Intramonomer Polarization Transfer: Calibrating Spin Diffusion Coefficients in Mobile Polyolefins and Their Blends

Xingwu Wang and Jeffery L. White*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

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Polyolefins and their blends are a commercially important class of materials, and new polymer architectures now accessible via metallocene catalysis ensure that a growing number of novel blend compositions are forthcoming.[1−3] Analysis of morphology in such blends may be addressed using solid-state NMR methods, and nondestructive spin diffusion techniques are particularly attractive since isotopic labeling is not a requirement.[4] As such, commercial research and pilot scale blends may be interrogated without any sample modification. In a typical $^1H-^1H$ spin diffusion experiment, a polarization gradient is created between polymer phases or domains, and the diffusive flow of magnetization as the spin reservoir seeks equilibrium during subsequent time periods is measured. The rate at which polarization equilibrium is reached, treated mathematically using an initial-rate approximation scheme and Fick's second law of diffusion, reveals the size of the domain or repeating structure. While many simplified versions of the diffusion equation have been used, a favored form in recent investigations of two-component polymer blend studies for the determination of the domain size x_{dis} is

$$x_{\mathrm{dis}} = \left(\frac{\rho_1\varphi_1 + \rho_2\varphi_2}{\varphi_1\varphi_2}\right)\left(\frac{4\epsilon\varphi_{\mathrm{dis}}\sqrt{D_1D_2}}{\sqrt{\pi}(\rho_1\sqrt{D_1} + \rho_2\sqrt{D_2})}\sqrt{\tau_{\mathrm{m}}}\right)$$

where ρ is the proton density of each component, φ is the volume fraction, D is the spin diffusion coefficient, τ_{m} is the equilibration time, and ϵ is the number of orthogonal directions for polarization transfer to occur. Particularly detailed analyses of spin diffusion behavior, and the relationships with morphology in polymeric systems, have been published by Clauss,[5] VanderHart,[6] and Cheung.[7] In all cases, the choice of the value of the spin diffusion coefficient D in the analysis of the time-dependent data is critical to obtaining accurate dimensional information for the sample. This is particularly important for mobile (low T_g) polymers, since the dipolar coupling between the protons involved in the spin diffusion process is attenuated due to molecular motions.[8] Typical schemes reported in the literature in which static line widths for the sample of interest are compared to known samples can lead to erroneously large values for the spin diffusion coefficient and, therefore, inflated length scales of mixing. Diffusion coefficients are typically calibrated via comparison of the NMR spin diffusion data on known, well-characterized block copolymers with scattering or electron microscopy data on the same samples.[4,5] In a recent article, Spiess and co-workers have demonstrated that comparing transverse relaxation time constants between unknown and known samples is superior to static line widths, since in many mobile, amorphous polymers, inhomogeneous contributions to the line width greatly exceed the homogeneous spin diffusion contribution.[9] Again, independent scattering or microscopy analysis of the domain sizes in the known materials is required, just as in the static line width method.

Since we are interested in measuring the length scale of mixing in amorphous, mobile polyolefin blends, the experimental determination of accurate spin diffusion coefficients D is paramount. Further, the independent determination of the diffusion coefficient using only NMR data would be possible if a unique, invariant reference volume or distance existed in the polymer sample that could be used to quantitatively define the diffusive length scale. In other words, *an internal distance calibration on the sample itself would eliminate the need for independent validation of the mixing length scale by scattering or microscopy experiments*. In this contribution, experimental results are reported that indicate the length of the cylinder inscribing a monomer unit in a chain-extended polymer can serve as this reference distance, thereby resulting in calculation of an accurate spin diffusion coefficient in cases where a polarization gradient may be prepared within the monomer itself. Two different methods for generating the intramonomer polarization gradient will be discussed: one based on mobility differences and the other using ^{13}C chemical shift selection.

The polyisobutylene sample used in this study was a commercial sample ($M_w = 1\,000\,000$), and the 10% PIB/90% PIB-d_8 blend was prepared by toluene dissolution, followed by film casting and evaporation to dryness in a vacuum oven. All experiments were done on a Bruker DSX-300 instrument; 70 kHz radio-frequency power levels (3.5 μs $\pi/2$ pulses) and 4 kHz magic-angle spinning were used for the dipolar filter/CP measurements.[10] Cross-polarization times of 500 μs were used. In the dipolar filter measurements, T_1 contributions to the signal decay were eliminated by applying π pulses on alternate scans following the dipolar filter sequence, but prior to the spin diffusion mixing time. For the MREV-8 CRAMPS experiment, $\pi/2$ pulse widths were 2 μs with an interpulse spacing of 2 μs.[11] Spinning speeds were controlled at 1.5 kHz, and the experiment was calibrated using monoethylfumarate.

A reasonable assumption in any study of polarization transfer via $^1H-^1H$ spin diffusion is that the process may be followed using some direct ^1H observation scheme. However, for polyolefin blends containing no functional groups, this is not the case as the data in Figure 1 demonstrate. A comparison of the ^1H spectra obtained for a blend of PIB and hhPP using either 14 kHz MAS with single-pulse excitation or CRAMPS is shown in Figure 1.

While the homonuclear dipolar interactions between protons are eliminated using the CRAMPS MREV-8 sequence, no improvement in resolution exists relative to the fast MAS experiment. In both cases, only one featureless, inhomogeneously broadened signal is observed. As such, it is impossible to distinguish signals from the specific blend components by observing proton spins directly. Even if CH_3, CH_2, and CH hydrogens could be resolved (with resulting decrease in the overlap integral), experimental distinction of spin diffusion within a blend component or between components would

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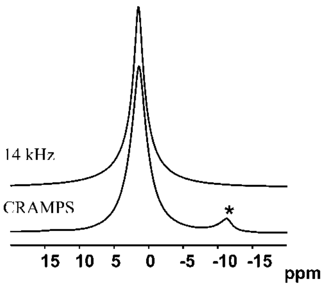

Figure 1. Comparison of ^{1}H CRAMPS experiment and fast magic-angle experiment on a 50:50 blend of PIB and head-to-head polypropylene (hhPP), demonstrating the lack of resolved features from either blend component using direct ^{1}H detection.

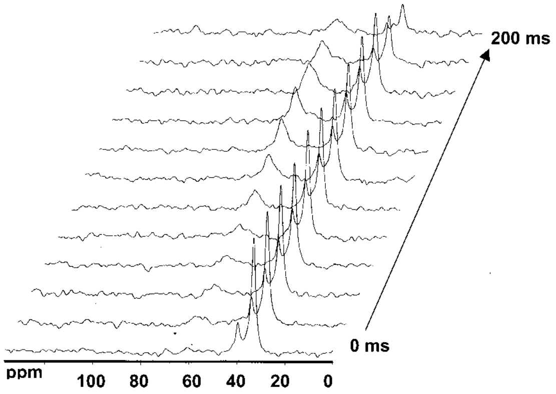

Figure 2. ^{13}C cross-polarization spectra for neat PIB, obtained following preparation of the ^{1}H spin system using 10 cycles of a dipolar filter sequence with an interpulse spacing of 10 μs. The spin diffusion mixing time is increased from 0 to 200 ms, resulting in an initial increase in the CH_2 (polarization sink) peak intensity, and decrease in the CH_3 (polarization source) peak intensity. See Figure 3 for specific spin diffusion time values.

not be possible. Therefore, all subsequent experiments reported in this contribution will indirectly probe ^{1}H–^{1}H spin diffusion via polarization transfer to nearby carbons.

Figure 2 shows a series of cross-polarization spectra for neat PIB as a function of the spin diffusion time following dipolar-filter preparation. PIB was chosen as the initial polymer to demonstrate the concept for two reasons: (1) PIB is an important polymer in fundamental studies of the origins of miscibility, as it displays very unusual mixing behavior with polypropylene and ethylene–α-olefin copolymers,[12] and (2) only two types of protons exist in the monomer unit, so a clear identification of polarization source and sink is possible. Initially, only CH_3 proton magnetization (32 ppm) exists following the dipolar filter period (10 cycles of the 12-pulse sequence, using 10 μs interpulse spacings), as demonstrated by the absence of the CH_2 peak at 60 ppm. As increasingly long spin diffusion periods are introduced, the CH_3 peak intensity decreases, while the CH_2 peak increases in intensity. Ultimately, all peaks decay at long mixing times due to the cancellation of magnetization arising from spin–lattice relaxation and the phase cycling of the π-pulses (at the end of the dipolar filter sequence) on alternate scans.

Spin diffusion curves from the data in Figure 2 are shown in Figure 3, in which the intensities of the proton polarization source (CH_3) and the sink (CH_2) are plotted as a function of the square root of the mixing period.

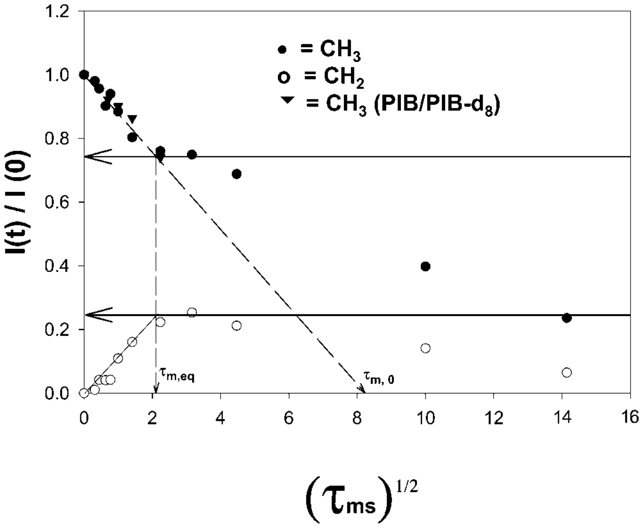

Figure 3. Graphical representation of the peak intensities in Figure 2 for neat PIB as well as the CH_3 peak intensity for a similar dipolar filter experiment on a 10% PIB/90% PIB-d_8 blend. For the protonated PIB data from Figure 2, one should observe that extrapolation of the initial slope of the CH_3 decay, or CH_2 rise, leads to the same plateau value, corresponding to the equilibrium ratio of proton magnetization in a PIB monomer unit. This is indicated by the arrows on the y-axis and corresponds to a 3:1 ratio of CH_3:CH_2 magnetization. The CH_3 decay from the PIB/PIB-d_8 blend is, within experimental error, identical to the fully protonated PIB. Finally, the difference between the extrapolated equilibration time values $\tau_{m,eq}^{1/2}$ and $\tau_{m,0}^{1/2}$ is noted on the x-axis.

Extrapolation of the initial slope at short mixing times to the dashed equilibrium line, i.e., that line denoting the equilibrium ratios of CH_3:CH_2 proton magnetization ($75{:}25 = 3{:}1$), provides the means of determining the equilibrium spin diffusion time $\tau_{m,eq}$. Again, it is worth noting that equilibrium is defined as the point at which proton polarization has been redistributed by spin diffusion in accordance with the 6:2 ratio of methyl:methylene hydrogens in the monomer unit. From the vertical arrow in Figure 3, the experimental value for $(\tau_{m,eq})^{1/2} = 2\ \mathrm{ms}^{1/2}$. Using these data along with the monomer unit size, an accurate spin diffusion coefficient D could be calculated. However, prior to this calculation, we would like to provide experimental data that demonstrate that the spin diffusion behavior shown in Figure 3 results from intrachain polarization transfer. If interchain spin diffusion were occurring on a time scale similar to polarization transfer within the chain/monomer unit, the utility of a reference spin diffusion dimension based solely on the monomer unit size would be limited.

Figure 3 also shows the results of a dipolar filter experiment on a 10% PIB/90% PIB-d_8 sample; these data points are indicated by the triangles for short mixing times. Given the decreased sensitivity of an experiment in which 90% of the protons have been replaced with deuterons, the CH_3 peak intensity is plotted for mixing times of 0, 500 μs, 1 ms, 2 ms, and 5 ms. The strategy for this isotopic dilution is to eliminate interchain proton spin diffusion as much as possible, thereby ensuring that the dominant pathway for magnetization exchange occurs only within the monomer unit of a single chain. From Figure 3, one observes essentially identical behavior for the fully protonated vs 90% deuterated polymer during the initial, short-time mixing period. This result indicates that polarization transfer in the mobile PIB polymer is dominated by intrachain spin diffusion, and interchain spin diffusion may be neglected at short times. As such, the use of a monomer dimension as a reference distance for calibration of the spin diffusion coefficient D is reasonable. It should be mentioned that, in the absence of neutron scattering data, we cannot prove that the PIB/PIB-d_8 blend is intimately mixed. Both polymers have molecular weights $M_n > 200$K, as they should if they are to reflect the chain dynamics, and therefore spin diffusion behavior, of commercial blends containing PIB. For this reason, we have not used low molecular weight materials (<50 000) to reduce the possibility of phase separation. Of course, any blend would be potentially suspect. It is our opinion that the only way to ensure that isolated protonated monomer units exist in a matrix of deuterated neighbors (thereby eliminating any interchain spin diffusion) is to prepare copolymers containing ca. 10% protonated monomer with 90% deuterated monomer. We are currently preparing this copolymer, and results will be reported in a subsequent contribution. However, relaxation experiments reveal that ^{1}H $T_{1\rho}$ time constants are not equal for the CH_2 vs CH_3 groups in PIB (500 μs vs 1.1 ms, respectively), indicating that spin diffusion *does not* equilibrate the proton magnetization over that time scale within a monomer unit. This is completely consistent with our spin diffusion dipolar filter data, which shows complete equilibration over a few milliseconds. As such, we feel it is appropriate to interpret the short-time spin diffusion behavior in terms of intrachain spin diffusion only.

Spiess and co-workers have recently discussed the use of two different forms of the diffusion equation, differing in that one uses the $\tau_m^{1/2}$ obtained by extrapolation of the initial slope to equilibrium vs the value obtained by extrapolation to $I/I_0 = 0$, as shown in Figure 3.[9] The form of the diffusion equation recently published by Spiess, in which the $\tau_{m,0}^{1/2}$ value for the CH_3 decay extrapolated to $I/I_0 = 0$ (not 0.75) is used, is shown:

$$x = 2\epsilon(D\tau_{m,0}/\pi)^{1/2}$$

Here, $x = 0.43$ nm for PIB monomer size, $\epsilon = 2$, $\tau_{m,0}^{1/2} = 8.2$ ms$^{1/2}$, and recognizing that this is a single-component system, we calculate a value for the spin diffusion coefficient $D = 4.4 \times 10^{-18}$ m^2/s. Again, for clarification, two values of the mixing time may be used, $\tau_{m,eq}^{1/2}$ and $\tau_{m,0}^{1/2}$ differing in that the former is derived from extrapolation of the initial slope to the equilibrium polarization ratio (defined by the monomer structure) vs extrapolation to zero for the latter.[9] Each of these are indicated on the x-axis of Figure 3. Also, the diffusion pathway for polarization transfer within the monomer involves vector components in two directions; therefore $\epsilon = 2$. As described by Spiess, sink:source volume ratios are not required when using $\tau_{m,0}^{1/2}$ in the diffusion equation.[9] In retrospect, we feel it is important to point out that, in a previous study of miscibility in a PIB/hhPP blend (obtained using a different instrument in a different laboratory), $\tau_{m,eq}^{1/2}$ for polarization equilibration within the PIB component in the blend was found to be 2.4 ms$^{1/2}$, in agreement with $\tau_{m,eq}^{1/2} = 2.2$ ms$^{1/2}$ in this work and consistent with the fact that this value should be invariant to blending.[13] For comparison, calculations based on the static $\Delta\nu_{1/2} = 4.1$ kHz gives a value of $D = 6.3 \times 10^{-17}$ m^2/s for PIB, greater than an order of magnitude in error.

In the rearranged form of the equation, it may be observed that errors in D scale as errors of the square of x. However, accurate values for the monomer dimension are easily obtained using any of a variety of molecular simulation software programs. The value of 0.43 nm for the PIB monomer size was determined via molecular dynamics calculation and dimensional measurements on a 100-unit chain, using the Insight II molecular modeling package (Polymer version 3.0.0) with PCFF force field parameters running on a Silicon Graphics IRIS Indigo workstation. Energy minimization was computed with 5000 iterations of an adjusted basis−steepest descents algorithm. Dynamics simulations were carried out at constant temperature of 300K for 5 ps with time step of 1 fs.

The use of monomer dimensions as a spin diffusion distance reference is not limited to mobile polymers. However, the strategy is particularly applicable for polyolefins and their blends, since such polymers have low T_g's. Even though the results as described here provide a diffusion coefficient for a single polymer instead of a blend, it also defines an accurate upper limit on the magnitude of spin diffusion coefficients *between* dissimilar chains in a polymer blend containing PIB. Given that the unique properties of PIB arise from anomalously dense chain packing in the homopolymer, it is unlikely that packing of PIB chains in a polyolefin blend will lead to reduced motion within a PIB chain. Any additional motional averaging of nuclear coordinates between polymer chains in a blend will only act to reduce the diffusion coefficient from the value defined by the size and motion of the reference monomer unit. The example presented in this paper in which a polarization gradient was established based on the dipolar filter sequence may not be applicable to all polyolefins. For example, the dipolar filter sequence will generate a "sharp" magnetization gradient in PIB, a-PP, and some PE-copolymers, but it does not work well for isotactic polypropylene, due to the lack of sufficient motional gradients between methyl and methylene groups. To circumvent this problem, we are pursuing new sequences, similar in concept to the CP3 sequence published by de Groot and co-workers,[14] that utilize ^{13}C chemical shift selection followed by periods of spin diffusion and isotropic (Lee−Goldburg) polarization transfer. In this way, proton magnetization from one specific monomer moiety may be cleanly prepared, based on its ^{13}C chemical shift, followed by isotropic polarization equilibration throughout the monomer. These experiments are in progress, and results from this work will be reported at a later time.

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