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Notes

Solid-State NMR Study on the Miscibility of Polystyrene and Tetramethyl-Bisphenol A Polycarbonate Blends

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Introduction

The miscibility and phase-separation behavior of polymer blends[1-3] have been of great interest since they are related to the physical performane of the materials. There are several techniques which can be applied to characterize the miscibility of polymer blends on the segmental level, such as small-angle neutron scattering (SANS),[4] solid-state NMR,[5] FT-IR,[6,7] etc. Among these techniques, solid-state NMR is a powerful technique to investigate the intermolecular distance and interactions of miscible polymer blends. In the last 2 decades, a large number of miscible polymer blends have been discovered.[1-3] For example, the polystyrene (PS) was found to be miscible with tetramethyl-Bisphenol A polycarbonate (TMPC) by Shaw.[8] The physical properties and miscibility of this polymer pair have since been studied by many authors.[9-14] In this paper, we report the use of CPMAS NMR spectroscopy to study the intermolecular behavior of the miscible PS/TMPC blends.

Experimental Section

PS was purchased from the Pressure Chemical Co., and its M_w = 105 000 and M_w/M_n = 105. TMPC was kindly supplied by General Electric Co., and its M_w = 67 000 and M_w/M_n = 2.0. Films of the PS/TMPC blend with compositions of 25/75, 50/50, and 75/25 wt % were cast from a dichloromethane solution. Then, the blend films were dried in a vacuum oven at 70 °C for 2 days in order to remove residual solvent.

Carbon-13 CPMAS NMR spectra for the component polymers and blends were obtained with the use of a General Electric instrument equipped with a probe for solid sample measurement manufactured by Chemagnetics Co. Measurements were made at 22 °C, with magic angle spinning at about 4.2 kHz.

Results and Discussion

The ^{13}C CPMAS NMR spectra of TMPC, PS, and a 50/50 wt % blend are shown in Figure 1. The spin–lattice proton relaxation times (T_1) and the rotating-frame relaxation times ($T_{1\rho}$) of the component polymers and their blends are listed in Table I. The experimental uncertainty in the relaxation time measurements is estimated to be 6–10%. For polystyrene, there is no difference between the values measured at two major resonance peaks, 127 (aromatic) and 40 ppm (backbone). The relaxation times determined from the resonance intensities at 15 (methyl), 41, 128, and 146 ppm for TMPC are also in good agreement with each other. A single-exponential decay of the intensity was found in every case. The exponential decay observed in both the T_1 and $T_{1\rho}$ (Figure 2) data of the blends is consistent with a single relaxation mechanism which comes about through the mechanism of magnetic spin diffusion between the component polymers.

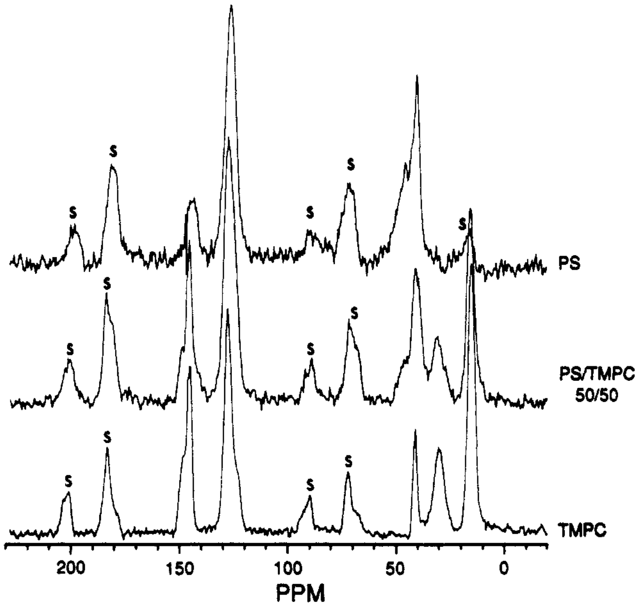

Figure 1. NMR spectra of PS, TMPC, and a PS/TMPC 50/50 wt % blend. The side bands are indicated as "s".

Table I

Proton Spin–Lattice Relaxation Times (T_1, s)

PS/TMPC	ppm 15	40	128	146	calc
0/100	0.34	0.33	0.33	0.33	
25/75	0.42	0.43	0.42	0.40	0.42
50/50	0.55	0.54	0.55	0.55	0.56
75/25	0.80	0.80	0.82	0.75	0.82
100/0		1.48	1.50		

Proton Spin–Lattice Relaxation Times in the Rotating Frame ($T_{1\rho}$, ms)

PS/TMPC	ppm 15	40	128	146	calc
0/100	39.8	43.8	40.0	41.1	
25/75	20.8	21.7	20.3		17.4
50/50	13.1	12.8	12.2	13.5	11.1
75/25	10.4	9.0	9.1	10.4	8.2
100/0		6.8	6.6		

If spin diffusion allows all the material to relax totally through the two component polymers in the blend, then the relaxation rate is related to the number of PS and TMPC protons by the following equation[15-17]

$$k = k_1N_1 + k_2N_2 \qquad (1)$$

where k is the observed spin–lattice (T_1^{-1}) or rotating-frame ($T_{1\rho}^{-1}$) relaxation rate of the blend, k_1 and k_2 are the

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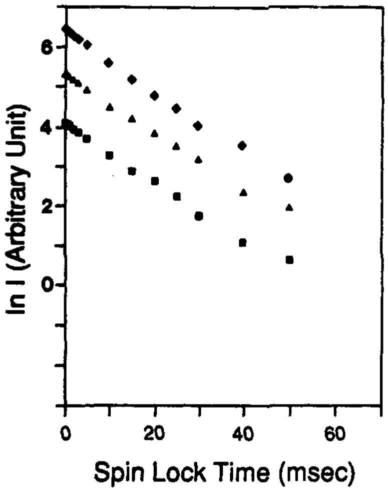

Figure 2. Exponential fitting for a 50/50 wt % PS/TMPC blend in $T_{1\rho}$ measurement. ■: 15 ppm. ▲: 40 ppm. ◆: 128 ppm.

rates for the component polymers, and N_1 and N_2 represent the mole fractions of the protons of the respective component polymers in the blend. In applying the above equation to our data, we find that the experimental T_1 values are in excellent agreement with the predictions of eq 1 (Table I). An estimate of the maximum diffusive path length L may be made from the approximate formula

$$L = (6D/k)^{1/2} \tag{2}$$

where D is the diffusion coefficient. For $k = 2\ \mathrm{s}^{-1}$, L is estimated as 17 nm for a typical D value of $\sim 10^{-12}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$;[18,19] a larger D value, for example, $10^{-11}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$, will give a diffusion length of about 55 nm. If domains of the component polymers are present in the blends, their linear dimensions are probably not larger than 15–60 nm on the basis of T_1 data.

The $T_{1\rho}$ results present a somewhat different picture. The relaxation times are longer than the calculated values. Although the differences are not large, they are believed to be beyond the limits of experimental error. Recently Li, Dickinson, and Chien[20] reported similar findings in PS/poly(2,6-dimethylphenylene-1,4-oxide) (PPO) blends. Earlier, McBrierty[15] and co-workers also found discrepancies between the experimental and calculated $T_{1\rho}$ values in blends of poly(methyl methacrylate) and poly(styrene-co-acrylonitrile).

The discrepancy between experimental and calculated $T_{1\rho}$ values may reflect a violation of the assumptions made in the derivation of eq 1. It should be noted here that FT-IR results have shown evidence of intermolecular interaction between the phenyl ring of PS and the carbonyl group of TMPC.[7] As a consequence of the interaction which restricts segmental motion, it is possible that the intrinsic relaxation rate of PS or TMPC (or both) is no longer the same as that in the neat state.[17] For example, an increase of $T_{1\rho}$ for PS to 8 ms would give a good fit to the calculated $T_{1\rho}$ values. This would suggest that the motional freedom of PS in the blend is reduced by the presence of TMPC. Changing the $T_{1\rho}$ value of TMPC to 60 ms, however, results only in a moderate improvement. However, the effect of local environment (including realistic geometries) on segmental motion needs additional study.

Finally, the single $T_{1\rho}$ value for each blend suggests homogeneity of mixing on a scale of a few nanometers. We note with interest that the correlation length of concentration fluctuation from SANS measurements[12] is about 2 nm which has the same order of magnitude.

References and Notes

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