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Two-Dimensional NMR Characterization of Local Structure in Two Polystyrene Blends

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ABSTRACT: Solid-state NMR spin diffusion measurements have been used to investigate the local structures in two miscible polymer systems, the isotopic polystyrene blend PS-d_5/PS-d_3 and poly(2,6-dimethylphenylene oxide)(PPO)/PS-d_3. The experimental spin diffusion build-up curves were compared with theoretical ones based on a number of structural models. It was found that a Gaussian correlation model furnished the best agreement with the experimental data, and this implies the existence of some short-range ordering in the local environment in such nominally miscible blend systems. The best fit of the spin diffusion curves gave a correlation length of 0.5–0.6 nm for the PS-d_5/PS-d_3 blends and 0.4 nm for the PPO/PS-d_3 blends. The correlation lengths for the PS-d_5/PS-d_3 blends were found to be independent of the blend compositions. The result also suggests that the concentration fluctuation in a 50/50 PPO/PS-d_3 blend is weaker than that in a 50/50 PS-d_5/PS-d_3 blend, indicating a molecular interaction less favorable to homogeneity in the latter.

Introduction

Miscible polymeric blends are usually diagnosed as such by their single T_g's and transparency.[1–3] These criteria, even though practical, only imply a homogeneity on a scale of tens of nanometers or larger.[4–8] The local structure of such miscible blends on a smaller scale, on the other hand, is less understood. Despite the lack of knowledge about the fine structure, many theoretical assumptions regarding polymer blends are explicitly or implicitly derived on the assumption of totally homogeneous segmental mixing.[9–11] Although this assumption may be entirely reasonable for small molecules, it is questionable for high molecular weight polymers. Various attempts have been made to investigate the local structures of miscible polymer blends.[12–16] The Ornstein–Zernike approximation, which assumes a random-phase structure, provides a methodology to calculate the correlation length of concentration fluctuation from SANS.[17–19] It was found that most polymer blends well within the miscible regime in their phase diagram still exhibit correlation lengths from 30 to 150 Å.[12–16] If this implied structure is inherent in polymers only, then it is important in understanding the nature of the structure and the thermodynamics and properties of the polymer blends.

The development of theories for polymeric blend structures is not as well established as it is for small molecular mixtures. The local structure of the latter mixtures has been studied in great detail.[20–30] The results show generally that the clusters of one component are approximately the size of the molecule itself.[20–22,25–29] In other words, each molecule is essentially surrounded by a concentration-dependent fraction of dissimilar molecules as might be anticipated. The local structure of the mixture is thus dependent on the nature of the interaction of the molecules and the molecular structure of each component.[21]

Polymers obviously differ from small molecules in terms of the connectivity of segments, which dramatically reduces the entropy of mixing.[10] This produces a very strong effect of molecular interaction on the local structure. Unless the reduced interaction parameter χ_{ij} is very small or negative, immiscible blends will be obtained. The connectivity of polymers limits the dispersion of segments among dissimilar species, resulting in structures differing from low molecular weight molecule mixtures. de Gennes has shown that the segmental density fluctuation decreases as $1/r$ in the regime $b \ll r < R_g$ for polymer chains,[11] where b is the Kuhn segment length, and R_g is the radius of gyration. Recently Schweizer and Curro applied the "reference interaction site model" theory to polymer blends.[31–35] They predicted a nonrandom intermolecular packing associated with large-scale weak fluctuations of the polymer chain concentration. A nonmonotonic correlation function was predicted on a scale of the radius of gyration of the macromolecules.

Solid-state NMR spin diffusion has been used to study the inhomogeneity of polymer blends for over 2 decades.[36–43] For example, some inhomogeneity in miscible PPO/PS blends has been implied from the nonlinearity of the proton $T_{1\rho}$(H) decay.[36,37] Recent developments in spin diffusion studies of polymer blends have been summarized by Vanderhart.[44,52] However, relatively few studies have been made of the detailed structure of local inhomogeneities in nominally miscible polymeric blends. In a previous study,[39] we have investigated the local structure in the miscible polymer blend PPO/PS-d_5 using multidimensional pulse techniques for the measurement of spin diffusion. Similar techniques have also been used for the study of polycarbonate blends[61] and poly(vinylphenol)/poly(methyl methacrylate) blends.[62] In the present paper, we investigate the local structure of two miscible polymeric blends, PS-d_5/PS-d_3 and PPO/PS-d_3, by a more extensive analysis of solid-state NMR spin diffusion. A simulation of the spin diffusion process was carried out for various structural models and compared to the experimental data.

Experimental Section

The polymers used in this study were (a) a ring deuterated polystyrene-d_5 (Cambridge Isotope; MW = 200 000), (b) a backbone deuterated polystyrene-d_3 (MW = 225 000; Lark Enterprises, Inc.) and (c) poly(2,6-dimethylphenylene oxide) (Scientific Polymeric Products, Inc.; MW = 27 000). The deuterated polymers have an isotopic purity higher than 98%.

The PPO/PS-d_3 blend was prepared by dissolving the appropriate amount of polymers in toluene and casting films at room temperature. The isotopic polystyrene blends were pre-

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Table 1. Correlation Functions Used and Their Parameters from the Best Fit of the Experimental Spin Diffusion Data

sample	fitting function	D ($\times 10^{-12}$ cm^2/s)	L (Å)	b (Å^{-1})	l (Å)[a]	$G_{AA}(R_{segment})$	expt error[c] (±)	SD[d]
PS-d_5/PS-d_3 25/75	cosine Gaussian[e]	3.2	5.3	0.0084	4.4	0.61	10%	7.1%
PS-d_5/PS-d_3 50/50	exponential[f]	2.9	6.9	0.0	6.9	0.42	5%	31.8%
PS-d_5/PS-d_3 50/50	Gaussian[e]	2.9	5.7	0.0	5.1	0.68	5%	1.1%
PS-d_5/PS-d_3 50/50	cosine[e]	2.9	∞	0.182	17.3[g]	0.79	5%	24.3%
PS-d_5/PS-d_3 50/50	cosine Gaussian[e]	2.9	5.7	0.012	5.1	0.68	5%	1.5%
PS-d_5/PS-d_3 75/25	cosine Gaussian[e]	2.7	5.4	0.011	4.8	0.65	10%	6.7%
PPO/PS-d_3 50/50	cosine Gaussian[e]	3.8	7.2	0.164	4.0	0.34	10%	0.8%

[a] $l = \int_0^\infty G_{AA}(R)\,dR$. This definition of the correlation length is different from the Ornstein–Zernike approximation where $G_{AA}(R) = e^{-r/L}/r$ and L is the correlation length. [b] $G_{AA}(R_{segment}) = (\langle P_{AA}{}^2\rangle - \langle P_{AA}\rangle^2)_{R=R_{segment}}/(\langle P_{AA}{}^2\rangle - \langle P_{AA}\rangle^2)_{R=0}$. The values are determined from the $G_{AA}(R)$ at $R = 0.6$ nm for PS-d_5/PS-d_3 blends and at $R = 0.7$ nm for the PPO/PS-d_3 blend. [c] The experimental error was estimated from the NMR signal-to-noise. [d] Standard deviation of fittings [e] $G_{AA}(R) = \exp(-R^2/L^2)\cos(bR)$. [f] $G_{AA}(R) = \exp(-R/L)$. In this case L is equivalent to the correlation length l. [g] l represents the radius of domain size for a periodical structure.

pared from chloroform solution. The cast films were dried at approximately 100 °C in vacuum for complete removal of the solvent. The PPO/PS-d_3 samples (and, of course, the isotopic PS blends) prepared in this way were transparent and possessed the characteristic single glass transition temperatures as observed by DSC. The dried materials were ground into a fine powder in liquid nitrogen on a Spex mill for measurement.

Solid-state two-dimensional NMR spectra of the spin diffusion process were obtained on a Bruker MSL 300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75 MHz) using a HETCOR pulse sequence with magic angle spinning (MAS) conditions. The spinning rate was approximately 4.5 kHz. Full experimental details have been reported elsewhere.[45]

The correlation functions of the polymer blends were obtained through curve fitting of the spin diffusion data. The required spin diffusion constants D for the polymer blends were estimated from the relation:[53]

$$D \propto \omega^{1/2} a^2 \tag{1}$$

where ω is the spin transition rate, and a is a lattice constant. The spin diffusion constants of the polymer blends used in this study were calculated using a reference value for D of 6.6×10^{-12} cm^2/s[41,58] for polyethylene and taking into account the differences of proton density in the present systems. The calculated spin diffusion constants for several blends in this study are listed in Table 1.

Results and Discussion

Aromatic and aliphatic protons in a magnetic field resonate at different energy levels and permit the observation of a spin diffusion from aromatic to aliphatic protons.[53] Selectively deuterated polystyrenes were used in this study which can thus be distinguished by the type of protons contained, allowing the study of spin diffusion from one polymer chain to another. Figure 1 shows the two-dimensional heterogeneous nuclear correlation spectrum of a 50/50 wt % PS-d_5/PS-d_3 blend at two mixing times, 0.3 and 10 ms. The spin diffusion time (mixing time), t, determines the spatial range of observed spin diffusion, given by the following relation:[44]

$$\langle r^2\rangle^{1/2} = \left(\frac{4}{3}Dt\right)^{1/2} \tag{2}$$

where $\langle r^2\rangle^{1/2}$ is the root mean square spin diffusion length and D is the spin diffusion constant. At zero time, no diffusion occurs, and the proton signals observed in the HETCOR spectrum are only associated with the respective directly attached carbons. For finite spin diffusion times, the proton signals are also associated with protons attached to more distant carbons. As discussed in the previous study,[39] a spin can diffuse over average segmental distances for these polymer systems in times on the order of 0.3 ms. Thus the HETCOR spectrum at $t = 0.3$ ms corresponds to spin diffusion at the segmental level (Figure 1a). A spin diffusion time at either too short or too long a scale does not properly represent the segmental miscibility which is of interest. If there is no contact between the unlike segments of the two polymers, as will occur in a phase-separated structure, there can be no spin diffusion between protons in the two polymers at a spin diffusion time on this time scale. It is seen from the spectrum in Figure 1a that there can only be very weak energy transfer between the aromatic protons of PS-d_3 located at 7 ppm and the aliphatic protons of PS-d_5 at 2 ppm since it is not visible above the background noise. This indicates that the number of heterosegmental contacts at the segmental scale is small.

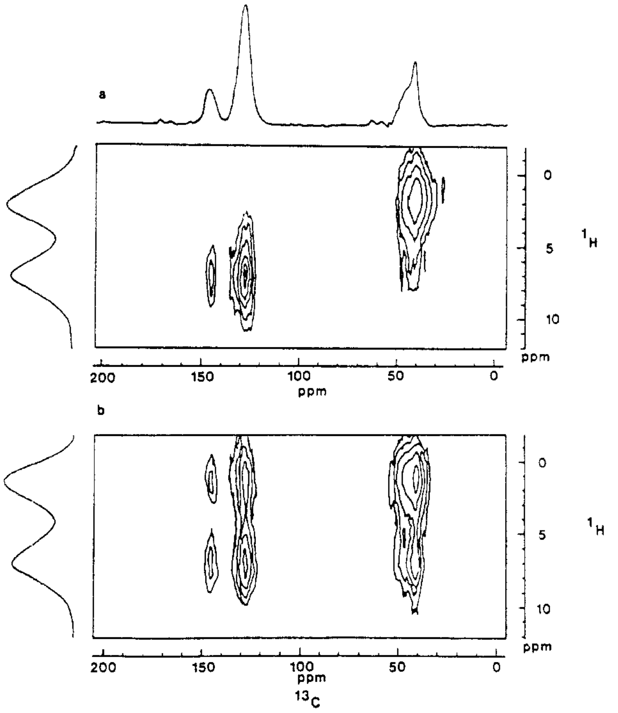

Figure 1. HETCOR spectra of a 50/50 PS-d_5/PS-d_3 blend at two different mixing times: (a) 0.3 ms; (b) 10 ms.

The HETCOR spectrum at a mixing time of $\tau = 10$ ms is taken as an extreme in which spin diffusion is well equilibrated. This is evidenced by the observation that the same ratios of the aromatic to the aliphatic proton signal intensities are reached at 40 ppm (methylene carbons) and 127 ppm (aromatic carbons) in the ^{13}C spectrum.

The correlation intensity $I_{AB}(t)$ for spin diffusion of aromatic proton character to protons attached to an aliphatic carbon may be defined by $I^{H}{}_{arom}(^{13}C)/(I^{H}{}_{arom}(^{13}C) + I^{H}{}_{aliph}(^{13}C))$. Figure 2 shows the aromatic to aliphatic proton correlation intensity for the 50/50 PS-d_5/PS-d_3 blend at 40 ppm (aliphatic carbons) of the ^{13}C spectrum as a function of mixing time.

The correlation intensity $I_{AB}(t)$ is given by the following integration through space:

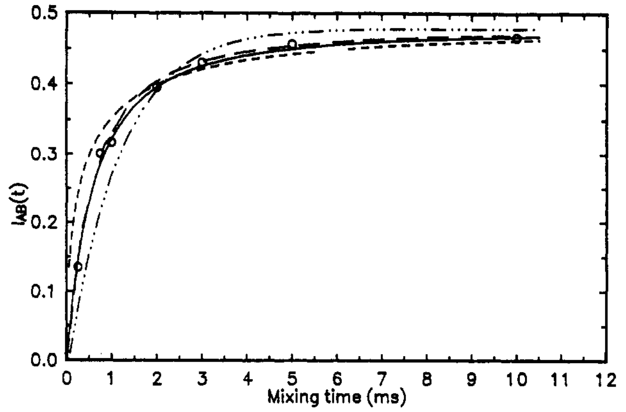

Figure 2. Aromatic to aliphatic proton correlation intensity at 40 ppm ^{13}C resonance as a function of mixing time for the 50/50 PS-d_5/PS-d_3 blend. The circles are experimental data. The lines are the best fits calculated from several structural correlation models: (—) simple Gaussian; (– –) cosine Gaussian; (- - -) exponential; (· · · –) cosine.

$$I_{AB}(t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P_B(X,Y,Z)\, M_A(X,Y,Z,t)\, dX\, dY\, dZ \tag{3}$$

where $M_A(X,Y,Z,t)$ is the time-dependent ^1H proton magnetization density at position (X, Y, Z) associated with proton A, $P_B(X,Y,Z)$ is the density function of proton B at the same position (X, Y, Z) which equals $M_B(X,Y,Z,0)$. The subscripts A and B are arbitrarily assigned to the aromatic and aliphatic protons, respectively.

The time dependence of the proton magnetization density $M_A(X,Y,Z,t)$ is given by the diffusion equation:[53]

$$\frac{\partial M_A(X,Y,Z,t)}{\partial t} = D\left(\frac{\partial^2 M_A(X,Y,Z,t)}{\partial X^2} + \frac{\partial^2 M_A(X,Y,Z,t)}{\partial Y^2} + \frac{\partial^2 M_A(X,Y,Z,t)}{\partial Z^2}\right) \tag{4}$$

The solution of eq 4 takes the general form

$$M_A(X,Y,Z,t) = \frac{1}{(4\pi Dt)^{3/2}}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P_A(X,Y,Z) \times \exp\left(-\frac{(X-X')^2 + (Y-Y')^2 + (Z-Z')^2}{4Dt}\right) dX'\, dY'\, dZ' \tag{5}$$

where $P_A(X,Y,Z)$ is the density function of proton A and X', Y', and Z' are the integration variables. By substituting eq 5 into eq 4, the correlation intensity can be written as

$$I_{AB}(t) = 1 - \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} G_{AA}(X,Y,Z) \frac{1}{(4\pi Dt)^{3/2}} \times \exp\left(-\frac{X^2 + Y^2 + Z^2}{4Dt}\right) dX\, dY\, dZ \tag{6}$$

where $G_{AA}(X,Y,Z)$ is the density correlation function of proton A:

$$G_{AA}(X,Y,Z) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P_A(X,Y,Z) \times P_A(X+x,Y+y,Z+z)\, dx\, dy\, dz \tag{7}$$

For isotopic systems $G_{AA}(X,Y,Z)$ can be replaced by $G_{AA}(R)$, which is proportional to the probability of finding an aromatic proton A at a distance R from a second aromatic proton. The local structure of polymer blends can thus be characterized by the proton density correlation function.

The form of the correlation function depends on the type of structure. A simple exponential correlation function was suggested by Debye for materials of totally random phase structure.[46] Similar correlation functions have also been used in neutron scattering calculations.[19,47] A structure with localized clusters may be represented by a Gaussian correlation function, which implies a relatively high correlation at short distances and in ordered structures may be simply described by a periodic cosine function. More complicated structures may be represented by a combination of the above functions.[48,49,59] In this study, several structural correlation models were used to test different possible structures.

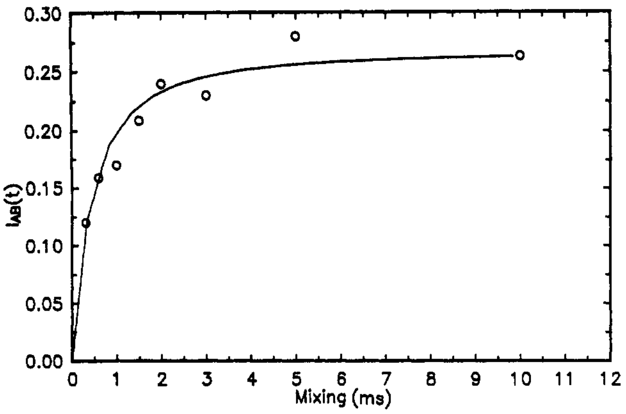

Figure 3. Aromatic to aliphatic proton correlation intensity at 40 ppm ^{13}C resonance as a function of mixing time for the 25/75 PS-d_5/PS-d_3 blend. The circles are experimental data. The line is the best fit calculated from the cosine Gaussian correlation structure model.

Figure 2 shows the best fit curves of the experimental spin diffusion data for the 50/50 PS-d_3/PS-d_5 blend. The best fits were calculated from several structural correlation models, using eq 6. The relevant parameters and the corresponding correlation functions are listed in Table 1. As discussed earlier, an exponential correlation represents a homogeneous structure which inevitably results in a rapid buildup in spin diffusion. The best fit curve based on the exponential model (- - -) is also shown in Figure 2. The initial buildup is about 20–40% faster than the experimental data, a disagreement outside the experimental error of ±5%. Similarly, a simple cosine correlation structure provides a poor fit (· · · –) of the spin diffusion data, with a deviation of 15% from the experimental data. The failure of both the exponential and the cosine forms as a correlation function seems to exclude the possibilities of both a structural randomness and a long-range ordering in this 50/50 PS-d_3/PS-d_5 blend.

The best fit curves using the Gaussian and the cosine Gaussian correlation functions (— and – –) are shown in Figure 2. Both curves fit the entire spin diffusion data well. The deviation of these functions from the experimental data is virtually indistinguishable. The simulations using the cosine Gaussian and a simple Gaussian correlation function can also correctly describe the spin diffusion data for the 25/75 PS-d_5/PS-d_3 and 75/25 PS-d_5/PS-d_3 blends. Figures 3 and 4 show the best fits from the cosine Gaussian correlation function for the spin diffusion data of 25/75 and 75/25 PS-d_5/PS-d_3 blends. The corresponding parameters are listed in Table 1.

The best fit cosine Gaussian correlation functions for the PS-d_5/PS-d_3 data for various compositions are shown in Figure 5. However, the periodicity of the cosine functions is much longer than the correlation length of the Gaussian function. Thus the curves are essentially Gaussian functions. It appears that a structural periodicity is not required in this system and suggests that a long-range ordering is inconsistent with the spin diffusion data. A short-range-ordered structure in the blend is implied by the good fit of the Gaussian correlation function.

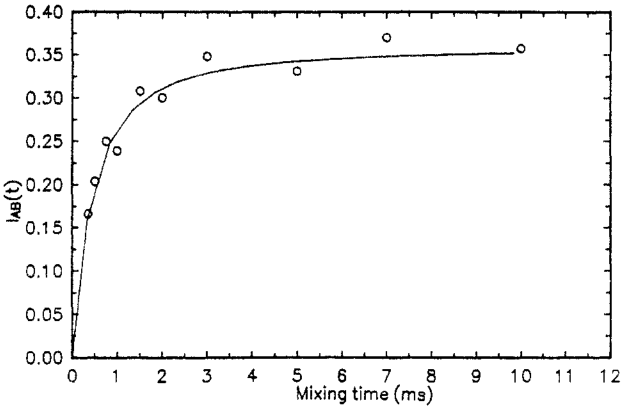

Figure 4. Aromatic to aliphatic proton correlation intensity at 40 ppm ^{13}C resonance as a function of mixing time for the 75/25 PS-d_5/PS-d_3 blend. The circles are experimental data. The line is the best fit calculated from the cosine Gaussian correlation structure model.

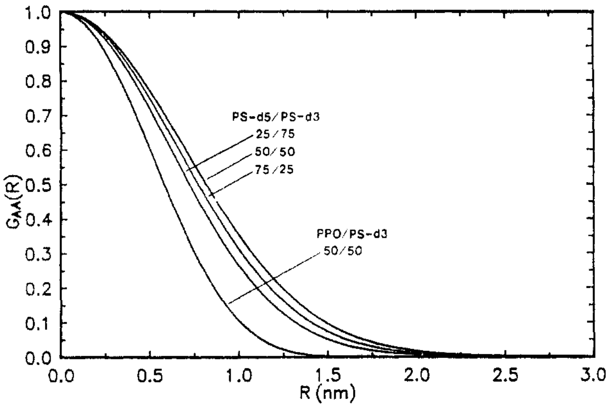

Figure 5. Magnetization density correlation function for PS-d_5/PS-d_3 and PPO/PS-d_3 blends from the best fits of the experimental data based on a cosine Gaussian correlation structural model. The curves are essentially Gaussians due to the weak periodicity in the blend structure.

It is useful to examine the intensity of the concentration fluctuations of the short-range-ordered structure of the blend at the segmental level. The proton density fluctuation at the segmental level can be characterized by the correlation on the segmental scale, $G_{AA}(R_{segment})$. For polystyrene, $R_{segment}$ is on a scale of 0.6 nm.[65] The $G_{AA}(R_{segment})$ value ranges from 1.0 for fully ordered structure to 0.0 for a completely random structure. Table 1 lists the characteristic values of $G_{AA}(R_{segment})$ for the three compositions of PS-d_5/PS-d_3 blends. It is seen that the 50/50 PS-d_5/PS-d_3 blends have a proton density fluctuation magnitude $G_{AA}(R_{segment})$ of 0.68. The corresponding values for the 25/75 and 75/25 blends on the same scale are 0.61 and 0.65. These high magnitudes of proton density fluctuation again indicate that the number of heterosegmental contacts of the isotopic PS-d_5/PS-d_3 blends are small and the mixing at the segmental level is not completely homogeneous. This conclusion is consistent with the weak spin diffusion intensity in the HETCOR spectrum at τ = 0.3 ms, as shown in Figure 1a. The dependence of the proton density fluctuation on the blend compositions is small, and the difference is within the experimental error.

The local ordered structure of the blends can also be characterized by the correlation length. The correlation lengths of PS-d_5/PS-d_3 blends are also listed in Table 1, and it is seen that the correlation length is in the range of 0.5–0.6 nm. The apparent composition dependence of the correlation length is not significant considering the experimental error.

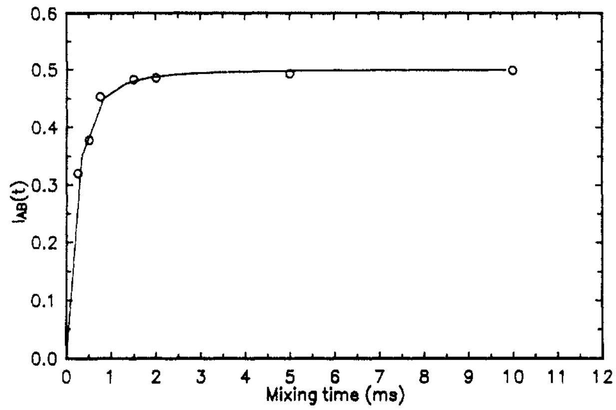

Figure 6. Aromatic to aliphatic proton correlation intensity at 16 ppm ^{13}C resonance as a function of mixing time. The circles are experimental data. The line is the best fit calculated from the cosine Gaussian correlation structural model.

A locally ordered structure in a miscible polymer blend has been postulated in earlier investigations for the PPO/PS-d_5 blend.[39] However, recent theoretical models also support this concept. As noted, Curro and Schweizer applied a "reference interaction site model" integral theory (RISM) to polymer blends. They predicted that a weak local fluctuation can exist in athermal polymer blends.[32] A Monte Carlo simulation by Cifra et al. implies that athermal polymer blends have a tendency toward segmental segregation.[50,51] In other words, athermal blends are not completely randomized on the segmental level. Our spin diffusion results experimentally support the above theoretical prediction and the simulation. Larger scale concentration fluctuations with correlation lengths on the order of 8 nm have been reported by SANS for isotopic polystyrene blends.[14] However, if the difference of the correlation function is taken into account and the correlation length is recalculated as defined in the present study, both experiments give essentially the same correlation length.

The studies of the local structure of polymer blends were extended to the PPO/PS-d_3 system, for which the macroscopic miscibility parameters are well-known (assuming no isotopic effect).[60] Figure 6 shows the aromatic to aliphatic proton correlation intensity at 16 ppm ^{13}C resonance as well as the best fit curve calculated using the cosine Gaussian structural correlation model for the 50/50 PPO/PS-d_3 blend. The results are listed in Table 1. The PPO/PS-d_3 blend differs from the PS-d_3/PS-d_5 blend in that in the former the PPO chains contain both aromatic and aliphatic protons. Proton spin diffusion can occur within the PPO polymer chains as well as between PPO and PS-d_3 segments. However, because the dipole–dipole interaction of protons is proportional to the cube of their separation,[53] spin diffusion from adjacent protons on the same polymer chain is much faster than any intermolecular spin diffusion. As discussed earlier, it takes less than 0.3 ms to reach equilibrium for intramolecular spin diffusion.[39] Therefore, it can be assumed that the protons in the PPO segments have reached equilibrium before they "communicate" with protons of the PS-d_3 segments.

Figure 5 also shows the correlation function for the PPO/PS-d_3 blend. As in the case of the PS-d_3/PS-d_5 blend, even though a cosine Gaussian correlation function was used for the fitting, the resulting correlation function was essentially Gaussian, a result indicating the lack of periodicity in the structure. The mean square proton density fluctuation at the segmental scale, $\langle G_{AA}\rangle(R_{segmental})$, is 0.34, much lower than that found for the PS-d_3/PS-d_5 blend. The higher degree of segmental mixing for the former is also inferred from the considerably greater spin diffusion energy transfer at a mixing time of 0.3 ms (Figure 6). The weak segmental fluctuation in the PPO/PS-d_3 blends can be explained by their difference in segmental dimensions. Even though both systems are found to be miscible by the conventional criterion of single T_g's, there is evidence that the partial deuteration of polystyrene results in a small unfavorable interaction with a hydrogenated polystyrene chain,[14,54,55,63,64] and this leads to macroscopic phase separation for isotopic polystyrene blends of high enough molecular weight.[56] This result may well extend to the isotopic mixtures studied here. Though the effect of deuteration of polystyrene in PPO blends has not been examined, the favorable interaction of the PPO chain with protonated polystyrene is well established.[57] It is probably this favorable interaction that results in a weaker concentration density fluctuation and, hence, the weaker magnetization density fluctuation. It is also possible that the lower molecular weight of PPO used here would favor the miscibility in PPO/PS-d_3 compared to PS-d_5/PS-d_3.

Conclusions

A novel NMR spin diffusion technique has been used to study the local structure of two miscible polymer blends, PS-d_5/PS-d_3 and PPO-PS-d_3. The correlation functions of the magnetization density fluctuation have been calculated by numerically fitting the experimental data. The simulations based on the Gaussian correlation model were found to properly represent the experimental spin diffusion data. It is concluded from the model that there are short-range-ordered structures in these miscible blend systems. A correlation length of 0.5–0.6 nm was found for PS-d_5/PS-d_3 blends and 0.4 nm for the PPO/PS-d_3 blend. Further analysis of the spin diffusion data found that the PPO/PS-d_3 blend system possesses a higher miscibility as indicated by a lower segmental mean square proton density fluctuation at the segmental level. This result is in accord with the very small unfavorable interaction presumed to occur in the isotopic polystyrene blends as a result of differential deuteration.

NMR spin diffusion has proved to be a powerful tool for the analysis of the local structure of polymer blends. It will be noted that, together with other approximations, the structures calculated are determined by the assumption of constant spin diffusion coefficients that were calculated on the basis of the measured value of polyethylene. Solid evidence is needed to verify these assumptions. The results of these experiments will be reported in future publications.

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