPS10/PA6, LiSPS5/PA6, NaSPS10/PA6,

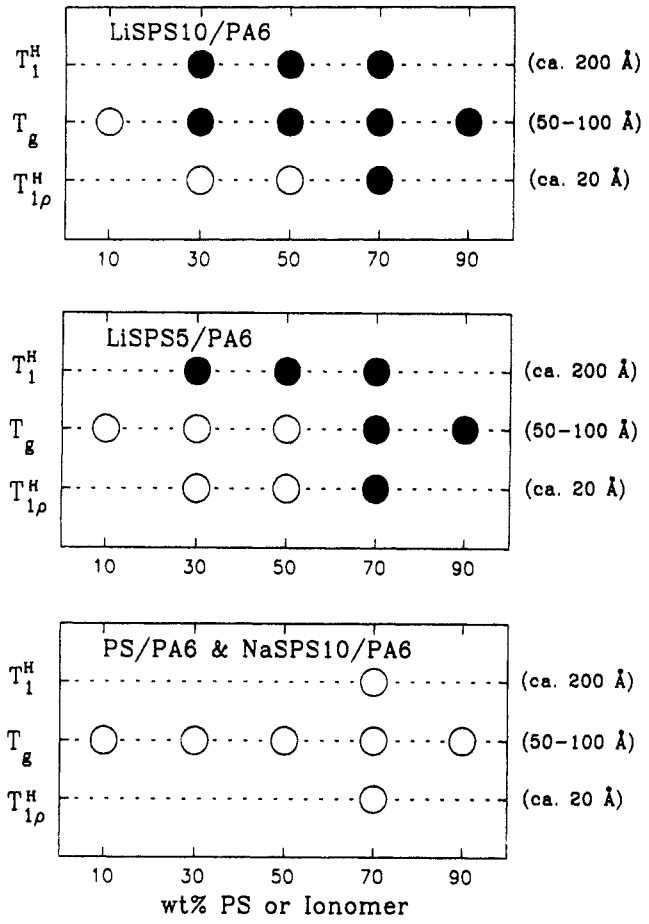

Figure 4. Miscibility diagrams of LiSPS10/PA6, LiSPS5/PA6, NaSPS10/PA6, and PS/PA6. The open and filled symbols represent multiple- and single-phase systems, respectively.

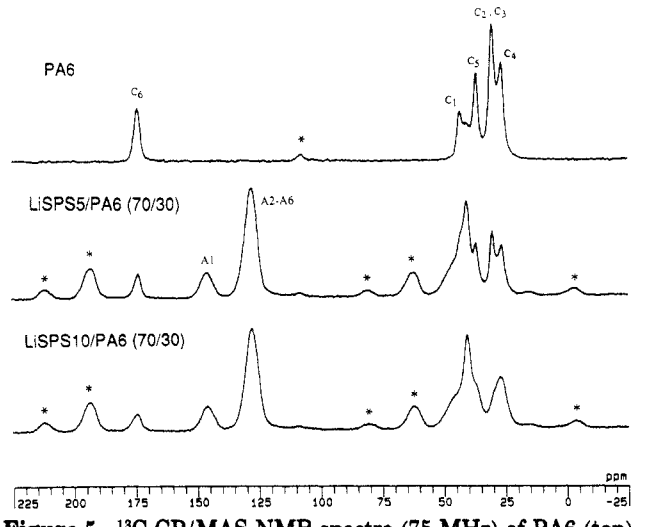

Figure 5. ^{13}C CP/MAS NMR spectra (75 MHz) of PA6 (top), LiSPS5/PA6 (70/30) after annealing at 140 °C (middle), and LiSPS10/PA6 (70/30) after annealing at 140 °C (bottom). Asterisks denote spinning sidebands. The other symbols used are the same as those in Figure 1.

and PS/PA6 based on the DMTA (T_g) and NMR results ($T_{1\rho}^H$ and T_1^H) are given in Figure 4. One should also bear in mind that DMTA results only reveal miscibility in the amorphous phase.

Effect of Annealing. ^{13}C NMR spectra of LiSPS10/PA6 70:30 and LiSPS5/PA6 70:30 blends, after 4 days of annealing at 140 °C, are given in Figure 5. The C_4 resonance of nylon 6 is clearly shown in the LiSPS5/PA6 70:30 spectrum at 24 ppm,[17,18] which is characteristic of crystalline PA6 in the α form.[18] Also, in this blend, all the ^{13}C resonances of PA6 are quite narrow, as compared to those from polystyrene. On the other hand, for the LiSPS10/PA6 70:30 blend, the C_2–C_4 resonances overlap and only a broad peak is observed at 28 ppm, indicating that a minimum amount of α form crystalline PA6 is present in the blend. Spin–lattice relaxation times in the rotating frame were also measured for these two samples, and the results are given in Table II. For the LiSPS5/PA6 blend, single-exponential decays were observed for both PA6 and polystyrene protons in the rotating frame, and the $T_{1\rho}^H$ values for LiSPS5 and PA6 were determined to be 7.05 and 20.2 ms, respectively. The single relaxation in the rotating frame for PA6, with a relaxation time of 20.2 ms, clearly indicates that a very large fraction of PA6 in the blend was converted to the crystalline form during the annealing process. However, for the LiSPS10/PA6 blend, both the LiSPS10 and the PA6 signals display single-exponential decays in the rotating frame with relaxation times of 7.45 and of 9.04 ms, respectively. The slightly higher relaxation time for PA6 may be due to the conversion of a small amount of PA6 from the miscible phase to the crystalline phase. Please note that, as was mentioned in a previous section, the LiSPS5/PA6 70:30 and LiSPS10/PA6 blends were found to be miscible on a 20-Å scale before annealing, with the $T_{1\rho}^H$ values of LiSPS and PA6 being equal within experimental error. The annealing experiments also confirm our earlier assignments of the PA6 relaxation times in the rotating frame; i.e., the longer relaxation time belongs to the protons in the crystalline phase.

As reported in a previous paper, the crystallization temperatures of PA6 in the LiSPS5/PA6 and LiSPS10/PA6 blends decreased as the sulfonated polystyrene contents increased,[3] indicating that LiSPS10 is more effective than LiSPS5 on the depression of the crystallization temperature of PA6. The substantial difference in crystallinity between the LiSPS5/PA6 70:30 and the LiSPS10/PA6 70:30 blends after annealing may be related to the different decomplexation temperatures. However, no decomplexation endotherms, as reported by Simmons and Natansohn[36] on the blends of (*N*-ethylcarbazol-3-yl)-methyl acrylate and 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate, were observed for these sulfonated polystyrene and PA6 blends in DSC measurements. The difference in crystallinity may also be due to the fact that the sequential free repeat units of PA6 in the LiSPS5/PA6 70:30 blend are long enough to initiate a crystallization process, while this is not the case for the LiSPS10/PA6 70:30 blend. In the LiSPS10/PA6 70:30 blend, the ratio between the ionic groups in LiSPS10 and the amide groups in PA6 is approximately 1:4, while in the LiSPS5/PA6 70:30 blend, this ratio is approximately 1:8. If 1:1 binding between the ionic group and the amide group is assumed, there are, on average, 7 free repeat units of PA6 in sequence in the LiSPS5/PA6 70:30 blend. In contrast, there are only, on average, 3 sequential free repeat units of PA6 in the LiSPS10/PA6 70:30 blend. Generally, ca. 8 sequential free repeat units are considered necessary for crystallization to occur.

Conclusions

On the basis of the NMR measurements of the ^1H spin–lattice relaxation time in the rotating frame ($T_{1\rho}^H$) and in the laboratory frame (T_1^H), we find that in 70:30 LiSPS5/PA6 and LiSPS10/PA6 70:30 blends, the two polymers are highly miscible and the separated domains, if present, are smaller than 20 Å, while for PS/PA6 and NaSPS10/PA6 at the same ratio, the two components in the blends

are not miscible with separated phase dimensions larger than 200 Å. The miscibility of LiSPS5 or LiSPS10 with PA6 in these blends depends significantly on the ratio of the two polymers. At the ratio of 30:70 or 50:50, the blends of both SiSPS5/PA6 and LiSPS10/PA6 are not miscible on the scale of 20 Å ($T_{1\rho}^{H}$), but are miscible on the scale of 200 Å (T_1^{H}). From comparison with earlier DMTA data,[1,3] we can conclude that the separated amorphous phases in the 30:70 and 50:50 LiSPS5/PA6 blends are within 50–200 Å, while those in the 30:70 and 50:50 LiSPS10/PA6 blends are within 20–100 Å. Annealing at 140 °C had a significant effect on the 70:30 LiSPS5/PA6 blend; most of the PA6 in the blend was found to be converted to a crystalline phase. On the other hand, for the 70:30 LiSPS10/PA6 blend, only a very small fraction of the PA6 was converted to the crystalline phase after annealing at 140 °C.

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