

Microheterogeneity in PPO/PS Blends

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SYNOPSIS

Proton spin magnetization relaxation in the rotating frame is a simple exponential for poly(2,6-dimethylphenylene ether) (PPO) (23K)/polystyrene (PS) (9K) blends of various compositions; these blends are truly homogeneous at the spin-diffusion distance scale of a few nanometers. Blends of PPO with high molecular weight PS exhibit nonexponential decays for the PS component but exponential decays for the PPO component, indicating compositional fluctuation for PS. In some blends, the relaxations are nonexponential for both components. Three factors have been identified to promote microheterogeneity of nanometer dimensions: high polymer molecular weight, increase of temperature, and preparation of blend using solvent that induces crystallization of PPO such as toluene.

INTRODUCTION

Poly(2,6-dimethylphenylene ether) (PPO) has excellent tensile strength, modulus, chemical resistance, and high-temperature dimensional stability but poor processability. Polystyrene (PS) is an extremely brittle substance. Blending of PPO with PS gave a tough material with good processability. PPO is also blended with high-impact polystyrene (HIPS) and other polymers to give a family of engineering plastics of high impact strength. Therefore, the miscibilities of these component polymers are of both scientific and technological interest.

There have been many studies using various techniques to investigate the PPO/PS blends. Differential scanning calorimetry and thermo-optical analysis of PPO/PS blends¹⁻⁸ found a single T_g transition as well as did dielectric relaxation⁹ and dynamic mechanical thermal analysis.^{1,3,10} Small-angle neutron scattering measurement^{11,12} yielded a large and positive second virial coefficient (A_2), indicating that PS is a good solvent for PPO. A_2 decreases linearly with an increase of temperature, consistent with a lower critical solution temperature of about 345°C.

The above results led some authors to conclude that PPO and PS are miscible in all proportions. However, the plot of T_g versus the blend composition

is convex.⁸ The T_g transitions of the blends are very broad. The breadth of the T_g transition has been associated with the intimacy of mixing in compatible blends, which may reflect thermodynamic composition fluctuations or long-range concentration gradients.¹² Dynamic mechanical studies on mechanically mixed PPO/PS blends² indicate the existence of a PPO-rich phase and a PS-rich phase. The behavior had been suggested by Shultz and Gendron⁴ to be due to poor mixing. MacKnight et al.⁹ responded that while a certain level of miscibility is achieved in the PPO/PS blend, compositional fluctuations were prevalent enough to yield data indicating definite microheterogeneity.

Solid-state nuclear magnetic relaxation can detect the existence of microheterogeneity at the nanometer scale.¹³⁻¹⁶ The central purpose of this work is to investigate the nanometer scale microheterogeneity in PPO/PS blends by solid-state NMR over a wide range of compositions and the molecular weight (MW) of PS. The effect of the MW of PS, annealing temperature, and solvent used in the blend preparation are described. In another paper,¹⁷ solids NMR results in PPO/HIPS blends are presented and a theory for compositional fluctuation is formulated.

EXPERIMENTAL

PPO, MW = 23K, $\bar{M}_w/\bar{M}_n = 1.9$ (determined by GPC), and MW = 6.4K, were obtained from General

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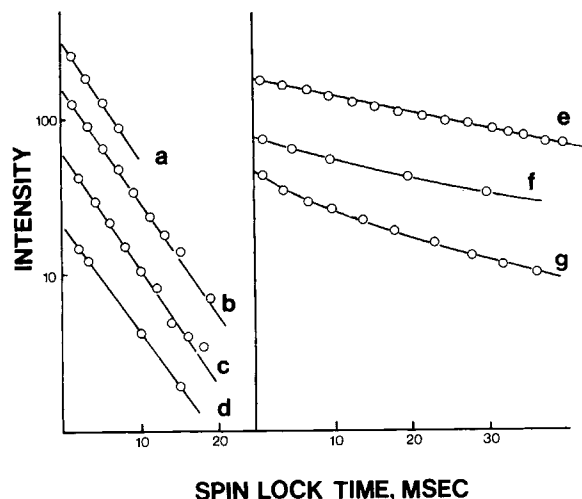


Figure 1 Logarithmic intensity plots vs. the spin-lock time for different MW polystyrene and PPO: (a) PS (9K); (b) PS (90K); (c) PS (900K); (d) PS (10K); (e) PPO (23K) cast from chloroform; (f) PPO (23K) cast from toluene; (g) PPO (6.4K) as received.

Electric Company. Monodisperse PS standards with MW of 9K, 90K, and 900K were purchased from Pressure Chemicals. A polydisperse ($\bar{M}_w/\bar{M}_n = 2.0$) of MW = 10K was extracted from an HIPS sample provided by GE.

Blends were prepared by dissolving the desired proportion of polymers into a common solvent to obtain a homogeneous solution, casting this solution onto a glass or aluminum surface at room temperature in air for 1 day, then vacuum drying at 60°C for 2 days to completely remove the residual solvent. Unless otherwise stated, chloroform was used as a solvent to avoid crystallization of PPO that can be promoted by solvents such as toluene.¹⁷ Blends prepared in this way show only a single DSC transition T_g and no observable amount of crystalline phase.

¹³C-NMR spectra were obtained on an IBM AF200 spectrometer with a solid accessory at 50.3 MHz using 5 μ s 90° pulses (50 kHz) for both carbon and proton nuclei. The pulse sequences used for the determination of $T_{1\rho}$ have been described previ-

ously.¹³ The data are presented as the decay of ¹³C-magnetization in the rotating frame versus the spin-lock time of proton as described by Stejskal et al.¹⁸ The resolved resonance intensities of PS and PPO in the blend spectrum at 40 ppm and 16 ppm, respectively, are monitored independently. All determinations were done at 21°C with magic angle spinning near 4 kHz. Typical signal-to-noise ratio is 70 to 80, and there is no sideband problem.

RESULTS AND DISCUSSION

Homopolymers

Figures 1(a-d) gave magnetization plots of logarithmic carbon-13 intensities versus the spin-lock time for PS of various MW that are all single exponential. The experimental error in the measurement of resonance intensity is about 10%. There is no difference between the decay of the aromatic carbon resonance at 127 ppm and that of backbone carbon resonance at 40 ppm in all the samples. This is as expected because the relaxation rates of these nuclei are equalized by the efficient proton spin diffusion.¹⁷ Therefore, only the $T_{1\rho}(H)$ results of the 40 ppm resonance are listed in Table I.

PS of MW from 9K to 900K have the same $T_{1\rho}(H)$ values in accord with expectation because no chain-end effect is likely to influence the motion of the chain with lengths exceeding 100 bonds.¹⁷ The accuracy of $T_{1\rho}(H)$ is better than ± 1 ms.

The relaxation of PPO (23K) cast from chloroform is a simple exponential with $T_{1\rho}(H) = 20$ ms [Fig. 1(e)]. In contrast, the magnetization decay of PPO (23K) cast from toluene showed slight curvature [Fig. 1(f)]. This is attributable to the known behavior of toluene that it induces crystallization of PPO¹⁹; protons in the crystalline and amorphous domains would differ in their relaxations. The relaxation of PPO (6.4K) as received showed marked biphasic decay, which may be due to the sample being partially crystalline. PPO (6.4K) cast from chloroform exhibits simple exponential decay.

Table I Relaxation Time in Rotating Frame for Homopolystyrene

	MW							
	9K		90K		900K		10K	
ppm	40	127	40	127	40	127	40	127
$T_{1\rho}(H)$ (ms)	6.0	5.8	6.4	6.0	5.7	5.7	6.2	

Blends

We have obtained relaxation data for a series of blends of PPO (23K) and PS with a range of MW from 9K to 900K. The logarithmic intensity decay in the rotating frame is shown in Figure 2 for the PPO and PS components in each blend.

The three blends with PS (9K) all exhibit single exponential decays for both components. The $T_{1\rho}(H)$ values for the two polymers are within the accuracy of ± 1 ms. Therefore, these blends are homogeneous. However, the relaxation rates are not those expected according to the additivity rule:

$$[T_{1\rho}(H)]_{\text{blend}}^{-1} = \frac{M(H)_{\text{PPO}}}{[T_{1\rho}(H)]_{\text{PPO}}} + \frac{M(H)_{\text{PS}}}{[T_{1\rho}(H)]_{\text{PS}}} \quad (1)$$

where $M(H)_{\text{PPO}}$ and $M(H)_{\text{PS}}$ are the mol fractions of protons in the polymer and $[T_{1\rho}(H)]_{\text{PPO}}$ and $[T_{1\rho}(H)]_{\text{PS}}$ are the homopolymer relaxation times for PPO and PS, respectively. According to eq. (1), the 75PPO/25PS and 25PPO/75PS blends should have $[T_{1\rho}(H)]_{\text{blend}}$ values of 12 ms and 7 ms, re-

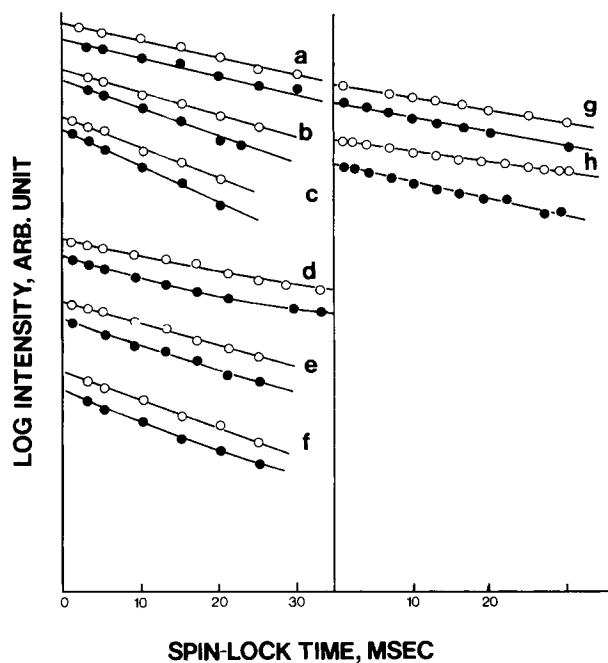


Figure 2 Logarithmic intensity plots vs. spin-lock time for blends of PPO (23K) with different MW PS: (a) 75PPO/25PS (9K); (b) 50PPO/50PS (9K); (c) 25PPO/75PS (9K); (d) 75PPO/25PS (90K); (e) 50PPO/50PS (90K); (f) 25PPO/75PS (90K); (g) 50PPO/50PS (900K); (h) 25PPO/75PS (900K); upper curves of open circles are for PPO and lower curves of filled circles are for PS.

spectively, which are much shorter than the observed rates. This means that the $T_{1\rho}(H)$ of the polymer component in the blend are much longer than they are in the neat polymer.

The relaxation time of a polymer below T_g is increased if its motional freedom is reduced. The conformation-sensitive IR bands of PPO at 1186 cm^{-1} become skewed toward lower frequency upon blending with PS,²⁰ suggesting an interaction of the ether oxygen with the ring of PS. For instance, an increase of $[T_{1\rho}(H)]_{\text{PS}}$ to 10 ms could account for the differences between relaxation times for the blends expected by eq. (1) and those observed. Of course, the same effects can be achieved by increasing $[T_{1\rho}(H)]_{\text{PPO}}$ or both.

In so far as interactions between polymers in a blend restricts motional freedom, then $[T_{1\rho}(H)]_{\text{blends}}$ should be greater than expected by eq. (1) below T_g . Conversely, it would be smaller above T_g according to theory.²¹ The contrary behaviors would be seen if one component plasticizes the other polymer in the blend.

Blends of PS (90K) with PPO have relaxation behaviors as shown in Figure 2(d-f). The decay of the PPO resonance is exponential, but the decay of the PS deviates from the simple exponential. The relaxation times of the latter given in Table II are that of the slow component obtained by analysis of data according to two exponential processes. In the case of PS (900K) blends [Fig. 2(g) and (h)], the PS component also relaxes nonexponentially. Moreover, the 25/75 blends with this high MW PS have nonexponential decay for the PPO relaxation. These nonexponential nuclear relaxations in com-

Table II Relaxation Time^a in the Rotating Frame for PPO (23K) Blends with Various MW PS

PS MW	$T_{1\rho}(H)$ (ms)					
	PPO/PS					
	75/25		50/50		25/75	
	PPO	PS	PPO	PS	PPO	PS
10K ^b	18.0	14.4	9.6	11.5	9.3	7.6
9K	20.3	18.9	12.2	10.2	9.6	8.2
90K	18.1	17.9	14.0	14.3	10.0	10.9
900K	16.9	15.4	11.5	8.9	14.4	9.1

^a For nonexponential decays, the values given are for the slow component.

^b PS (10K) is extracted from HIPS.

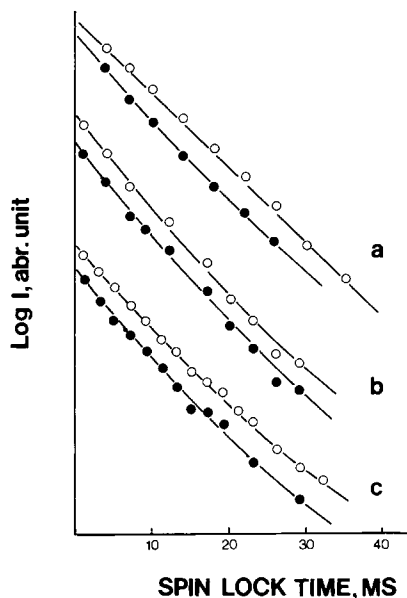


Figure 3 Logarithmic intensity plots against spin-lock time for PPO (6.4K) blends with different MW PS. Open circles: intensity of PPO; filled circles: intensity of PS. (a) 50PPO/50PS (9K); (b) 50PPO/50PS (90K); (c) 50PPO/50PS (900K).

patible blends have been attributed to compositional fluctuations; the theoretical treatment of this subject is given in the succeeding paper.¹⁷ Other behaviors observed by dynamic mechanical thermal analysis⁹

and differential scanning calorimetry¹² have also been thought to reflect this fluctuation.

The MW dependence described above is consistent with the Flory-Higgins theory. The configurational entropy for mixing is more probable toward composition homogeneity for low MW PS blends with PPO resulting in simple exponential relaxations. High MW PS blends are less homogeneous and exhibit nonexponential decay.

There are factors other than MW that can also contribute to microheterogeneity. Figure 3 gives the magnetization decay plot for blends prepared from 6.4K MW PPO with equal amounts of PS of MW 9K, 90K, and 900K. The results of 50 PPO (6.4K)/50 PS (9K) in Figure 3(a) already has nonexponential decay for PS as compared to Figure 2(b). Furthermore, the PPO (6.4K) blends with higher MW PS have nonexponential relaxations for both PPO and PS resonances. In other words, even though PPO (6.4K) has a lower MW than does PPO (23K), the blend of the former with PS of a given MW is less homogeneous than those of the latter. This behavior may be related to the crystallizability of the low MW PPO mentioned above.

Thermal Effects

The lower critical solution temperature for the PPO/PS blend was estimated at 345°C.^{11,12} There

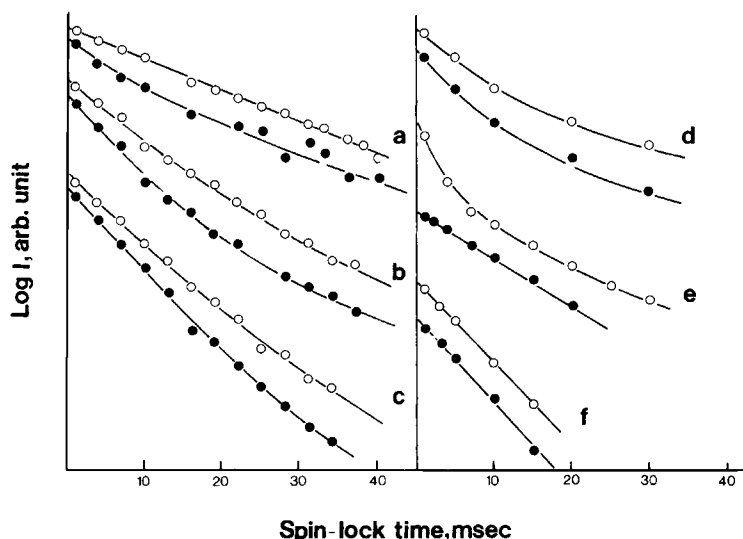


Figure 4 Logarithmic intensity plots against spin-lock time for blends of thermal effect and solvent effect on blends of PPO (23K) with PS of various MW. Open circles: intensity of PPO; filled circles: intensity of PS. (a)–(c) Annealing at 150°C for 1 h: (a) 75PPO/25PS (9K); (b) 50PPO/50PS (9K); (c) 25PPO/75PS (9K). (d)–(f) Films cast from toluene solution: (d) 75PPO/25PS (10K); (e) 50PPO/50PS (10K); (f) 25PPO/75PS (10K).

should not be phase separation under this temperature. However, we have annealed the PPO (23K)/PS (9K) homogeneous blends for 1 h at 150°C. The resulting sample showed definite compositional fluctuation as manifested in nonexponential proton relaxations [Fig. 4(a-c)]. The curvature of the magnetization decay plots of the PS component increases with increasing PPO content. The fact that both polymer components became more inhomogeneous at the nanometer scale with annealing may seem to be in contradiction to the negative enthalpy of mixing in compatible blends. However, if the system is characterized by two shallow minima around the minimum free energy of mixing at elevated temperature, then it is still possible to enhance the fluctuation of composition by thermal annealing. Hopfenberg et al.²² had observed density increases upon annealing PPO/PS blends.

The temperature dependence of slopes of the decay plots was investigated for a PPO (23K)/PS (9K) blend, as shown in Figure 5. Below 7°C, the relaxation of both the PPO and PS components are within experimental error; above that temperature, a larger separation of the two is seen, indicating that there is some increase in the incomplete mixing of the two components on a segmental level. This increase in difference of $T_{1\rho}(H)$ is further evidence for compositional fluctuation with the increase of temperature as a driving force.

Solvent Effects

Figure 4(d-f) shows the magnetization decay for PPO (23K)/PS (10K) blends cast from toluene solution. The relaxation data are compared with those found for blends prepared from chloroform solution (Table III). The toluene-cast blends exhibit pronounced biphasic decay for the 75/25 and 50/50

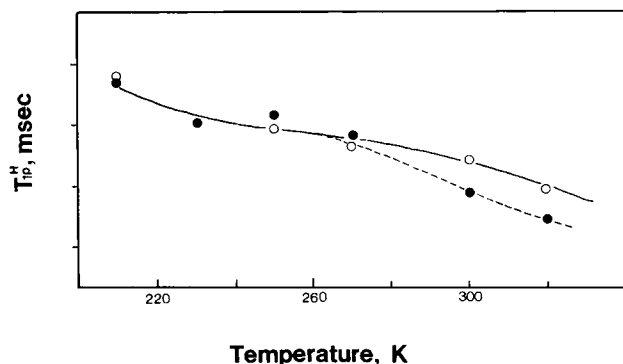


Figure 5 Plots of $T_{1\rho}(H)$ as a function of temperature for PPO (23K) and PS (900K) 50/50 blend.

Table III Effect of Solvent Used in Blend Preparation

PPO/PS (10K)	Solvent	$T_{1\rho}(H)$ (ms)	
		PPO	PS
75/25	Chloroform	18	14.4
	Toluene	19.8, 3.6	18.8, 3.6
50/50	Chloroform	9.6	11.5
	Toluene	13.6	11.6, 4.8
25/75	Chloroform	9.3	7.8
	Toluene	7.7	8.3

compositions. They are simple exponential decays in the chloroform-cast film. Interestingly, both the PS- and PPO-blend components show this curvature. Similar data not shown here were obtained for PPO (23K)/PS (9K) blends where the curvature was somewhat smaller. Toluene is known to induce crystallization in PPO²; thus, the most likely explanation for the curvature of the PPO component is the presence of both amorphous and crystalline PPO, with the latter relaxing more rapidly than the former. The rapidly decaying PS component may result from PS segments that lie within a spin diffusion radius of the crystalline PPO. Some peculiar liquid-liquid phase separation in PPO toluene solutions has been reported.²³

CONCLUSIONS

Most investigations of PPO/PS blends led to the conclusion that it is compatible at all compositions. There are one or two studies that yielded results indicative of microheterogeneity or a long-range concentration gradient. The degree of homogeneity at the nanometer scale has been examined by solid NMR. The blends are truly homogeneous at this dimension for samples obtained with low MW PS, i.e., 9K, and cast from chloroform. In most other cases, the magnetization decay is nonexponential for the PS component but is exponential for the PPO component. Both components relax nonexponentially for very high MW PS (900K), samples cast from toluene and thermally annealed, or NMR relaxation measured at elevated temperature. The nonexponential decay may be ascribed to compositional fluctuation at the spin-diffusion distance scale. A theory for it is given in another paper.¹⁷

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