5424 *Macromolecules* **1998,** *31,* 5424−5429

Direct Detection of Miscibility in Saturated Polymer Blends

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Received February 24, 1998; Revised Manuscript Received May 18, 1998

ABSTRACT: We have used variable-temperature solid-state NMR methods to determine that amorphous polypropylene (a-PP) is miscible with blends of poly(ethylene)ethylethylene (PEE) and poly(ethylene-*co*-octadecene) (PE-OD). Rothwell−Waugh line-broadening effects and selective ^{1}H $T_{1\rho}$ measurements indicate that the frequency of reorientational chain dynamics increases for a-PP upon blending with PEE and PE-OD but remains unchanged for blends with poly(ethylene-*co*-dodecene) (PE-DD). We infer partial miscibility on the basis of converged but incompletely averaged relaxation curves for the a-PP/PEE and a-PP/PE-OD blends, while the a-PP/PE-DD blends were found to be immiscible. Dipolar filter experiments in which spin-diffusion was used to monitor polarization transfer provided direct evidence for miscibility in the a-PP/PE-OD blends and immiscibility in the a-PP/PE-DD blends. From these data, domain sizes were calculated to be 5.1 nm (i.e., on the order of chain dimensions) for the miscible regions of the PP/PE-OD blend.

Introduction

Binary mixtures of high molecular weight, saturated hydrocarbon polymers are generally not miscible due to the lack of any significant enthalpy of mixing. Recently, there have been reports of single phase melt mixtures of isotactic polypropylene (i-PP) and some poly(ethylene/ethylethylene) copolymers.[1] Experimental verification of miscibility in these blends came from neutron scattering data. Given the relative difficulties associated with neutron scattering work, i.e., deuterium labeling and access to a neutron source, we have initiated work to determine to what degree solid-state NMR is useful in miscibility studies of saturated polyolefin blends. Given the large-scale manufacture, development, and application of saturated polyolefins, tailoring of blends in these commodity systems is critical.

Although the recent literature includes many references to blend studies by solid-state NMR,[2−6] most if not all of these reports focus on binary mixtures in which at least one of the polymer pairs contains some type of functional group or unsaturation. While this observation surely reflects the lack of saturated blends that are known to be miscible, it also reflects the unique constraints placed on standard NMR methods and their analyses, which are most commonly used to identify miscibility. The absence of any olefinic or aromatic functionality in these systems makes it difficult to establish polarization gradients with which to directly follow spin diffusion.[7,8] This report describes the analysis of miscibility in solid blends of high molecular weight amorphous polypropylene (a-PP) and polyethylene copolymers (poly(ethylene/ethylethylene) or PEE, poly(ethylene-*co*-octadecene) or PE-OD, and poly(ethylene-*co*-dodecene) or PE-DD) using variable-temperature ^{1}H−^{13}C CP/MAS, relaxation, and spin-diffusion NMR spectroscopy.

Experimental Section

a-PP/polyethylene copolymer blends (50/50 wt/wt %) were prepared in toluene solutions containing a BHT stabilizer and dried under nitrogen at ambient temperature, with further drying at 50 °C in a vacuum for at least 48 h. The M_n data for a-PP, PEE, PE-OD, and PE-DD were 83k, 50k, 76k, and 60k, respectively. Polydispersities of a-PP, PE-OD, and PE-DD were all ≈2.0, whereas that of PEE was 1.07. The PEE copolymer contained 83 mol % butene comonomer, the PE-OD copolymer contained 11 mol % octadecene comonomer, and the PE-DD copolymer contained 19.5 mol % dodecene. The a-PP contained 60% racemic diads and 6% 2,1 regio errors.

Solid-state NMR data were collected on a Bruker DSX-500 spectrometer using a variable-temperature 4-mm MAS probe. Radio frequency power levels were 70 kHz for spin-locking and decoupling, corresponding to a ^{1}H $\pi/2$ pulse width of 3.5 μs. Data were collected at MAS speeds of 4.3 kHz. Depending on the temperature, anywhere from 100 to 2000 scans were collected per relaxation time increment. ^{1}H $T_{1\rho}$ measurements were made using standard ^{13}C cross-polarization observation experiments, in which the length of the ^{1}H spin-lock pulse was incrementally varied prior to cross-polarization.[9] $T_{1\mathrm{H}}$ measurements were made using inversion−recovery measurements via cross-polarization.

Results and Discussion

Variable-temperature CP/MAS experiments may be used to investigate the change in polymer chain dynamics which occurs upon mixing. Information about mixing and miscibility may be inferred from dynamics information, since local polymer chain dynamics are controlled by intermolecular packing constraints. However, even for blend components that are miscible at a molecular level, a similar distribution of motional time scales for blend components does not necessarily exist, as has been demonstrated for several blend systems.[3,10,11] In fact, for most cases the dynamics of the individual homopolymers do change significantly, but still maintain unique temperature dependencies. In our investigations of a-PP blends, we have observed a shift in the temperature-dependent dynamics for backbone reorientation in a-PP upon blending with poly(ethylethylene) and poly(ethylene-*co*-octadecene). Cross-polarization spectra can be sensitive to small changes in reorientational dynamics since random molecular motions interfere with the application of coherent radio frequency pulses. Rothwell and Waugh first reported on the conflicts between incoherent molecular motions and coherent averaging methods such as decoupling,

S0024-9297(98)00287-3 CCC: $15.00

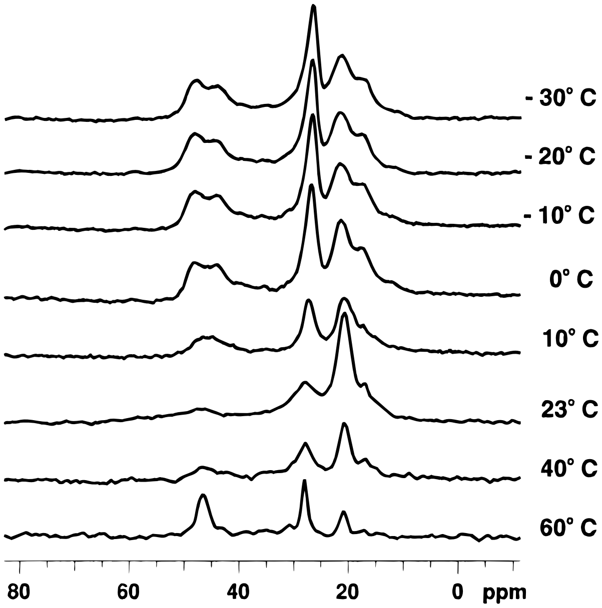

Figure 1. Variable-temperature $^1H \rightarrow ^{13}C$ cross-polarization spectra of atactic polypropylene. Note in particular the temperature dependence of the methylene signal at 46 ppm.

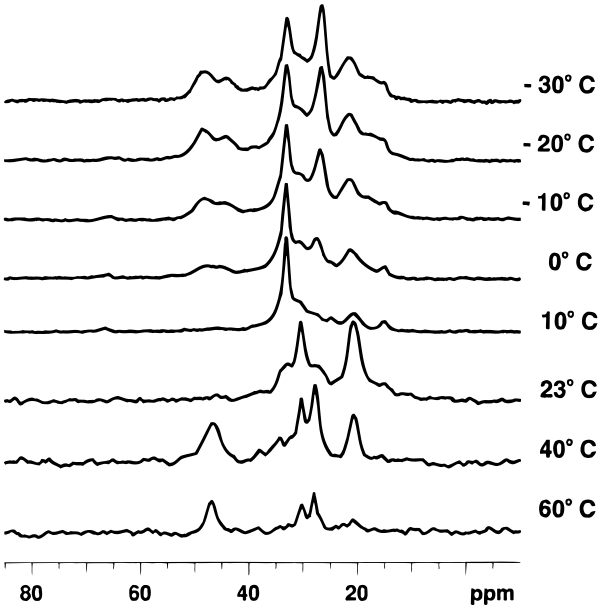

Figure 2. Variable temperature cross-polarization spectra for the atactic PP/poly(ethylene-*co*-octadecene) blend.

magic-angle spinning, and multiple-pulse sequences.[12] When the frequency of chain motion approaches that of the radio frequency field strength (usually 40−80 kHz) or spinning rate (ca. 3−15 kHz), line widths in the CP spectrum reach their maximum value and, in some cases, become broad beyond detection.

Shown in Figure 1 are the CP/MAS spectra for a-PP obtained over a temperature range of −30 to +60 °C. We are particularly interested in the methylene signal at 46−47 ppm, since this group is situated on the polymer backbone. Conformational splitting of this signal is observed at lower temperatures, as trans−trans and trans−gauche conformations are not averaged below the glass transition.[13] The most interesting features of this peak are observed at higher temperatures, as the methylene signal converges to a single peak at 10 °C, broadens significantly at room temperature, becomes unobservable at 30 °C (not shown), and begins to sharpen again as the temperature is raised to 60 °C. These data indicate that the density of chains with a correlated reorientational frequency of 70 kHz is maximized at 30 °C. While we realize that there exists a broad distribution of chain reorientation rates, we rule out the MAS time scale as most relevant based on variable-temperature T_{1pH} measurements (vide infra).

For comparison, CP spectra obtained over the same temperature range for the a-PP/poly(ethylene-*co*-octadecene) blend are shown in Figure 2. Here, the methylene signal is unobservable at both 10 and 23 °C, and the onset of broadening occurs at 0 vs 10 °C for the a-PP homopolymer. Further, the 46 ppm signal for the blend is well-resolved once the temperature reaches 40 °C. Clearly, the frequency distribution of motion is shifted to a lower temperature for a-PP upon blending and appears to be broadened as well since the peak is absent in both the 10 and 23 °C spectra for the blend, and only the 30 °C spectrum for the homopolymer. The relaxation data presented below are consistent with this observation.

The degree to which polymers are mixed in binary blends is often determined via solid-state NMR relaxation methods. In particular, ^1H T_1 and $T_{1\rho}$ measurements may be used to establish upper and lower limits on the length scales of polymer mixing.[2] The technique relies upon application of a standard diffusion equation for polarization transfer, where the time input corresponds to an experimentally measured composition-weighted average of the relaxation time constants for the two homopolymers. One limitation of this technique, however, is that the relaxation time constants for the separate homopolymers should differ by a factor of 2−3. In our study of the a-PP/polyethylene copolymer blends, we have found that the $T_{1\rho H}$ relaxation time constants for the neat blend components are almost identical near room temperature. Recall that the 46 ppm peak in a-PP is too broad at room temperature to measure its relaxation decay.

To more carefully interrogate the change in the distribution of molecular motions that occurs upon blending, and to determine the level of molecular scale chain mixing, we have collected $T_{1\rho H}$ relaxation data over the temperature range −30 to +60 °C. The a-PP homopolymer, the blend with PE-OD, and two additional blends were measured. The two additional blends were a-PP/PEE and a-PP/PE-DD. Previous neutron scattering work by Bates and co-workers on i-PP/PEE blends in the melt suggests to us that the a-PP/PEE blend may be miscible in the bulk.[1]

The temperature-dependent rotating-frame relaxation times $T_{1\rho H}$ for a-PP, PEE, and either polymer in the a-PP/PEE blend are shown in Figure 3. Since separate peaks are resolved in the CP/MAS spectrum, the effect of blending on chain dynamics for either polymer component may be interrogated separately, thereby providing chain-selective information not available from standard thermal or rheological measurements. The methylene signal at 46 ppm was used to determine the $T_{1\rho H}$ for PP, while both the backbone CH_2 and terminal CH_3 signals were used for the PEE (the same value was determined for either PEE signal, as expected due to proton spin diffusion). Note that the apparent minima in the relaxation curves are observed at or near room temperature, as expected since the Rothwell−Waugh line broadening is maximum at those temperatures (the $T_{1\rho H}$ experiment probes the same time scale of

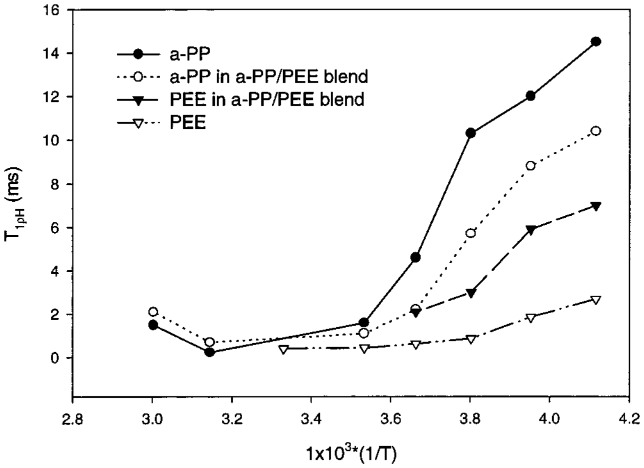

Figure 3. Variable-temperature $T_{1\rho H}$ plots for atactic polypropylene (a-PP) and its 50:50 wt % blend with poly(ethylene)-ethylethylene (PEE). Note the convergence of relaxation times to intermediate values for either polymer upon blending. Most data points are the result of triplicate measurements, and the standard deviation $\sigma = 150$ μs.

molecular motion). The relevant time scale is defined by the strength of the ^{1}H radio frequency field strength, which in this case was 70 kHz.

The most significant observation from the data in Figure 3 is that the relaxation times for either polymer in the blend fall between the extremes observed for the a-PP or PEE homopolymers over the temperature range below that complicated by the Rothwell–Waugh effect. However, the relaxation times do not converge to the same average value, as seen from the −10, −20, and −30 °C data points. The data points at −20 and −30 °C are especially significant, as they are below the glass transition for the a-PP homopolymer, and therefore spin-diffusion should be effective. The a-PP value decreases toward the PEE homopolymer value, and vice versa for the PEE. Typically, if the two polymers are miscible at the molecular level, the relaxation times converge to the same value since spin diffusion acts to distribute polarization from specific relaxation sinks. Although the two polymers may have significantly different chain dynamics, the relaxation times would be the same. The incomplete averaging observed for the data in Figure 3 suggests that all chains from each polymer are not completely mixed at a chain level with length scales longer than the spin-diffusion length scale in some areas of the blend. Using the standard diffusion equation (vide infra),[14] we calculate a minimum domain size of 2–3 nm in the PP/PEE blend. We were not able to observe multiple components in the relaxation curves (*M(y) vs* τ) for the blends, however, presumably due to the relatively small difference between the homopolymer and blend $T_{1\rho H}$ values. Regressions yielded correlation coefficients for single-exponential fits of >0.98 for all data points at −10, −20, or −30 °C in the PP/PEE blend. Also, the ^{1}H T_1 values for the neat a-PP and PEE were too similar at 40 °C (650 and 450 ms, respectively) to accurately measure a converged relaxation value for the blend.

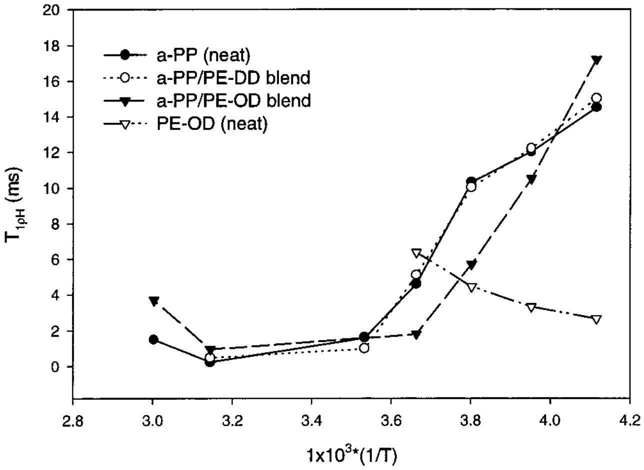

Figure 4. Variable-temperature $T_{1\rho H}$ plots for blends of a-PP with poly(ethylene-*co*-dodecene) (PE-DD) and poly(ethylene-*co*-octadecene) (PE-OD). Note the complex low-temperature behavior of the a-PP/PE-OD blend. See text for details.

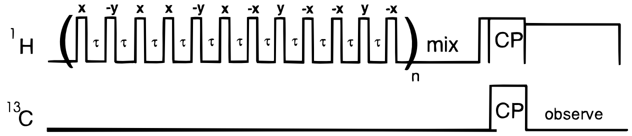

Figure 5. Pulse sequence used for the dipolar filter[15] experiments. Typically, $\tau = 10$ μs and the number of cycles, *n*, was 20.

Figure 4 shows the temperature dependence of the $T_{1\rho H}$ values of the a-PP CH_2 group in blends with PE-DD and PE-OD. The a-PP homopolymer and PE-OD curves are shown for reference. The a-PP homopolymer and its blend with PE-DD show identical behavior over the entire temperature range, which indicates that the frequency distribution for polypropylene backbone motion is not changed relative to the homopolymer and that spin diffusion is not operative between the two polymers. Therefore, this blend is not mixed at a molecular level. Figure 4 also shows that the relaxation times for the a-PP methylene groups in the a-PP/PE-OD blend decrease significantly at temperatures greater than −30° C, analagous to that observed for PP in the a-PP/PEE blend of Figure 3. We note that for the 50:50 PP/PE-OD blend, T_{1H} relaxation times for the a-PP, neat PE-OD, and the blend were 650, 280, and 450 ms, respectively. Clearly, the length scale of mixing is below the 20 nm range defined by the averaged T_{1H} value for the blend (vide infra). The low-temperature relaxation data for the neat PE-OD copolymer is also shown in Figure 4 and indicates that the relaxation minima for this copolymer occurs at a much lower temperature than for the other polymers. Together, these data suggest the complex low-temperature phase behavior for the PP/PE-OD blend, with phase separation at −30° C and partial misciblity at temperatures greater than −20 °C. This interpretation in consistent with our initial DMTA experiments, in which we have observed a single tan δ peak at −15 °C for a 2 °C/min scan over the temperature range −130 to +40 °C. For reference, the T_g for the neat a-PP and PE-OD were measured to be 0 and −40 °C, respectively.

To more conclusively determine the length scale of mixing in the a-PP/PE-OD blend, dipolar filter experiments were employed to directly follow the polarization transfer rate. These data were collected at 40 °C. The dipolar filter experiments have recently been introduced by Egger and co-workers as a novel way to select magnetization from the mobile components in a heterogeneous blend.[15] The pulse sequence is shown for reference in Figure 5. The effect of this sequence depends strictly on the number of cycles applied on the ^{1}H channel (i.e., *n*), and the spacing between the

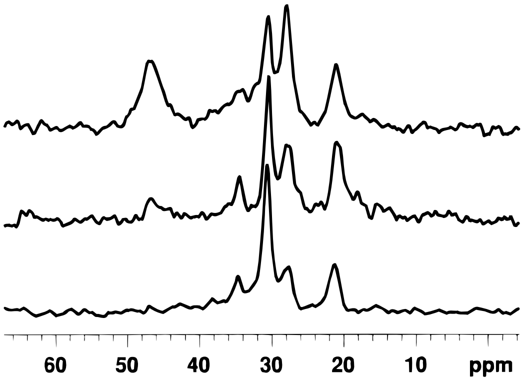

Figure 6. Effect of the dipolar filter sequence length on the PP signals in the a-PP/PE-OD blend: (top) normal CP spectrum; (middle) dipolar filter with 10 cycles using a 10 μs τ value; (bottom) dipolar filter with 20 cycles using a 10 μs τ value.

individual 90° pulses in the cycle. In short, this sequence prepares magnetization based on the strength of the proton dipolar couplings in the particular polymer phase of the blend. We have used $n = 10-20$ and the interpulse spacing τ of 10−15 μs. Rigid polymer phases will lose magnetization during the application of the sequence, as the effective cycle time is too long to average homonuclear proton dipolar couplings. The polarization from more mobile polymers, which have reduced dipolar coupling strengths due to molecular motion, will be preserved. This polarization may be transferred back to the rigid phase during an appropriate mixing time in which $^1H-^1H$ spin diffusion is operative.

Shown in Figure 6 is the effect of varying the dipolar filter cycle length on the discrimination between the PE-OD and PP components in the a-PP/PE-OD blend. The normal CP/MAS spectrum is shown in Figure 6a for reference. Application of a 10 cycles of the dipolar filter with a 10 μs spacing (Figure 6b) results in only partial attenuation of the PP CH_2 signal at 46 ppm and CH signal at 28 ppm. Increasing the number of cycles to 20 completely attenuates all PP backbone signals, with only a small CH_3 signal at 21 ppm remaining. Complete suppression of the PP CH signal at 28 ppm is confirmed by the 1:1 ratio for the signal intensity of the PE-OD α (34 ppm) and β (28 ppm) carbons (relative to the branch).

Figure 7 shows the results for the dipolar filter experiment during which increasing mix times are inserted to allow spin diffusion to occur. As the mixing time is increased from 0 to 50 ms, the main-chain CH_2 peak for PP at 46 ppm continues to increase in intensity, as does the PP CH signal at 28 ppm. As was shown in Figure 6, complete suppression of the PP methyl signal is not achieved using the 20 cycle filter. Further increasing the strength of the filter by increasing the interpulse spacing did not lead to selective attenuation of the PP methyl signal relative to the PE-OD signal. Therefore, the analysis of the time dependence of polarization transfer in the PP/PE-OD blend must account for the intramolecular effect from the PP methyl signal. As a control for this intramolecular effect, we also ran the same dipolar filter experiment used to generate the data in Figure 7 on neat a-PP.

Figure 8 shows the spin-diffusion curves for buildup of PP CH_2 magnetization as a function of mixing time in neat a-PP and the a-PP/PE-OD blend. The plot is a measure of percent recovery to equilibrium intensity as a function of mixing time, where the equilibrium peak height is that measured at long mixing times. It is immediately apparent from the graph that the time required to reach equilibrium for the PP CH_2 in the blend is 3−4 times longer than in the neat a-PP (based on comparisons of time to 90% recovery). Although we do not achieve complete suppression of the PP CH_3 signal at time = 0, the fact that the time scale for complete equilibration of the PP CH_2 signal is significantly longer in the blend relative to the purely intramolecular effect in the homopolymer indicates an additional polarization source. The additional source must be the intermolecular spin-diffusion from the PE-OD copolymer chains in the blend. These data provide direct evidence for miscibility in the a-PP/PE-OD blend.

Our observation that the purely intramolecular effect arising from incomplete suppression of the PP CH_3 signal occurs on a ca. 10-ms time scale is consistent with our findings from applying the dipolar filter/spin diffusion experiment to an immiscible blend of a-PP/PE-DD.

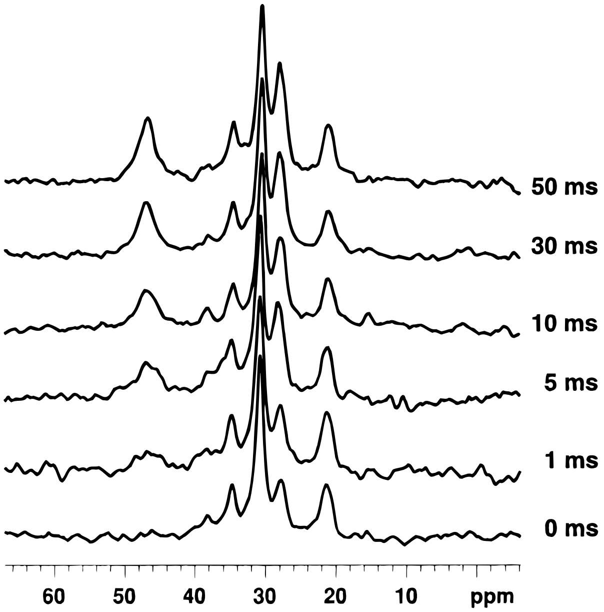

Figure 7. Dipolar filter spectra of the PP/PE-OD blend as a function of the spin-diffusion mixing time.

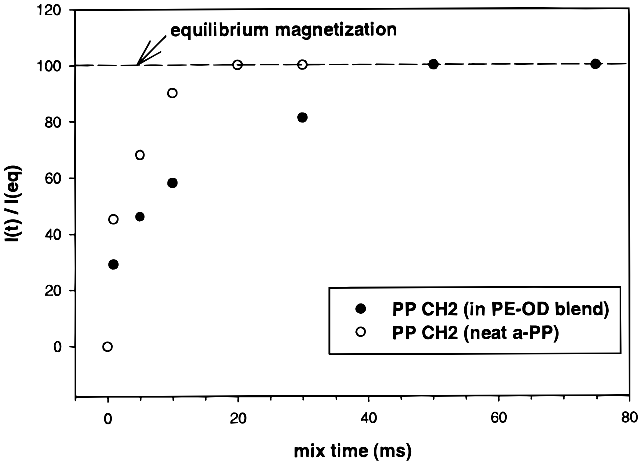

Figure 8. Comparison of spin-diffusion polarization transfer curves for the methylene signal of polypropylene in neat atactic PP and the atactic PP in the blend with PE-OD. Note that complete transfer essentially occurs after 10 ms for the neat a-PP, while in the blend it takes ≈40−50 ms.

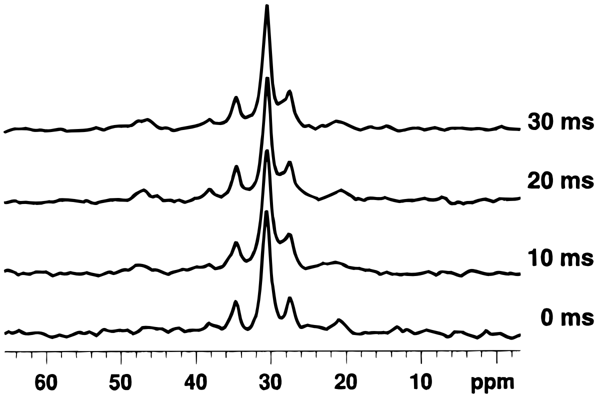

Figure 9. Dipolar filter spectra of the PP/PE-DD blend as a function of the spin-diffusion mixing time. Note the lack of any significant increase in the a-PP methylene signal at 45 ppm at long spin-diffusion times.

Recall the relaxation data presented in Figure 4, which indicated that there was no change in the $T_{1\rho H}$ values for PP in the PE-DD blend relative to the neat polymer. Our conclusion from that data concerning the immiscibility of that particular blend is supported by the dipolar filter experiments, the spectra from which are shown in Figure 9. There are two things to note from these spectra. First, the suppression of the PP CH_3 relative to the PE-DD signals is much greater than was observed in Figure 7 for the PE-OD blend. This indicates a greater difference in motional time scales for the a-PP relative to the PE-DD, as expected from the relaxation data shown previously. Such behavior, especially compared to our results for the PE-OD blend, supports our conclusion that there is no chain level mixing of the two polymers. Second, Figure 9 shows that the PP CH_2 signal reaches equilibrium intensity in only 10 ms, versus 40−50 ms in the blend with PE-OD. This result is in complete agreement with our measurements of intramolecular transfer in the neat a-PP polymer and clearly shows that there is no additional intermolecular polarization transfer from the PE-DD phase. The spin-diffusion data directly confirm the immiscibility of this particular blend that was inferred from the relaxation data.

Our evaluation of the spin-diffusion growth data in Figure 8 for the PP/PE-OD blend follows that published by Schmidt-Rohr and Spiess for a two-component system.[16] The characteristic domain size, L, is defined as the ratio of the total phase volume, V_{tot}, to the total interfacial surface area, S_{tot}, between polymer phases. In terms of the relationship between L and the polarization transfer rate, the following equation applies:

$$L_a = (\epsilon/f_a)(4D\tau/\pi)^{1/2} \qquad (1)$$

where ϵ is the number of orthogonal directions available for spin diffusion, f_a is the volume fraction of phase A (0.5 here), D is the spin-diffusion coefficient, and τ is the mixing time required to reach equilibrium polarization transfer and is determined by extrapolating the initial rate from the spin-diffusion curve to the equilibrium polarization (i.e., $I(t)/I(\mathrm{eq}) = 1$). D was determined experimentally by measuring the static ^{1}H line width for the blend ($\Delta\nu_{1/2}$ = 2.7 kHz, single component line shape) and for rigid polystyrene ($\Delta\nu_{1/2}$ = 51 kHz). Clauss et al. has reported the spin-diffusion coefficient for polystyrene based on microscopy, NMR, and simulation data to be 8×10^{-16} m^2/s.[17] By appropriate ratio, we calculate D for the PP/PE-OD blend to be 4.3×10^{-17}m^2/s.[18] Substitution into eq 1, with $\tau = 30$ ms and $\epsilon = 2$, gives $L = 5.1$ nm for the PE-OD domain size. This domain size is in agreement with the relaxation data, since unique $T_{1\rho H}$ but common T_{1H} values were measured in the blend, and domain sizes based on these values must be between 2.1 and 20 nm.

A relevant aspect of these experimental data concerns the fraction of total polymer chains that are miscible, i.e., partial vs total miscibility. Examination of the Rothwell−Waugh behavior in Figure 2 seems to indicate that all the PP chains experience a shift in dynamics upon blending with PE-OD, as the methylene signal is completely absent at 10 and 23 °C. However, the low-temperature relaxation data show incomplete $T_{1\rho H}$ averaging. Finally, comparison of the equilibrium dipolar-filtered spectrum for the PP/PE-OD blend after 50 ms of spin-diffusion (Figure 7) to the normal CP spectrum in Figure 6 shows that relative intensities of the PP and PE-OD signals are different. Such an observation indicates that some of the PP chains are not within the spin-diffusion length scale of 5.1 nm defined by the dipolar filter experiment at 40 °C. Our interpretation of the relaxation and dipolar filter results is that partial miscibility exists. However, the cooperative dynamics of the polymer chains are sensitive to changes in interchain type and arrangement on length scales greater than 5.1 nm, but less that 20 nm. For this reason, the Rothwell−Waugh line-broadening results of Figure 2 show a more homogeneous response to blend formation.

Conclusions

The selective interrogation of chain dynamics coupled with the spin diffusion analysis from the solid-state NMR relaxation data represents a relatively easy method for probing miscibility in saturated PP/PE blends and does not require specific isotopic labeling. Our current work is focused on outlining the complete phase behavior for these blends, as well as miscibility studies for a-PP and commercial ethylene copolymers.

Acknowledgment. The authors would like to thank Professor Frank Bates for valuable discussions and for the PEE sample, and John Ashbaugh for gathering some of the experimental data in this report.

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(14) $L = (\epsilon/f)(4)D\tau/\pi)^{1/2}$, where ϵ is the morphology (1 for lamellar, 2 for cylindrical, 3 for spherical), f is the volume fraction of the initial component, D is the diffusion constant, and τ is the relaxation or equilibrium spin diffusion time.

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MA9802879