Polymer-Polymer Miscibility Determination via CP-MAS NMR in Blends of Deuteriated and Protonated Polymers

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Polymer-polymer blends, both miscible and semimiscible or phase-separated systems, are important materials from both industrial and academic viewpoints. A better understanding of the important factors affecting polymer-polymer miscibility is essential for the development of new blend systems. DSC, DMTA, microscopy, light and neutron scattering, and other methods have been used to determine miscibility on the dimensional scale limitations of each technique. However, miscibility in blends of polymers having similar T_g's and blends in which one polymer is present in amounts less than 5-10% is difficult to characterize.

Solid-state NMR has already been demonstrated to be a valuable tool for the characterization of polymer-polymer miscibility. In favorable cases, Goldman-Shen pulse sequences[1-4] and 2D proton NMR[5] can provide domain size estimates, as also can measurement of proton relaxation processes in blends compared to the component polymers.[6,7] One excellent method involves cross-polarization studies in mixtures of deuteriated and protonated materials[8] and has been used to study mixing in polymer-plasticizer mixtures[9,10] and in block copolymer systems.[8,9] The central purpose of this work is to further apply intermolecular cross polarization to high molecular weight polymer-polymer blends in order to obtain useful information about miscibility at the molecular level and to show that the method is applicable to blends in which one component polymer is present in small quantities (less than 5-10%).

In solid-state CP-MAS ^{13}C NMR the dipolar interactions between the abundant proton spins and the rare ^{13}C spins are utilized to polarize the latter by the Hartman-Hahn technique[11] through spin polarization transfer. This brings about significant gains in ^{13}C signal intensity and reduction in data acquisition time. The efficiency of this cross polarization depends on the strength of the proton-carbon magnetic dipolar coupling and thus on the proximity of the protons to the ^{13}C nuclei.[12,13] Of course, the absence of protons, such as for a perdeuteriated polymer, deprives the system of this benefit. Fortunately cross polarization can also occur if the average proton-carbon distances in two different molecules are on the order of 10 Å or less. Thus if a perdeuteriated polymer is mixed with a second protonated component, ^{13}C spectral features of the former are cross polarized and become observable if the system is sufficiently miscible on a molecular scale.

NMR spectra were obtained on an IBM AF 200 spectrometer at ambient probe temperatures of 22 ± 2 °C with 5-μs 90° pulses for both ^{1}H and ^{13}C nuclei (50-KHz rotating frame).

Blends of PS and PVME have been well characterized to be compatible. Figure 1a shows a ^{13}C spectrum (2500 accumulations) for PS-d_8 of 110 000 MW obtained with CP contact time of 3 ms. The sample contains ca. 2% of protonated PS which gives the weak resonance at 127 ppm from the aromatic proton impurities. A spectrum for protonated PS is shown in Figure 1c (2-ms CP time, 256 accumulations) for comparison (methylene carbons, 39 ppm; aromatic C_{2-6}, 127 ppm; aromatic C, 145 ppm).

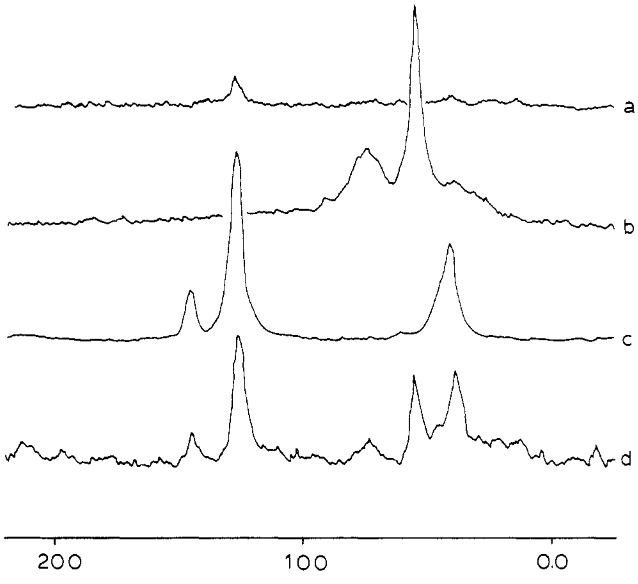

Figure 1. (a), (c), and (d) CP-MAS ^{13}C spectra of PS-d_8, PS, and 65 PS-d_8/35 PVME blend, respectively. (b) DP-MAS ^{13}C spectrum of PVME.

Table I
Normalized ^{13}C Signal Intensities for Polystyrene and Polystyrene-d_8 in PVME Blend

resonances		normalized ^{13}C NMR intensities	
chemical shift, ppm	nuclei	PS	PS-d_8/PVME
145	aromatic, C_1	0.24	0.22
127	aromatic, C_{2-6}	1.00	1.00
39	methylene C	0.51	0.51

Figure 1b is for PVME obtained by using direct carbon polarization (DP) (methylene carbon, 45 ppm; methine carbon, 75 ppm; methyl carbon, 55 ppm). Motional freedom in PVME, a viscous liquid at room temperature, renders polarization by the Hartman-Hahn method ineffective.

A blend of 65 PS-d_8/35 PVME (the number preceeding the polymer is its weight percent in the mixture) was prepared by casting a film from dilute toluene solution and drying it in vacuo for 48 h at 60 °C and 4 h at 125 °C. The ^{13}C spectrum for the blend is shown in Figure 1d. The normalized intensities of the resonances for the PS-d_8 in the blend are 12 times that of pure PS-d_8. This experiment demonstrates the occurrence of significant intermolecular cross polarization of the carbon spins of PS-d_8 by the proton spins of PVME. This is possible when the proton-carbon internuclear distances are on the order of 10 Å or less. Furthermore, PVME resonances are observable by CP conditions, indicating restriction of its main chain motions in the blend. It is concluded that there is molecular scale mixing for this blend. The same conclusion was reached by solid-state NMR studies on blends of protonated PS/PVME.[14,15] The present results obtained with PS-d_8/PVME are at the same time simple and direct.

Table I shows that the relative normalized ^{13}C NMR intensities of pure protonated PS are identical with those of PS-d_8 in the PVME blends. This indicates that the *relative* CP efficiencies for the PS-d_8 in the blend are approximately the same as the relative efficiencies in the protonated PS and that the proton-carbon dipolar interactions are comparable in the two systems. The actual dynamics of the CP process are slower for the PS-d_8 than for PS, and a study will be discussed in detail elsewhere.

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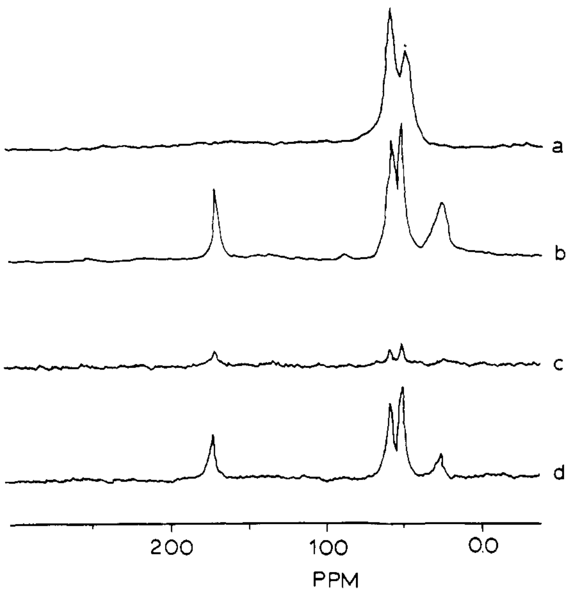

Figure 2. (a), (b), (c), and (d) CP-MAS ^{13}C spectra of PVC, PMMA, PMMA-d_8, and 95 PMMA-d_8/5 PVC blend, respectively. (d) Obtained with a dipolar decoupling delay of 40 μs.

Miscibility information can also be obtained from relaxation times of the blend if the component polymers have very different relaxation times. For instance, our $T_{1\rho}^{H}$ measurements on PMMA/PVC blends and the pure components indicate miscibility on a scale of about 40–50 Å.[16] Albert et al.[6] reported heterogeneity in syndiotactic PMMA/PVC blends below the 25–30 Å level. However, proton-relaxation experiments are of little value if the component polymers have similar characteristic relaxation times or if the sample contains low volume fractions of either component.[17] To demonstrate the value of CP with perdeuteriated polymer, we have performed CP-MAS on atactic PMMA-d_8/PVC blends containing only 5% of PVC.

Figure 2a shows the CP-MAS NMR spectrum for PVC. The chlorinated carbon resonance is at lower field. The spectrum of PMMA (Figure 2b) has resonances in the order of decreasing field for the α-methyl, quarternary main chain, methoxy, and carbonyl carbons. Figure 2c is the spectrum of 110 000 MW atactic PMMA-d_8 from Polymer Laboratories (4110 accumulations) due to a small amount of protonated PMMA in the material. A blend of 95% of this PMMA-d_8 and 5% PVC was prepared by methanol precipitation of a THF solution of the polymers. The CP-MAS spectrum of the blend is shown in figure 2d (3-ms CP time, 2000 accumulations). In this instance the PVC resonances are suppressed by a delayed dipolar decoupling sequence. Even though Figure 2d is the spectrum from less than half of the transients used to obtain Figure 2c, the resonances are 3–4 times more intense. This result establishes not only miscibility at the molecular level but also the applicability of the technique to blends containing only a few percent of protonated polymer component.

Blends of PS and PMMA, which have found usage in decorative applications due to their pearlescent appearance,[19] are reported to be phase separated according to microscopy studies.[20] This system should exhibit only minimal intermolecular cross polarization in contrast to the two compatible systems above.

A simple physical mixture of 65% PS-d_8 and 35% PMMA by weight gave the ^{13}C spectrum shown in Figure 3a. The small peak at 127 ppm is due to the PS aromatic carbons which are the same as seen in Figure 1a for PS-d_8 alone. The remaining resonances are those of PMMA. The mixture was dissolved in THF and a blend obtained by methanol precipitation. The aromatic region of the CP-MAS ^{13}C NMR spectrum of this blend (2-ms CP time, 2500 FID accumulations) is shown in Figure 3b. The resonance intensity in the blend is about twice that of the mixture, indicating a small degree of interfacial mixing.

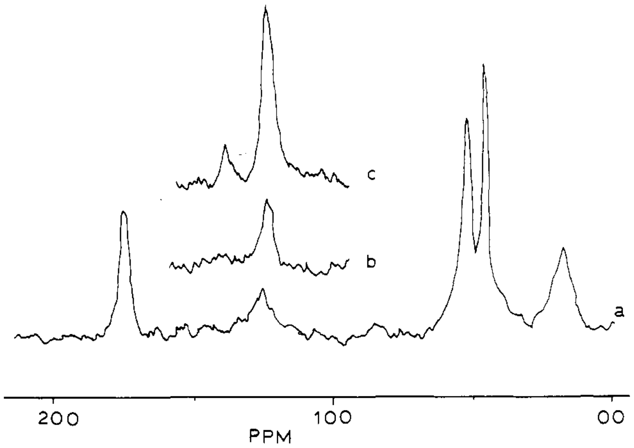

Figure 3. (c) CP-MAS ^{13}C spectrum of a 65/35 mixture of polystyrene-d_8 and poly(methyl methacrylate) powders. (b) PS-d_8 aromatic signal after blending the two polymers. (a) Aromatic region for PS-d_8 in the 65/35 PVME blend (× $^{1}/_{2}$) for comparative purposes.

The intermolecular cross polarization in this 65 PS-d_8/35 PMMA blend is much less than it is in the 65 PS-d_8/35 PVME blend. The aromatic carbon resonance in the latter (Figure 3c scaled by one-half) is more than 6 times more intense than the former. The small interfacial mixing in the PS/PMMA system is in contrast with the deuteriated polyether–polyester block copolymers, which although phase separated show extensive interfacial mixing according to CP-MAS NMR.[9]

A second blend, incorporating 75% PMMA-d_8 and 25% PS, was also prepared. In this case, there was no observable increase in the intensity of the PMMA-d_8 resonances under identical accumulation conditions. Therefore, the PMMA-rich blend has either a smaller degree of intermixing at the interface, or a reduced interfacial area. Microscopy studies show that the PS-rich end of the composition range has a smaller average domain size of a dispersed PMMA phase.[20] This would mean a greater interfacial area as compared to the PMMA-rich blends.

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Registry No. PMMA-d_8, 63541-79-7; PVC, 9002-86-2; PS-d_8, 27732-42-9; PVME, 9003-09-2; PMMA, 9011-14-7.

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(16) Single component proton T_1 relaxation times in the rotating frame of 7–8 ms were observed for 30/70 and 60/40 blends of PMMA/PVC which were intermediate in value between those for the pure components. This allows an upper limit for phase separation to be estimated at about 40–50 Å, cf. ref 6.
(17) The uncertainty in the measurement of proton relaxation times is greater than the expected or observed change after blending with small amounts of either blend component.
(18) The PMMA-d_8 was synthesized by Dr. Claude Picot, CNRS, France. Cumylpotassium was used as an initiator and the MW was determined by GPC to be 100 000.
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Activation Energies of Local Conformational Transitions in Polymer Chains

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In recent years, much effort has been devoted to understand the mechanism for rapid relaxation processes in polymers. Various theoretical and experimental studies have accumulated on the dynamics of local orientational motions. The fact that these local motions result from conformational transitions of the skeletal bonds from one isomeric state to another is now well established. However, still some controversy remains as to the exact nature and extent, along the chain, of these motions. High frictional resistance naturally prevents the propagation of the configurational rearrangements beyond a finite sequence. However, crankshaft[1,2] or three-bond[3] motions, which leave the tails of the motional unit unchanged, necessitate the passage through at least two barriers between conformers, which is incompatible with the experimentally observed activation energies. Although the scale of motions probed depends on the specific experimental technique (NMR, ESR, fluorescence depolarization, dielectric relaxation, etc.), most experiments reveal an activation energy of about 5 kcal/mol for rapid relaxation processes.[4] Simulation studies by Helfand and collaborators[5] demonstrated that isolated single-bond motions accompanied by the translation of chain ends dominate the relaxation behavior. The activation energies associated with those motions, referred to as type 2 motions, are slightly larger than the barrier height between the gauche and trans states. Also, relying on an activation energy of 2.6 kcal/mol measured by NMR for aryl aliphatic esters, Tĕkély et al.[6] concluded that type 2 motions are highly probable in long aliphatic subchains, while the higher activation energy (5.6 kcal/mol) for molecules with shorter motional sequences was attributed[6] to the occurrence of three-bond or crankshaft-like motions. Skolnick and Yaris calculated,[7] on the other hand, an activation energy of about 2 kcal/mol for the dissipation of the diffusive mode, by parameterizing the Bendler–Yaris[8] and Skolnick–Yaris[9] models to NMR experiments on PVA; in comparison, an activation energy of 4 kcal/mol was measured[10] by dielectric relaxation.

More investigation is clearly required to elucidate the relative contributions of (i) barriers through conformational isomeric states, (ii) frictional resistance of the surroundings, and (iii) constraints imposed by chain connectivity to the observed activation energies. The first two effects are present in small molecules, too, while the latter is characteristic of polymeric chains. The fact that temperature dependence of the excimer fluoresence intensity parallels that in a small molecule analogue, as pointed out by Liao et al.,[11] suggests that the apparent activation energy is independent of effect (iii). In fact, calculations reported below yield, invariably, a definite activation energy slightly larger than the barrier to internal rotation of a skeletal bond, regardless of the degree of constraints imposed by the connected tails.

The internal orientational autocorrelation function (OACF) is given by

$$M_{2,\text{int}}(t) = \frac{1}{2}\langle 3\cos^2\theta(t) - 1\rangle \qquad (1)$$

where $\theta(t)$ denotes the angular separation between the initial and final (at time t) orientations of the bond investigated and the brackets represent the ensemble average. The subscript int indicates that the global or external reorientation of the sequence to which the bond belongs is not considered. Calculations are performed by keeping the first two bonds of the sequence fixed relative to a laboratory-fixed coordinate system. In experiments such as NMR, ESR, and fluorescence depolarization, $M_{2,\text{int}}(t)$ is measured, during the short time windows of observation.

In recent work,[12] the OACF of the central bond of a finite motional sequence was investigated, with special emphasis on the influence of factors such as first neighbor interdependence and strength of constraints imposed by chain connectivity. The evaluation of the ensemble average in eq 1 necessitates the analysis of all possible transitions between conformers. To this end, the complete set of sequences with various configurations was generated, and normalized stochastic weights or time-delayed joint probabilities were assigned to each transition between those configurations. In accordance with the scheme first introduced by Jernigan,[13] joint probabilities were obtained as the solution of a master equation describing local dynamics. The parameters such as the chain geometry, the height of saddles between isomeric states, etc., were determined from real chain characteristics. The method allows for the calculation of any dynamic property associated with local conformational transitions. For the complete description of the calculation scheme, the reader is referred to ref 12.

In this note, the above simulation method[12] is used to calculate the activation energy associated with conformational transitions. A finite sequence of n bonds belonging to a polyethylene chain is considered. $M_{2,\text{int}}(t)$ for the last bond of the sequence, whose first bond is held fixed, is calculated for various degrees of constraints: In one extreme case, only transitions conserving the coordinates of the end point of the sequence are allowed. In the other extreme, possible constraints on the motion of the sequence imposed by the connected tail are ignored; i.e., all transitions of the sequence are considered. Neither of the two extremes is a realistic representation of the chain behavior. The end of the motional sequence is not necessarily fixed at its original position during conformational transition (e.g., type 2 motions), while, on the other hand, large swinging motions of the tails are precluded by high frictional resistance. In the intermediate case, only those

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