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^{7}Li static and MAS n.m.r. studies on blends of polyamide-6 and lithium sulfonated polystyrene ionomers

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Abstract

^{7}Li nuclear magnetic resonance (n.m.r.) spectra obtained in static mode were used to characterize blends of polyamide-6 (PA6) and lithium sulfonated polystyrene ionomers (LiSPS) with 5.4 and 9.7 mol% sulfonate groups; for the blends with the higher degree of sulfonation a linear relation was found between full n.m.r. line width at half-maximum (FWHM) and the glass transition temperature (T_g, as determined by differential scanning calorimetry, d.s.c.). Magic angle spinning (MAS) spectra were also recorded and it was shown, in particular, that the line width of the central transition provides information on polymer miscibility on a scale smaller than 2 nm. Based on simulations of the ^{7}Li spectral data, it is suggested that three lithium species are present, whose concentration is determined by the sulfonated polystyrene/PA6 ratio in the blend; the miscibility of the blend is shown to be mainly correlated with one of the species. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Ionomer; Polyamide; Miscibility

1. Introduction

Since the demonstration in 1983 [1] that ion–ion interactions can be used very effectively to control the miscibility of otherwise immiscible polymers, a large number of papers have been devoted to the topic. One of the blends that has recently been studied quite extensively involves sulfonated polystyrenes (SPS) and one of the polyamides (PAs). Molnár and Eisenberg showed that while styrene-*co*-styrene sulfonic acid copolymer could be mixed very effectively with polyamides, with the miscibility enhancement resulting from proton transfer, the sulfonic acid was found to lead to chain scission at elevated temperatures [2,3].

Lithium sulfonated polystyrene (LiSPS) was also found to show effective miscibility enhancement. In addition, the neutralized sulfonated polystyrenes are not involved in bond scission at elevated temperatures. A number of studies were devoted to the specific miscibility enhancement mechanism involved in SPS salts, including mechanical property studies [2–4], and infra-red studies [5]. A number of other investigations of the PA-6/SPS system have been carried out, in which various counterions were employed [6–8] as well as other PAs [9,10]. A lower critical solution temperature (LCST) type behaviour was also found for a number of PA-6/SPS blends [8]. Because of the commercial interests in materials of this type, it is not surprising that the melt rheology was also investigated [11]. In contrast to the miscibility enhancement found in the lithium sulfonated polystyrene as well as a number of transition metal ions, it was seen that the sodium sulfonated polystyrene, in general, does not lead to miscibility enhancement [2,4,5,11,12]. This was ascribed to the weak interaction between the Na$^+$ ion and the amide groups, which is unable to interact strongly enough with the amide group to leave the sulfonate environment [5].

Nuclear magnetic resonance (n.m.r.) is a powerful tool to study the miscibility of polymer blends at a molecular level. For example, a recent n.m.r. study on compatibilization mechanisms between polystyrene (PS) and polyamide-6 (PA6) by functionalizing 12–14% of PS repeat units with Li$^+$ sulfonate groups was presented, based on ^{7}Li observation, and changes in microphase separation of the two blend

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components were observed [13]. Miscibility n.m.r. studies using techniques like ^{13}C CP/MAS have already been reported on PA6 and sulfonated polystyrene (5–10% sulfonated) [12]. Depending on the counterion (Li^+ or Na^+), different results were obtained on the degree of mixing. In the present paper, new evidence on the role of the counterion is presented, through the observation of lithium nuclei, specifically the ^{7}Li isotope, in the static or in the MAS mode at magnetic field strengths of 7.0 or 9.4 T.

^{7}Li is a 3/2 spin nucleus, with a small quadrupole moment ($eQ = -4.5 \times 10^{-30}$ m^2) and a small chemical shift range (ca. 6 ppm). The chemical shift anisotropy (CSA, represented by the shielding tensor σ with σ_{XX}, σ_{YY} and σ_{ZZ} as eigenvalues) results from the coupling of the nuclear spin with the magnetic field, shielded by the electrons. The interaction between the nuclear quadrupole moment (eQ) and the electric field gradient at the nucleus (EFG described by the tensor $\mathbf{V}$ with V_{XX}, V_{YY} and V_{ZZ} as eigenvalues) produces the quadrupolar interaction. In the polymer blend, the ensemble of Li^+ ions experiences a distribution of EFGs. The lone-pair electrons from SO^{3-} group in sulfonated PS or from the carbonyl group in PA6 contribute to the EFG, therefore the mobility of either the Li^+ or of the polymer backbone will influence the n.m.r. spectra. Among the few reports on ^{7}Li MAS n.m.r. observation from polymeric materials, those on polymer electrolytes should be mentioned where, in particular, it was pointed out that ^{7}Li line widths could be used as an indicator of the glass transition temperature (T_g) (see for instance Ref. [14]). However, as far as we know, this is the first report on ionomer blends that correlates differential scanning calorimetry (d.s.c.), dynamic mechanical thermal analysis (DMTA) and ^{7}Li n.m.r. results, including also the first simulation of ^{7}Li spectral data reported on polymeric materials in order to extract the relevant parameters related to the distribution of electric charge in the surroundings of the nuclei.

2. Experimental

The LiSPS and PA6 blends were prepared according to the method already described [4]. For the synthesis of the lithium ionomer, polystyrene functionalized with sulfonic acid to 5.4 or 9.7 mol%, and quantitatively neutralized with lithium hydroxide (LiSPS5 and LiSPS10) was used. The polymers (LiSPS/PA6) were blended in the following proportions (w/w): 10/90, 30/70, 50/50, 55/45, 70/30 and 90/10.

N.m.r. experiments were performed on a MSL 300 Bruker spectrometer, operating for the observation of ^{7}Li resonances at 116.6 MHz; the data recorded at 155.5 MHz, and shown in Table 1, were obtained using an ASX 400 Bruker spectrometer. A single RF pulse was used for the static or magic angle spinning (MAS) spectrum acquisition, with typical parameters for pulse width and delay between pulses of 1 μs (corresponding to a 45° tip) and 1 s, respectively. High-power proton decoupling was occasionally used. Spinning rates were selected in the range 3–15 kHz, and are indicated in the text for each experiment. As an external reference for the chemical shifts, a LiCl (aq) solution (0 ppm) was used. All the spectra were obtained at the probe temperature ($\approx$ 293 K). Spin-lattice relaxation times were obtained from exponential fits to the signal intensities, measured in spectra run with different relaxation delays (from 100 μs to 8 s). MAS spectra were simulated using the program QUASAR [15], after the introduction of the experimental data as the program input.

3. Results and discussion

^{7}Li spectra from LiSPS/PA6 blends were acquired in the static mode, without proton decoupling, and only one signal with an asymmetric shape was identified in all the cases. Fig. 1 shows the variation of the full width at half-maximum (FWHM) of the n.m.r. signal as a function of the ionomer concentration in the blends. In Fig. 1, the minimum FWHM value is assigned to the LiSPS10/PA6 blend containing 90% ionomer; on the other hand, concerning LiSPS5 data, the narrowest line was obtained for the pure ionomer.

Using d.s.c. and DMTA measurements [4], it was previously reported that the glass transition temperature (T_g) of the LiSPS10/PA6 blends increases smoothly with the ionomer content, reaching a maximum precisely for the blend with 90% ionomer (145°C)[4]. We report here that a correlation was found between the FWHM of the single resonance in ^{7}Li static spectra from the LiSPS10/PA6 blends and the T_g (from d.s.c. data) [4]. A linear fit to the experimental data, plotted in Fig. 2, yields:

$$^{7}\text{Li Line width (Hz)} = -30T_g\ (^{\circ}\text{C}) + 5660$$

It is worth noting that the observation by DMTA of a single

Table 1
The FWHM (Hz) measured for the single line and for the central line from ^{7}Li static and MAS spectra, respectively, obtained from LiSPS10/PA6 with the composition 50/50 (w/w)

116.6 MHz			155.5 MHz				
Static	MAS/kHz		Static		MAS/kHz		
	3	10			3.5	9.5	15
1960	290	150	2150	900[a]	470	230	< 230

[a] Run with proton decoupling

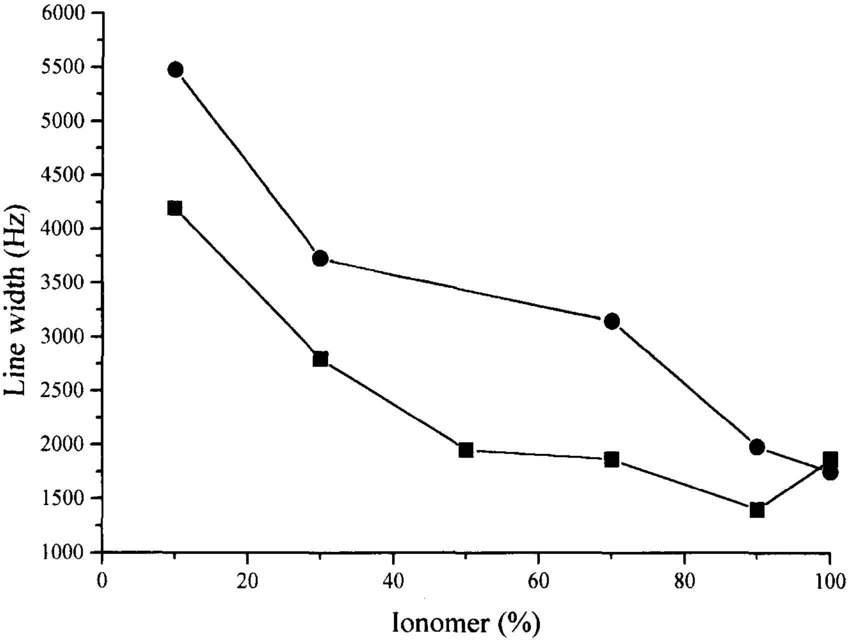

Fig. 1. Plot of the FWHM of the single ^{7}Li resonance obtained in the static mode, without proton decoupling, from LiSPS5/PA6 (●) and LiSPS10/PA6 (■) polymer blends. The lines are guides to the eye.

T_g for the LiSPS10/PA6 blends, containing at least 30% ionomer, is expected for a material not microphase separated on the 5–10 nm level [4].

In the next step, ^{7}Li static spectra were recorded with proton decoupling (not shown); it was found that the line width remains approximately constant for all the blends (770 ± 20 Hz), except the one containing 10% ionomer (840 Hz). This result indicates that the correlation between the ^{7}Li line width and the T_g is determined by Li–H dipolar interaction. It must be pointed out here that the results shown in Figs 1 and 2 cannot be explained on the basis of differences in the degree of crystallinity of the samples, involving only polyamide domains, because T_g is only relevant for the amorphous phases. In fact, from DSC measurements, a degree of crystallinity less than 1% was obtained for the LiSPS10 50/50; for compositions higher than 50%, the blends are amorphous, the crystallization process of PA6 being hindered by the ionomer [4]. It would be reasonable to expect a ^{7}Li line narrowing effect when the T_g decreases, following the increase in non-cooperative motions of the polymer chains; on the contrary, the correlation between T_g and ^{7}Li n.m.r. data reported here can only be explained on the basis of the increasing concentration of restricted mobility domains with the increasing of PA6 content.

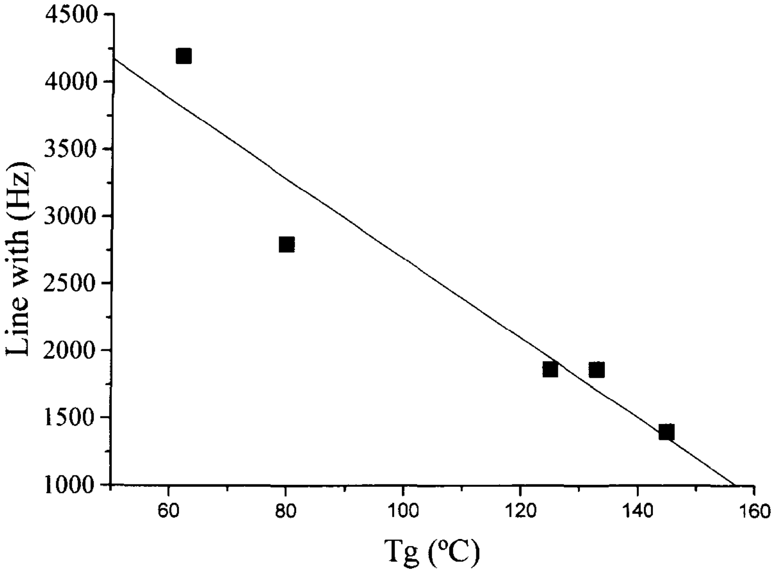

Fig. 2. The lithium resonance FWHM obtained in the static mode, without proton decoupling, versus T_g of the observed samples, LiSPS10 ionomer (133°C) and LiSPS10/PA6 blends, as determined by d.s.c.[4]. The line corresponds to a fit of the data to the linear expression described in the text.

An estimate of the dipolar coupling constant (DCC) between lithium and proton nuclei can be extracted from the observed decrease of the line width in the presence of RF proton irradiation. The approximate value of the averaged distance, r, between the lithium and the protons can thus be obtained. In the static mode, for the blend with 10% ionomer, we found a decrease of *ca.* 3.4 kHz, while for the blend with 90% ionomer the observed value is only 0.6 kHz; using the expression $\mathrm{DCC} = \gamma_H\gamma_{Li}/r^3$ (with γ_H and γ_{Li} representing the gyromagnetic ratios of proton and lithium nuclei, respectively), we have obtained an average lithium–proton interatomic distance of 0.42 nm and 0.25 nm for the blends containing 90% and 10% ionomer, respectively.

The influence of decoupling the protons from the lithium nuclei was also observed in ^{7}Li MAS spectra for the LiSPS10/PA6 blends. Fig. 3 shows a typical ^{7}Li MAS spectrum obtained with a spinning rate of 6 kHz, with proton decoupling, from the LiSPS10/PA6 blend at a composition of 30/70. Without proton decoupling, the FWHM of the central line obtained with a spinning rate of 6 kHz, increases monotonously with the PA concentration in the blend: from 407 Hz (PA6 = 10%) to 661 Hz (PA6 = 90%). On the other hand, ^{7}Li central lines with similar FWHMs (344 ± 12 Hz) were observed in the spectra of all the blends, run with the same MAS rate but in the presence of a RF decoupling field. Comparing this value with the one obtained in static mode (ca. 800 Hz) we verified that MAS at 6 kHz induced a line narrowing of ca. 450 Hz.

When the protons are decoupled, not only a second-order quadrupolar line broadening and a chemical shift distribution can explain the residual line broadening for the central $+1/2 \rightarrow -1/2$ transition, lithium isotropic motion not being fast enough to give optimal narrowing also needs to be taken into account; in which case MAS is only effective if the spinning rate is much higher than the molecular motion. In MAS spectra, first-order quadrupolar interaction and chemical shift anisotropy can both contribute mainly to the intensity of spinning side bands (SSBs) assigned to the satellite transitions.

MAS experiments at 10 kHz were also performed on LiSPS5 and LiSPS10 ionomers and on the blends with PA6, in the absence of proton decoupling. When comparing the intensities of the SSBs of the normalized spectra obtained from the LiSPS10 blends, it was clearly observed a minimum for the intensities of the SSBs in the spectrum of the blend containing 90% ionomer; this was not the case in the corresponding spectra obtained from LiSPS5 blends (not shown). The variation of the line width of the central transition observed in the spectra from the LiSPS5 and LiSPS10 blends as a function of the corresponding ionomer content is plotted in Fig. 4. For the samples with 5.4% sulfonation the line width of the central signal from the pure ionomer and from the blends (with an ionomer composition ranging from 30 to 90%) remains constant. Since the chemical shift anisotropy is averaged out and the second-order quadrupolar interaction is expected to be very small, this fact means that the Li–H dipolar interaction must be similar in all these samples. On the other hand, for the samples with 9.7% sulfonation, a variation of the line width with the ionomer content is observed; a minimum value is reached for the blend containing 90% ionomer.

The results concerning miscibility studies based on measurements of T_g[4] or spin–lattice relaxation times in the

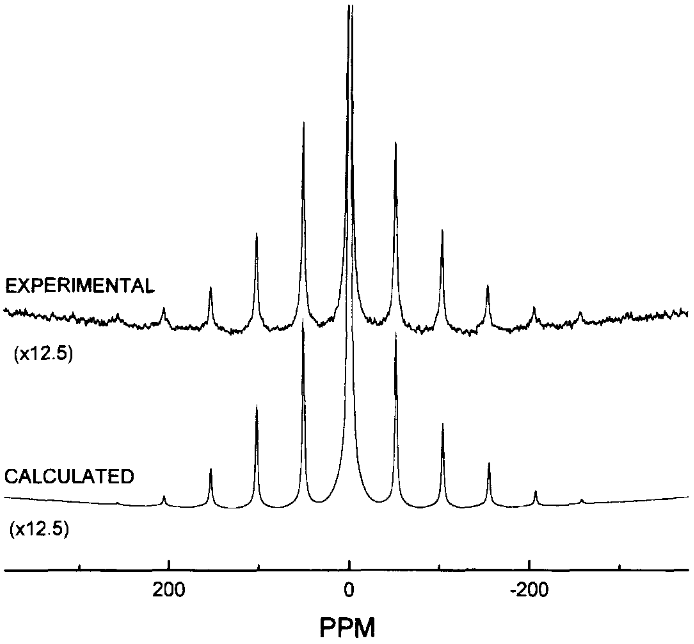

Fig. 3. Experimental and simulated ^{7}Li MAS spectra obtained with a spinning rate of 6 kHz, with proton decoupling, from the LiSPS10/PA6 polymer blend with a composition of 30/70 (w/w).

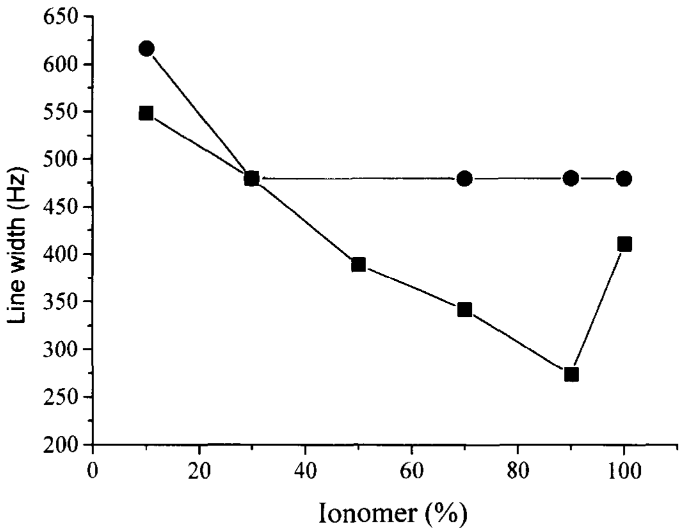

Fig. 4. Plot of the FWHM of the central line observed in ^{7}Li MAS spectra obtained with a spinning rate of 10 kHz (without proton decoupling) from the LiSPS5/PA6 and LiSPS10/PA6 blends versus the amount of LiSPS5 (●) and LiSPS10 (■), respectively. The lines are a guide to the eye.

rotating frame [12] ($^HT_{1\rho}$) are summarized, in part, in Table 2; the comparison with data shown in Fig. 4 leads to the conclusion that in LiSPS10/PA6 blends with an ionomer content from 70 to 90% the polymers are miscible in a scale smaller than 2 nm. In fact, similar FWHM values (ca. 470 Hz) are obtained for the LiSPS5/PA6 blends (from 30/70 to 10/90 compositions) and for the LiSPS5 pure ionomer (Fig. 4); this result shows that microregions of ion-rich phases, present in the ionomer, remain in those blends, in other words the polymers are not miscible on the FWHM MAS scale. Moreover, taking into account that in LiSPS5/PA6 blends with an ionomer content from 70 to 90% the polymers are miscible on a $^HT_{1\rho}$ scale (2 nm), it may be concluded that using FWHM MAS measurements it is possible to detect phases on a scale smaller than 2 nm. On the same basis, the observation of Fig. 4 leads to the conclusion that in LiSPS10/PA6 blends with 30/70 and 10/90 compositions the polymers are miscible on the FWHM MAS scale (smaller FWHM values than the ones obtained for the pure ionomer and for the blend with 50/50 composition).

The effect of annealing at 180°C during 1 h was also investigated on the blend of LiSPS/PA6 with the 55/45 composition; the ^{7}Li MAS spectrum was obtained with a spinning rate of 10 kHz and only a single line is observed (not shown). It should be pointed out that the appearance of spinning side bands is indicative of highly ordered lithium sites with non-cubic surroundings; annealing at 180°C ($> T_g$) induced an increase of lithium mobility, which creates approximately an isotropic environment, and thus only a resonance is observed in the MAS spectrum of this blend, after the thermal treatment. ^{13}C CP/MAS data were already reported on the effect of annealing at 140°C ($< T_g$) on the same blend with a 70/30 polymer ratio; on the basis of the slightly higher new $^HT_{1\rho}$ values, it was concluded that a small amount of PA6 had crystallized [12].

The spectra obtained from all the observed samples displayed similar features: a central line about 35 times more intense than the first spinning side band (SSB), with an asymmetric SSB envelope clearly visible for the first two SSBs in the spectra recorded at different frequency of observation (116.6 and 155.5 MHz), and a broad signal superimposed to the central line but with a much lower intensity. Spectral simulations from four LiSPS10/PA6 blends were performed on the experimental spectra obtained with a MAS rate of 6 kHz and with proton decoupling. Fig. 3 shows the simulated and the experimental spectra obtained from the 30/70 polymer blend. Relevant data on the following parameters were obtained: the concentration of the lithium nuclei in different environments ('lithium species'), the amplitude of the shielding anisotropy

Table 2
Range of miscible polymer blends, expressed by the ionomer content (%), based on the measurement of different n.m.r. parameters, correlated with different scales of polymer miscibility: T_g, 10 nm [4]; $^HT_{1\rho}$, 2 nm [12]; ^{7}Li static FWHM, 10 nm; ^{7}Li MAS FWHM < 2 nm

Blend	Miscibility scale			
	T_g	$^HT_{1\rho}$	^{7}Li static FWHM	^{7}Li MAS FWHM
LiSPS5/PA 6	70–90	70–90	70–90	–
LiSPS10/PA 6	30–90	70–90	30–90	70–90

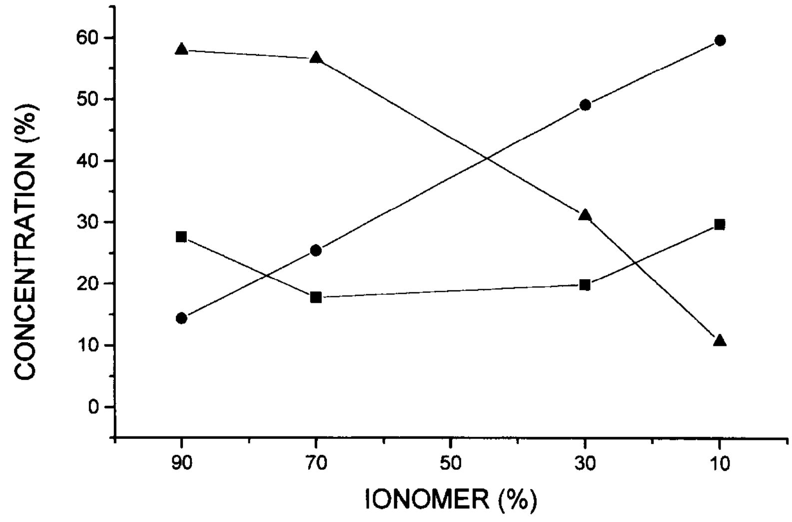

Fig. 5. Plot of the concentration of the three lithium species obtained as a percentage of the total lithium amount in each blend (assigned to 100% lithium) as a function of the LiSPS content in the polymer blends: ■, species 1; ●, species 2; and ▲, species 3. The lines are a guide to the eye.

($SA = \sigma_{ZZ} - \sigma_{XX}$) and the quadrupolar coupling constant ($C_q = eV_{ZZ}Q/h$).[2]

It was not possible to refine the results on the basis of the presence of a single species. In fact, two species were introduced to account for the very large magnitude ratio between the central line and the SSB envelope; one species generated the central line (species 1) while the SSB envelope was assigned to a second one (species 2). Concerning species 1, it was verified that a quadrupolar interaction smaller than 5 kHz could fit a single central line, without SSBs. The SSB envelope was assigned to species 2; in this case, lithium nuclei were considered to be mainly exposed to a quadrupolar interaction, which can be estimated to be *ca.* 50–100 kHz directly from the experimental spectra (from the simulated spectra it was obtained: $C_q = 42 \pm 2$ kHz) but a chemical shift anisotropy was also introduced to contribute to the asymmetric shape (from the simulation was obtained: $SA = -62 \pm 10$ ppm). A third species (species 3), with a fixed quadrupolar coupling constant (50 kHz) and a large lorentzian broadening (4000 Hz), was postulated to account for the overlapping of the central resonance (from species 1) with a much broader line (this broad line is not due to a residual heteronuclear dipolar broadening; in fact, it was previously pointed out that the dipolar interaction increases monotonously with the PA6 content, while the broadening at the bottom of the central line on the ^{1}H decoupled MAS spectra decreases). Another explanation for the appearance of species 3 is simply the existence of lithium ions involved in isotropic motion not averaged by MAS, the effect already mentioned above. The introduction of an anisotropic chemical shift to lithium nuclei in species 2 to account for the asymmetric shape of the SSB envelope can be criticized; another assumption that could explain that asymmetry is the presence of a third species with a quadrupolar coupling constant of the order of several MHz. In that case, the second-order quadrupolar interaction would cause both the asymmetric shape and the broadening observed at the bottom of the central line. However this hypothesis was not considered, since there are no known reports on such large values for C_q for lithium nuclei in diamagnetic samples. The variation of the concentration of the lithium species as obtained from the spectral simulations in function of the LiSPS concentration in the blends is represented in Fig. 5.

Table 1 summarizes the effect of the magnetic field strength and of the MAS rate for the blend with an equal content of PA6 and LiSPS10. Considering that for the FWHM values obtained at a MAS rate of about 10 kHz the dominant interaction that influences the line width is the second-order quadrupolar interaction, which is inversely proportional to the field strength, the increase of the line width with the magnetic field can be explained on the basis of an increasingly important contribution of species 3 to the measured FWHM, which is due to the corresponding line narrowing at higher MAS rates, as expected for the observation of lithium ions involved in isotropic motions. On the other hand, a large chemical shift anisotropy of species 2, increasing with the static magnetic field, also explains the observed effect.

Species 2 is characterized by the presence of rigid ordered domains, which are revealed by the appearance of SSBs in the spectrum, with an EFG interacting with the lithium nuclear charge much stronger than in species 1. Species 2 can thus be assigned to a rigid microphase.

^{7}Li spin–lattice relaxation time (T_1) measurement was performed on the LiSPS10/PA6 with 90% ionomer, in order to provide additional evidence for the formation of species 1 (mainly contributing to the central line) and 2 (assigned to the SSB envelope). However, similar T_1s (600 ± 20 ms) were obtained either from the central line or from the satellite lines. This result shows that motions in

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[2] Following the convention: $|\sigma_{ZZ} - \sigma_{iso}| \geq |\sigma_{XX} - \sigma_{iso}| \geq |\sigma_{YY} - \sigma_{iso}|$.

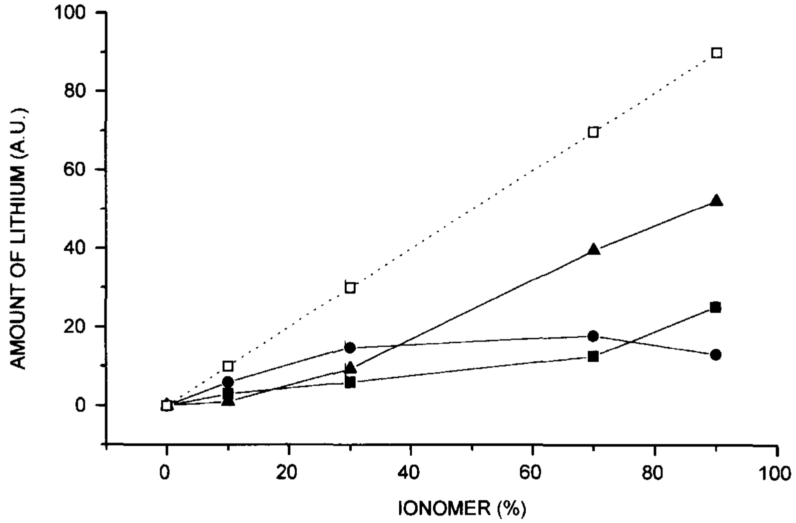

Fig. 6. Plot of the concentration of the three lithium species obtained as a percentage of the total lithium amount (approximately equal to the total amount of LiSPS) in each blend, as a function of the LiSPS content in the polymer blends: ■, species 1; ●, species 2; and ▲, species 3. The lines are a guide to the eye.

the MHz frequency range, probed by T_1 measurements, cannot be used to discriminate those species.

To simulate the ^{7}Li MAS spectra, it was thus necessary to postulate three different lithium species. It is worth noting that previously reported ^{23}Na n.m.r. studies on sodium-neutralized slightly sulfonated polystyrene have shown that sodium ions exist in up to three different environments: isolated ions; fully hydrated ions $Na(H_2O)^{4+}$ (FWHM equal to 160 and 270 Hz, respectively); and aggregated ions (FWHM = 1.8 kHz) [16,17]. Narrow lines were assigned to the first two species, accounting for the corresponding near-spherical symmetric electronic environments (EFG~0), while a strong quadrupolar interaction (C_q = 1.6 MHz in ionomers with 4.2% sulfonation) induces the breadth of the line assigned to aggregated ions. The relative amount of each type of sodium ion was found to be dependent on the sulfonation and neutralization levels. SSBs were not identified in ^{23}Na spectra from the SPS neutralized with sodium ions.

4. Conclusions

Lithium n.m.r. results clearly provide a new approach to probe the miscibility of polymer blends involving lithium ionomers. In principle, this method doesn't suffer from any restrictions; on the contrary, studies of blend miscibility based on relaxation studies demand that the starting polymers have different relaxation times before blending. The linear correlation found between the line width of the single ^{7}Li resonance and T_g, measured by d.s.c., shows that similar information about the size of separated phases (*ca* 5–10 nm) is obtained from both methods. The variation of the Li–H dipolar interaction with the amount of PA6 was observed and the monotonic decrease of the averaged Li–H distance with the PA6 content in the blends is in agreement with a disrupt of the ionic aggregates, i.e. with the presence of ionic aggregates with smaller sizes. In the blends, the increase of T_g, reflecting lower mobility of the two polymers and an increase of the polymer miscibility, is correlated with a smaller Li–H dipolar interaction which favours the hypothesis of a Li–PA6 interaction occurring through the oxygen atoms; this effect is expected to be more important when the counterion is lithium because of its higher charge to ionic radius ratio (ca. 17 nm^{-1}) in comparison with sodium (ca. 11 nm^{-1}). The line width of the central line of the MAS spectra provides another scale for the study of the miscibility of these polymer blends; blends that are miscible on a $^{H}T_{1\rho}$ scale show a different behaviour regarding MAS spectra, which is explained on the basis of the presence of microphases not detected from relaxation studies. Moreover, the spectral simulations give evidence for the presence of three different lithium species and also suggest that the composition of the blend determines the concentration of these species. Species 1 should be assigned to isolated and fully hydrated lithium ions. The progressive increase of PA6 favours an increase in the concentration of species 2; however, because this species is also identified in the spectrum of the pure ionomer, it must be assigned to lithium atoms interacting with SPS polymer chain. The miscibility of the polymers is correlated with the abundance of species 3, concentration of which increases monotonously with the amount of lithium in the blend (Fig. 6).

In order to get further evidence for the formation of two species with strongly different quadrupole coupling constants, work is now in progress using the 2D nutation n.m.r. technique.

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