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Spin Diffusion Analysis of Miscibility in an Anomalous Nonpolar Blend

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Phase behavior in blends of saturated hydrocarbon polymers has recently received much attention in the literature. These investigations are motivated by the great commercial potential for tailored properties in polyolefin blends, primarily those involving polypropylene and polyethylene copolymers. Despite the growing body of work in this area, the molecular origin of miscibility in completely nonpolar blends is not well understood. Graessley and co-workers have published extensively on mixing behavior in several polyolefin blends, using a Flory−Huggins χ parameter analysis of SANS, light scattering, and PVT data to establish miscibility windows.[1−4] Fredrickson and Bates have used radii of gyration and chain stiffness data to describe blend miscibility in homopolymer/copolymer blends.[5−7] Some insight into the miscibility of polyolefins has come from application of the PRISM theory[8] and detailed simulations,[9] but many questions remain.

Our goal is to develop accessible experimental strategies for measuring the length scale of chain mixing in completely saturated hydrocarbon polymer blends. To this end, we have recently reported a solid-state NMR approach based on dipolar filter[10] and spin diffusion[11] experiments to study miscibility in solid blends of atactic polypropylene and polyethylene copolymers.[12] While there has been little NMR work on saturated polymer blends (relative to functionalized blends) reported in the literature, we believe this technique is especially suited for these mixtures since it does not require isotopic labeling, a neutron source, or any special sample preparation treatments. Results for dipolar filter/spin diffusion solid-state NMR experiments are presented for blends of polyisobutylene (PIB) with head-to-head polypropylene (hhPP). PIB/hhPP blends have recently been found to exhibit anomalously large negative χ parameters by Graessley and co-workers,[1] and our experiments provide direct spectroscopic evidence for chain mixing in this blend with a length scale for concentration fluctuations $\leq$3.5 nm.

PIB/hhPP blends (50/50) were prepared by mixing known amounts of the individual polymers in dilute hydrocarbon solution and evaporating to dryness in a vacuum oven. The hhPP was prepared by hydrogenation of poly(2,3-dimethylbutadiene)[2] and had $M_w = 50\,000$. For PIB, $M_w = 1\,000\,000$.

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 cross-polarization 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, and 4 K scans were collected per spin diffusion time increment in the dipolar filter experiment. T_{1H} measurements were made using a cross-polarization version of the saturation-recovery experiment. Contact times for cross-polarization were 0.5 ms.

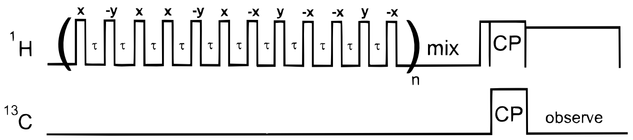

Figure 1. Pulse sequence used for the dipolar filter experiments. Additional experiments in which a ^{1}H π-pulse was inserted after the dipolar filter (prior to mix) on alternate scans were also used to eliminate T_1 effects. Typically, $\tau = 7$ μs and the number of cycles, n, was 10. The mixing time was varied from 0 to 50 ms.

Dipolar filter experiments were used to directly measure the rate of polarization transfer between the PIB and the hhPP polymer chains. The dipolar filter experiment[10] has recently been introduced as a robust method for selecting magnetization from the more mobile component in polymer blends or composites. The pulse sequence is shown in Figure 1. The goal for our study is to prepare an initial condition in which magnetization from only one blend component exists. Then, by inserting a variable spin diffusion time after the pulse train (the *mix* time in Figure 1), polarization can be transferred from the source phase to the sink phase if spin diffusion is operative. A version of the dipolar experiment in which π_x pulses were inserted on alternate scans (prior to the mix period) was also used to eliminate T_1 contributions to the measured spin diffusion; results were compared with the standard experiment shown in Figure 1.

Experimental results from the dipolar filter experiment on the PIB/hhPP blend are shown in Figure 2a. Resolved methyl peaks are observed at ca. 15 and 17 ppm for the two different tactic environments of the hhPP; these peaks provide a unique signal (free from overlap) with which to measure interchain transfer of polarization into the PP phase from the source PIB phase. One observes that, at mix time = 0, the PP signal is essentially eliminated. The PIB signals at 32 and 39 ppm are more clearly resolved after the filter application, since the hhPP backbone signals are also eliminated. (From variable-temperature control experiments on the PP and its blends, we know that the backbone methylene and methine signals are very broad at room temperature due to the Rothwell−Waugh effect.[13]) Further, the dipolar filter also suppresses magnetization from the backbone methylene groups of PIB; this resolved signal at 60 ppm provides a clear marker for PIB-to-PIB polarization transfer from the PIB methyl and methine hydrogens at ca. 32 and 39 ppm, respectively. Examination of the hhPP methyl signals as a function of increasing mixing time shows an intensity increase which indicates polarization transfer from the PIB hydrogens to the hhPP hydrogens via spin diffusion. Also, the PIB methylene signal at 60 ppm increases with increasing mixing time, while the 32 ppm methyl signal decreases.

As shown in Figure 2b, spectra obtained with a $\geq$10 ms mixing time were essentially identical to a normal CP/MAS spectrum, indicating that the equilibrium

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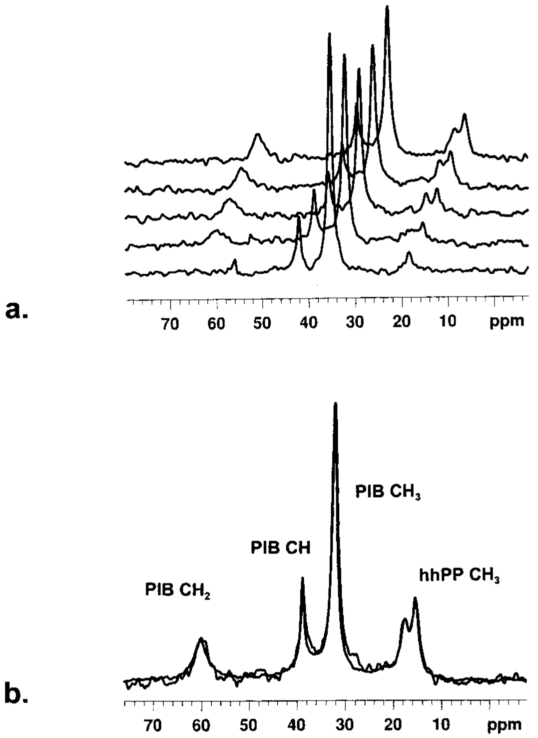

Figure 2. (a) Typical dipolar filter spectra of the PP/hhPP blend as a function of the spin diffusion mixing time. Each spectrum was obtained using 4096 scans. **(b)** Overlay plot of the normal cross-polarization spectrum for the hhPP/PIB blend and the 10 ms mixing time spectrum from the dipolar filter/spin diffusion experiment. As shown in Figure 3, equilibrium is essentially reached by 10 ms. The higher signal-to-noise trace is the normal CP spectrum.

condition has been reached corresponding to complete redistribution of proton polarization. T_{1H} values of 510 ms were measured for all protons in the blend via a saturation recovery/cross-polarization sequence. Initially, data were obtained using the basic dipolar filter sequence of Figure 1, and T_{1H} effects were neglected, given that the spin diffusion times (10−30 ms) were greater than 1 order of magnitude different than T_1. However, subsequent experiments showed that, at the longer mix times (20−30 ms), relaxation contributions could not be neglected (e.g., the decaying 32 ppm PIB signal began to increase in intensity at τ values >20 ms). As such, the data presented in Figure 3 were obtained using the sequence that utilized π pulses prior to the spin diffusion period on alternate scans.

As additional background information, one should also note at this time that the ability to establish a polarization gradient for well-mixed blends is not inconsistent with known results for differential mobilities of polymer chains in miscible blends. 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.[14−16] In fact, for most cases the dynamics of the individual homopolymers do change significantly upon blending but still maintain unique temperature dependencies. This is consistent with the unique intramolecular constraints to reorientation for each polymer type.

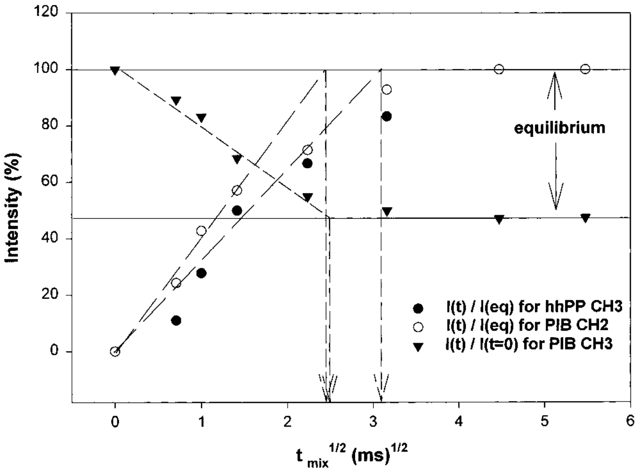

Figure 3. Comparison of spin diffusion polarization transfer curves for the methyl signal of hhPP (15−18 ppm) and the methylene signal of PIB (60 ppm) in the PIB/hhPP blend, as well as the decay curve for the 32 ppm PIB CH$_3$ signal. Note that the ordinate shows the percent of equilibrium signal intensity as a function of spin diffusion times for the rising signals, vs percent of initial (mix time = 0) intensity for the decaying signal. Also, the straight lines are the regression fits for the first 2 ms of mixing, which are extrapolated to obtain the equilibrium spin diffusion time.

A graphical representation of all of the spin-diffusion data is shown in Figure 3 for both PIB−PIB and PIB−hhPP polarization tranfer. We see that the time required for equilibration of hhPP magnetization (from the 15−18 ppm peak) is only slightly longer than that required for PIB equilibration (from the 60 ppm peak). Both the growth of the initially suppressed signals and the decay of the PIB methyl signal are plotted. (We did not plot the 39 ppm PIB CH signal, as its intensity is effected by the growth of a broad peak at longer spin diffusion times, arising from the hhPP backbone carbons.) As should be expected, the growth and decay curves mirror one another, consistent with polarization conservation during spin diffusion. We observe that (consistent with Figure 2b) the 32 ppm PIB methyl signal that initially survives the dipolar filter decays to 47% of its original intensity by about 10 ms and maintains that intensity at longer mixing times. Our initial evaluation of the spin diffusion growth data in Figure 3 for the PIB/hhPP blend follows that published by Schmidt-Rohr and Spiess for a two-component system.[17] The characteristic length for chain mixing, L, is defined as the ratio of the total phase volume, V_{tot}, to the total interfacial surface area, S_{tot}, between polymer domains. In terms of the relationship between L and the polarization transfer rate, the following equation applies:

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

where $\epsilon = 2$ 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, which is determined by extrapolating the initial rate from the spin diffusion curve to the equilibrium polarization (i.e., $I(t)/I(\text{eq}) = 100$). D was determined experimentally by measuring the static ^{1}H line width for the blend ($\Delta\nu_{1/2}$ = 4.1 kHz, single-component line shape) and for rigid polystyrene (($\Delta\nu_{1/2}$ = 51 kHz). Clauss et al. have reported the spin diffusion coefficient for polystyrene based on microscopy, NMR, and simulation data to be 8×10^{-16} m^2/s.[18] By appropriate ratio, we calculate D for the hhPP/PIB blend to be 6.3×10^{-17}m^2/s.[19] We note that the value of $\Delta\nu_{1/2} = 4.1$

kHz is large enough that the approach outlined here is valid; i.e., spin diffusion is efficient.[19] Substitution into the above equation, with $\tau = 9.6$ ms and $\epsilon = 2$, gives $L = 3.5$ nm for the minimum length scale of the PIB−hhPP intersegmental contact distance. For reference, a similar calculation based on the initial rate evaluation of the PIB−PIB spin diffusion data in Figure 3 gives a length scale of 2.8 nm. This same value is obtained whether one uses the initial growth slope of the PIB 60 ppm signal or the intitial decaying slope of the PIB 32 ppm signal, as should be expected.

Finally, we wish to comment on the types of saturated blends for which this particular experimental strategy is optimum. Obviously, there must be some difference in chain dynamics for the polymers in the blend which will enable selection of only one component by the dipolar filter. This requirement is more difficult to satisfy for saturated, nonpolar hydrocarbon blends relative to blends formed from polar polymers, since chain dynamics are usually more similar for polyolefins. In the work presented here, PIB is the more mobile component and therefore survives the same filter that suppresses hhPP signals. The dipolar filter/spin diffusion strategy is most applicable to blends that exhibit an LCST, since for blends that have a UCST, the temperature at which a single phase forms is usually high enough that spin diffusion is no longer efficient.

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