Independent Calibration of ^{1}H Spin-Diffusion Coefficients in Amorphous Polymers by Intramolecular Polarization Transfer

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ABSTRACT: We report a general method, based on intramolecular spin diffusion, for the measurement and calculation of spin-diffusion coefficients in amorphous polymers and their blends using only NMR data. The basic structural unit that defines ^{1}H polarization density in polymers is the monomer unit. Using appropriately selected internal reference distances calculated from energy-minimized chain dimension simulations, time scales for the redistribution of ^{1}H polarization *within* amorphous homopolymers may be used to *independently* calculate maximum values of the spin-diffusion coefficients D. This strategy represents an attractive alternative to current methods employed for domain size measurements in polymer blends, which require calibration of spin-diffusion coefficients based on comparisons of similar NMR data obtained on model compounds analyzed previously using scattering or microscopy techniques. In this way, many more polymer systems become amenable to study by NMR spin-diffusion methods, since X-ray scattering or microscopy calibrations on representative standards are no longer necessary to define quantitative limits on spin-diffusion coefficients. Experimentally, the fate of proton magnetization is followed with high selectivity using 2D ^{1}H−^{13}C solid-state HETCOR sequences incorporating controlled periods of ^{1}H−^{1}H spin diffusion.

1. Introduction

Spin-diffusion NMR experiments on solid polymers, blends, and composites are attractive methods for the interrogation of structure and miscibility, since isotopic labeling is not required.[1−3] Reports in which ^{1}H−^{1}H spin-diffusion rates are used to calculate “domain sizes” in heterogeneous polymer systems continuously appear in the literature,[4−9] and some excellent reviews of the area have been published.[1,10,11] The phenomenon of polarization transfer, or the spatial propagation of ^{1}H magnetization over some distance x_{dis}, is typically described for a binary polymer blend according to the following equation:[11]

$$x_{\mathrm{dis}} = \left(\frac{\rho_1\varphi_1 + \rho_2\varphi_2}{\varphi_1\varphi_2}\right)\left(\frac{4\epsilon\varphi_{\mathrm{dis}}\sqrt{D_1D_2}}{\sqrt{\pi}(\rho_1\sqrt{D_1} + \rho_2\sqrt{D_2})}\sqrt{\tau_{\mathrm{m}}}\right) \quad (1)$$

where ρ is the proton density of each component, φ is the volume fraction, D_i is the spin-diffusion coefficient for homopolymer component i, τ_{m} is the equilibration time, and ϵ is the number of orthogonal directions for polarization transfer to occur. In all cases, the choice of the value of the spin-diffusion coefficient D, which represents the rate of ^{1}H homonuclear spin diffusion in a pure polymer, is important for obtaining accurate dimensional information for the sample. While the length scale of mixing x depends only on the square root of D, and therefore, errors in D do not translate into large errors in x, the ability to *independently measure an upper limit for D on the sample of interest* is often more important than the exact knowledge of its precise value. Furthermore, placing an upper limit on D via a direct experimental measurement on the polymer itself results in a maximum distance for domain sizes, or heterosegmental contacts, in the blend.

The current strategy for determination of spin-diffusion coefficients in amorphous polymers, which has been discussed extensively by Spiess and co-workers, involves comparisons of static ^{1}H line widths (for rigid polymers) or ^{1}H T_2 values (for low-T_g polymers) to those obtained for well-characterized, model block copolymers.[1,12] The model block polymers have either lamellar, cylindrical, or spherical morphologies as measured by SAXS or electron microscopy. By ratioing the measured values of line width or T_2 obtained for the sample of interest to similar parameters in the literature for these standards, appropriately scaled values of the spin-diffusion coefficient may be estimated for the sample. While this approach is viable, and provides accurate values for D in most cases, we feel an alternative strategy in which direct measurement of spin-diffusion rates in the polymers of interest, and calculations of D based on that measurement, would be attractive. Such an approach would be particularly important for polymer systems in which scattering and microscopy contrast are poor or nonexistent, e.g., blends of amorphous polymers with similar chemical structures, or for which well-characterized block polymers of similar structure and molecular dynamics were not available.

In this contribution, we describe a general strategy for direct measurements of spin diffusion within the monomer units of rigid, amorphous polymers. In short, our approach represents a necessary class of control experiments on pure polymers, which heretofore have not been discussed and whose results are relevant to the most basic structural level of polarization transfer. On the basis of the time required for polarization to equilibrate between distinct chemical moieties in the monomer and knowledge of the characteristic dimension of the monomer, we can calculate a spin-diffusion coefficient D based on the assumption that intrachain spin diffusion is the dominant polarization transfer mechanism at short times. We have previously shown that this is a good assumption for low-T_g polyolefins like PIB.[13] However, we recognize that interchain contribu-

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tions also occur for rigid systems, and this is why we characterize the D values obtained in this way as maximum values. If interchain spin diffusion is operative on the same time scale as intramolecular spin diffusion within the monomer unit, then the rate at which polarization propagates must be lower and therefore characterized by a smaller D for the same experimentally measured τ_{eq} value. Conversely, even if interchain spin diffusion is occurring on similar time scales, polarization must still be equilibrated between all types of protons in the monomer unit at τ_{eq} for a given D. Since the monomer is the minimum structural dimension that defines polarization gradients, an upper limit for D is consequently also defined. The characteristic monomer dimension is determined by molecular simulation of the energy-minimized polymer chain structure. Typically, degrees of polymerization ranging from 20 to 100 are used, depending on the number of atoms that exist in the monomer unit. In this way, D values are determined by solving the spin-diffusion equation “in reverse” for each homopolymer; i.e., the dimension x is determined by force-field simulation of a single chain, and the polarization equilibration time τ_{eq} by the NMR spin-diffusion experiment.

While there are several strategies available for generating an initial ^1H polarization gradient in a polymer, particular attention is devoted to using 2D solid-state Hetcor methods for measuring intramonomer spin diffusion in rigid polymers. The main advantage of this experiment is that naturally occurring ^1H magnetization gradients are exploited.[14-16] In other words, no special manipulation of the proton spin reservoir is required to generate an initial polarization gradient; all local ^1H magnetization is preserved prior to the spin-diffusion period, and therefore one can be confident that the sampled spin response is representative of the bulk. The benefit of the Hetcor spin-diffusion experiment relative to direct ^1H-observe methods is much greater resolution in the ^1H dimension due to ^{13}C chemical separation, allowing different polarization-transfer processes (occurring over different length scales) to be detected simultaneously as might occur in blends or block polymers. Obviously, some of the results reported in this contribution could have been obtained using two-dimensional ^1H CRAMPS methods, particularly for materials like PC and PPO where there are essentially only two types of ^1H populations. However, in most cases of interest for polymer blends, sufficient ^1H resolution does not exist to follow individual spin-diffusion events, and therefore the additional resolution afforded by ^1H and ^{13}C shift separation in the Hetcor experiment is preferable and necessary. Also, changes in spin-diffusion coefficients induced by blending cannot be detected by running the constituent polymers separately, and as such, the Hetcor method is currently the best experimental choice for detecting spin-diffusion events in each of the polymer components of a blend, copolymer, or composite. Therefore, we felt that good experimental practice dictates that we use the Hetcor strategy for all experiments in this paper.

2. Experimental Section

Polymers. Polycarbonate (PC) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) polymers were obtained from Poly-Sciences (M_w = 100 000 and 60 000, respectively) and were used without further modification. The polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymers, prepared by Polymer Laboratories, Ltd., were monodisperse (M_w/M_n = 1.1) with each block have molecular weights $M_w \approx$ 55 000.

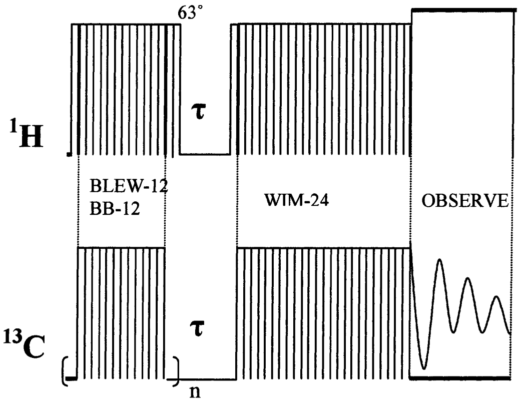

Figure 1. Pulse sequence diagram for the 2D solid-state $^1H-^{13}C$ heteronuclear correlation (Hetcor) experiment with isotropic polarization transfer and $^1H-^1H$ spin diffusion.

NMR Methods. The Hetcor experiment of Burum and Bielecki was used to obtain the 2D solid-state heteronuclear correlation data.[17] (Alternatively, more recent versions of the Hetcor experiment using Lee–Goldburg polarization transfer could also be employed and offer that advantage of better performance at high MAS rates.) The 90° pulse widths were 3.2 μs on each channel (Figure 1). In all experiments, only one windowless isotropic mixing (WIM) cycle (total polarization time = 76.8 μs) was used. All experiments were done on a Bruker DSX-300 instrument. The experimental verification of proper Hetcor performance was done using monoethyl fumarate (fumaric acid monoethyl ester), and carboxylic acid carbon correlations to both olefinic and acidic protons were observed.[18] For measuring spin diffusion throughout the monomer, controlled periods of $^1H-^1H$ spin diffusion were introduced prior to the isotropic $^1H/^{13}C$ polarization transfer step. The chemical shift scaling factor in the ^1H dimension was measured experimentally to be 0.42 (near the theoretical 0.47 value), and the proton frequency was shifted off-resonance by 5 kHz from the carrier to avoid any zero-frequency artifacts and take advantage of second averaging effects. Spinning speeds of 3.5–4.5 kHz were used to minimize potential sideband overlap with peaks of interest and to ensure good polarization transfer performance. The spinning speed periods (285–333 μs) were larger than twice the WIM cycle length, thereby preventing signal elimination or attenuation due to a refocusing of the C–H dipolar interaction at the end of each rotor period. Typically, 256–512 scans were taken for each of 64 points in the t_1 dimension, and recycle delays of 3–4 s were used. The total experiment time was typically 12–24 h. Quadrature detection was maintained in the t_1 dimension via use of TPPI. The data were processed with 50 Hz line broadening and zero-filled to 1024 points in the t_1 dimension prior to Fourier transformation. The spin-diffusion analysis was performed by extracting individual ^1H slices in the second dimension and quantitatively deconvoluting the aromatic:aliphatic intensity ratios using PeakFit software from Jandel Scientific.

Simulation of Polymer Chain Units. Monomer size was determined via molecular dynamics calculation and dimensional measurements on chains with degrees of polymerization ranging from 20 to 100, depending on the number of atoms, and therefore computational complexity, in the monomer structure. The Insight II molecular modeling package (Polymer version 3.0.0) with Discovery force field parameters was used for all polymers, and calculations were done 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 steps of 1 fs. The characteristic dimension of the monomer x is defined as follows:

$$x = (l_c d_c)^{1/2}$$

where l_c and d_c is the length and diameter, respectively, of the cylinder that inscribes the space-filling dimensions of the monomer. While it is conceivable that a sphere might best inscribe a monomer, and therefore the diameter of the sphere would be the appropriate dimension, such was not the case for the polymers in this work.

3. Results and Discussion

3.1. Spin-Diffusion Hetcor Experiments on Neat Polymers. We have previously shown that dipolar filter/spin-diffusion methods are effective strategies for calculating spin-diffusion coefficients and domain sizes in saturated polyolefins and their blends.[13,19] However, polyolefins like polyethylene, polypropylene, polyisobutylene, and their copolymers have low glass transitions and are therefore quite mobile at room temperature. This allows the dipolar filter sequence to effectively generate ^1H polarization gradients within monomer units of some polyolefins. Rigid, high-T_g polymers are not amenable to dipolar filter experiments since all structural moieties in the polymer have much longer correlation times for motions, and similar T_2 values, due to stronger homonuclear dipolar interactions. As such, methods like the dipolar filter sequence,[4] or traditional Goldman−Shen methods,[20] are not applicable for generating a ^1H polarization gradient within the monomer units of rigid, amorphous polymers.

As stated previously, two-dimensional solid-state Hetcor measurements are a particularly attractive technique for the determination of ^1H spin-diffusion coefficients via intramonomer polarization transfer for the following reasons: (1) no special manipulation of either ^1H or ^{13}C magnetization is required to generate a polarization gradient among the ^1H spins, i.e., all local ^1H magnetization is preserved; (2) multiple polarization transfer processes, occurring on different length scales, may be resolved; and (3) ^1H resolution is dramatically increased relative to direct observe ^1H spin-diffusion experiments like 2D CRAMPS. The spin diffusion/Hetcor sequence is shown in Figure 1.

Figure 2 shows selected spin diffusion/Hetcor spectra for neat PC obtained with 0, 0.1, and 3 ms mixing times. From the contour plots, one observes that the ^1H correlations at aromatic positions increase with mixing time at ^{13}C aliphatic chemical shifts, e.g., the CH_3 peak at 31 ppm, and conversely, ^1H aliphatic cross-peaks grow at aromatic ^{13}C chemical shift positions (120−130 ppm). At zero mixing time (Figure 2A), one does not observe any aromatic cross-peaks for the CH_3 peak or for the quaternary isopropylidene carbon at 42 ppm and no aliphatic cross-peaks for any of the three aromatic carbons (120−150 ppm region). From the full complement of mixing times, the spin-diffusion curves may be constructed by plotting ratios of the aromatic:aliphatic cross-peak intensities obtained from ^1H slices at any ^{13}C chemical shift. Alternatively, one could also take ^{13}C slices at the aromatic and aliphatic ^1H chemical shifts. Figure 3 shows a comparison of results for either slice type for PC methyl and aromatic shifts at conditions of no mixing vs equilibrium spin diffusion. In Figure 3a−d, the top slice shown comes from a methyl position, either ^1H or ^{13}C, and Figure 3a,b compares slice types for no spin diffusion, while Figure 3c,d compares those after equilibrium has been reached. In all slices, one observes that those taken at the CH_3 positions (the top slice) always have reduced signal-to-noise relative to their aromatic counterparts (lower slice in each set). This is due to the reduced isotropic H−C polarization transfer efficiency for a rapidly rotating methyl group relative to more rigid aromatic C−H spin pairs. The ^1H slices are straightforward to analyze since there are fewer peaks and no sidebands, and from such slices the spin-diffusion curves in Figures 4 and 6 were extracted.

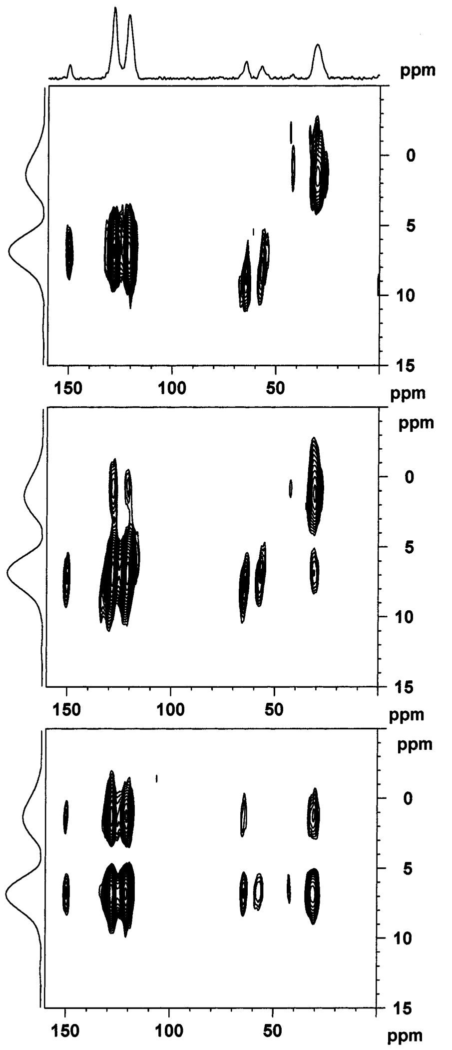

Figure 2. Two-dimensional $^1H-^{13}C$ Hetcor spectra obtained for polycarbonate (PC) using one C−H polarization cycle and with spin-diffusion times of **(**A**)** 0, **(**B**)** 0.1, and **(**C**)** 2 ms. Note in particular the time-dependent cross-peak intensities for the CH_3 and aromatic CH groups.

Quantitative analysis of the ^1H aromatic and methyl slices for each of the mixing times in the PC experiment results in the spin-diffusion curves shown in Figure 4. On the basis of a least-squares analysis of the first six data points for the rising curve obtained from the CH_3 slices, the intersection of that line with the equilibrium slice polarization ratio defines the equilibrium mixing time $(\tau_{m,eq})^{1/2} = 26\ \mu s^{1/2}$. The equilibrium aromatic:aliphatic ratio is defined by the PC structure, which contains eight aromatic and six aliphatic protons. The theoretical $(I_{aromatic}/I_{aromatic} + I_{aliphatic})$ ratio of 0.57 agrees very well with what is observed experimentally from aromatic:aliphatic slice ratios at long mixing times.

Hetcor contour plots are shown in Figure 5 for PPO at 0, 50 μs, and 3 ms spin-diffusion times. As with PC, ^1H cross-peaks at specific ^{13}C shifts increase at longer mixing times, as the methyl and aromatic protons

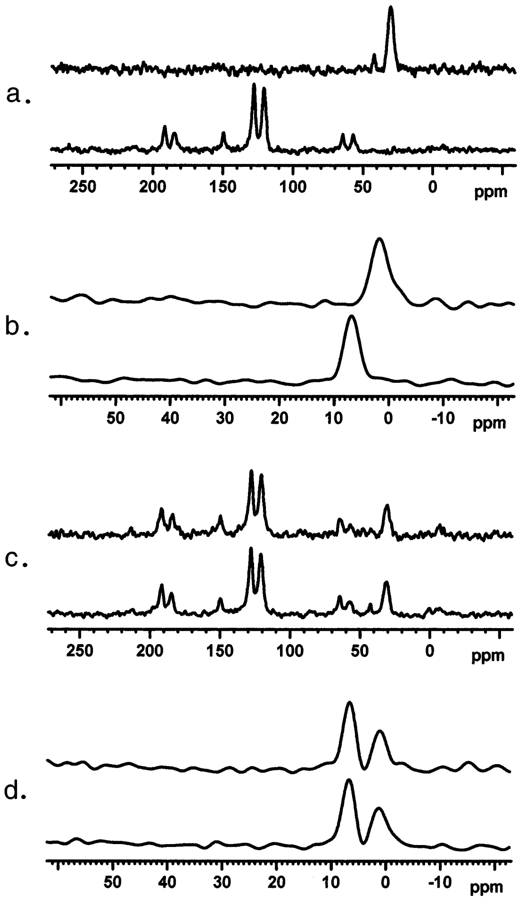

Figure 3. **(a)** Comparison of ^{13}C slices at the methyl ^{1}H peak (top) and the aromatic ^{1}H peak (bottom) for $\tau_m = 0$. **(b)** Comparison of ^{1}H slices at the 31 ppm methyl ^{13}C peak (top) and the 128 ppm aromatic ^{13}C peak (bottom) for $\tau_m = 0$. **(c)** Comparison of ^{13}C slices at the methyl ^{1}H peak (top) and the aromatic ^{1}H peak (bottom) for $\tau_m = 1$ ms. **(d)** Comparison of ^{1}H slices at the 31 ppm methyl ^{13}C peak (top) and the 128 ppm aromatic ^{13}C peak (bottom) for $\tau_m = 1$ ms.

undergo spin diffusion. In contrast to the PC experiment, quantitative analysis of the spin-diffusion rates were measured from aliphatic:aromatic ratios of ^{1}H slices through the 120 ppm aromatic ^{13}C peak, so as to eliminate any potential contributions from sidebands. On the basis of the spinning speed used in this experiment, a small aromatic sideband would contribute to ^{1}H aromatic intensity at CH_3 carbon slice positions and therefore should be avoided here. The complete PPO spin-diffusion curves are shown in Figure 6. Again, on the basis of least-squares analysis of the first six data points, and recognizing that the monomer structure defines the equilibrium ($I_{\text{aromatic}}/I_{\text{aromatic}} + I_{\text{aliphatic}}$) = 0.75, we find that $(\tau_{m,eq})^{1/2} = 23\ \mu s^{1/2}$. We note that, as expected, the PPO polymer equilibrates faster than PC (vide infra).

3.2. Data Analysis. The fact that we obtain fairly similar values for $(\tau_{m,eq})^{1/2}$ for both PC and PPO is consistent with our model, since the “effective” monomer size, i.e., the basic ^{1}H-bearing repeat unit, is nearly identical for each PC, while chemically a larger monomer unit requires only one-half of its monomer structure to define the ^{1}H polarization stoichiometry and is therefore very similar to PPO. As an example, Figure 7 shows the chain structure, and schematic for defining monomer dimensions, from the simulated PPO chain. From this model, we extract $x_{PPO} = 0.59$ nm. In a similar fashion, PC simulations yielded $x_{PC} = 0.61$ nm.

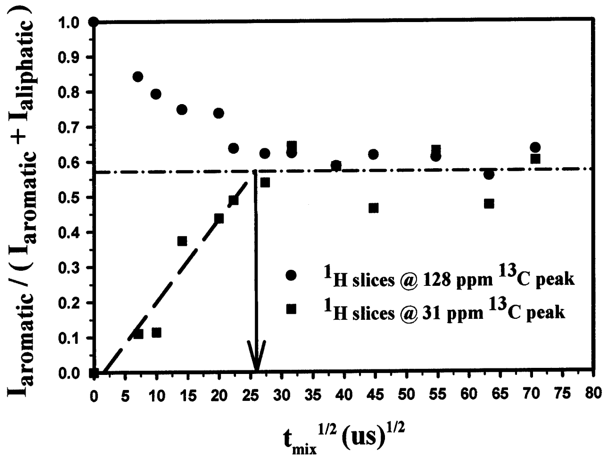

Figure 4. Spin-diffusion curves for PC constructed from deconvolution of the ^{1}H slices at the methyl (31 ppm) and aromatic (128 ppm) ^{13}C shifts in terms of the integrated intensity of the aromatic:aliphatic protons. Based on this choice of peak ratios, ^{1}H slices through the 128 ppm peak decrease from infinity to the equilibrium ratio of 0.57, while methyl slices increase from zero to 0.57. Experimentally, equilibrium is determined by equal aromatic:aliphatic ^{1}H slice ratios at longer mixing times, which is seen to agree with the stoichiometric ratio defined by the monomer structure.

On the basis of determination of $(\tau_{eq})^{1/2}$ from the Hetcor experiments, and x from simulation, one can now calculate the spin-diffusion coefficients D from the following equation:

$$D = (\pi x^2)/(4\tau_{eq}) \qquad (2)$$

This equation is identical that reported by Spiess,[11,12,23] except that we have not included the scaling factors which attempt to model the morphology or dimensionality of two-phase systems with finite domain sizes. We feel that this is justified for the case of intramonomer polarization equilibration, since the protons with the shortest internuclear distances will dominate polarization transfer, and there is no finite interface in pure polymers. For PC and PPO, the calculated values of D are 4.2×10^{-12} and 5.2×10^{-12} cm^2/s, respectively, based on the experimentally measured $(\tau_{eq})^{1/2}$. These results are in complete agreement with the published values of spin-diffusion coefficients for polymers, which are reported as ranging from 1×10^{-12} to 9×10^{-12} cm^2/s, with exact values dependent upon the polymer dynamics.[1,2,10,11,25] In particular, they agree almost exactly with values that would be calculated on the basis of the early theoretical models proposed by Cheung and Gerstein based on local dipolar fields,[2] and discussed more recently by Clauss,[1] Kaplan,[24] and Inglefield,[26] in which rigid polymers with static line widths exceeding 5 kHz could be approximated by $D = (1/3)[\Delta\nu_{1/2}(r_{HH})^2]$, where r_{HH} is the average interproton distance (taken as 0.23 nm). This model yields $D_{PC} = 4.4 \times 10^{-12}$ cm^2/s and $D_{PPO} = 5.2 \times 10^{-12}$ cm^2/s, in good agreement with our values reported above. More importantly, our experiments provide diffusion coefficients by direct observation of specific polarization transfer events within the polymer of interest under the experimental conditions of interest, i.e., magic-angle spinning, and not inferred from static measurements. The fact that our experiments and data analysis gives a slightly smaller D value for PC than for PPO is in complete agreement with its smaller static line width (22 and 25 kHz, respectively).

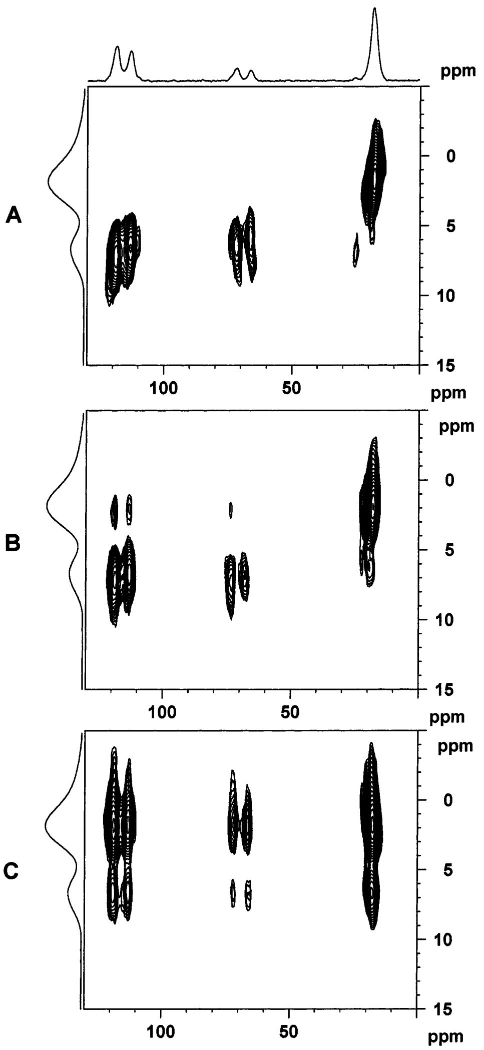

Figure 5. Two-dimensional $^{1}H-^{13}C$ Hetcor spectra obtained for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) using one C−H polarization cycle and with spin-diffusion times of (A) 0, (B) 0.05, and (C) 3 ms.

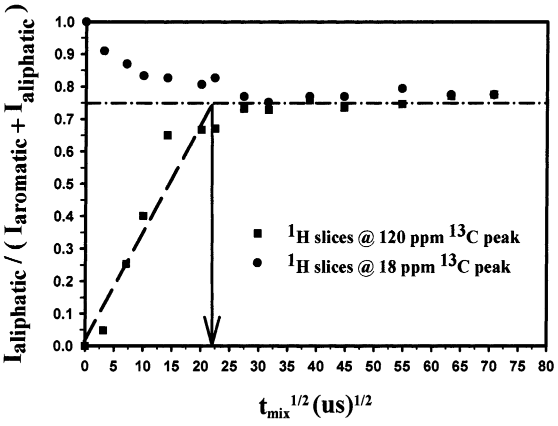

Figure 6. Complete spin-diffusion curves for the experiments represented in Figure 5 for PPO. Here, the growth of the aliphatic ^{1}H correlation at the 120 ppm aromatic ^{13}C chemical shift are plotted as a function of square root of the spin-diffusion mixing time.

We should also note that while the PC and PPO polymer exhibit reduced dipolar couplings relative to other glassy polymers due to their high methyl group content, we chose them as an initial model system since they only have two proton spin populations (aromatic and methyl). However, in retrospect, this is not a limiting or advantageous characteristic of a polymer system, since the Hetcor experiment will resolve the point at which all protons in the monomer unit, no matter how many chemically different ones there are, reach polarization equilibrium (see PS-*b*-PMMA discussion below).

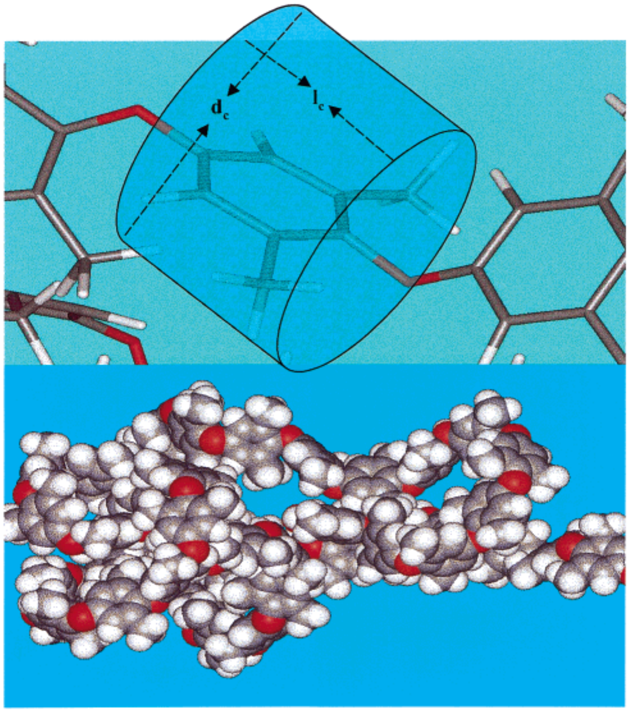

Figure 7. Simulated structure for the PPO chain demonstrating how the characteristic monomer dimension $x = (l_c d_c)^{1/2}$ was calculated.

3.3. Heterogeneous Systems. An important advantage of this experimental strategy is the ability to measure *changes* in *D* for a polymer once it is blended with another polymer. Unlike other methods based on ^{1}H relaxation or line width calibrations, the Hetcor/spin-diffusion experiment can resolve intramolecular and interchain spin-diffusion events. It is well-known that individual polymer chain dynamics can change upon blending, which in turn may alter the value of the spin-diffusion coefficient. As such, using *D* values obtained for neat polymers in eq 1 may lead to erroneous length scales of mixing, but revised *D* values determined from observing intramolecular spin diffusion for each polymer *in the blend* provide accurate dimensional quantification and referencing of intermolecular mixing. As might be expected, this is most relevant for blends of polymers that have large differences in T_g. We have found this to be true for several blends and copolymers, e.g., polyisobutylene−polystyrene copolymers,[21] polystyrene/poly(vinyl methyl ether), and polycarbonate/polycaprolactone blends (results not shown here).

The advantages of using intramolecular polarization as a reference point for heterogeneous systems are also apparent in blends or copolymers from polymers with similar T_g's. Figure 8 shows selected results from a symmetric PS-*b*-PMMA diblock copolymer, with each block having a molecular weight of ca. 55 000. Even in the absence of distinct cross-peaks between functional groups on the two different polymers, as long as there is one resolved peak in the ^{13}C spectrum, a quantitative length scale of mixing may be determined. In the PS-

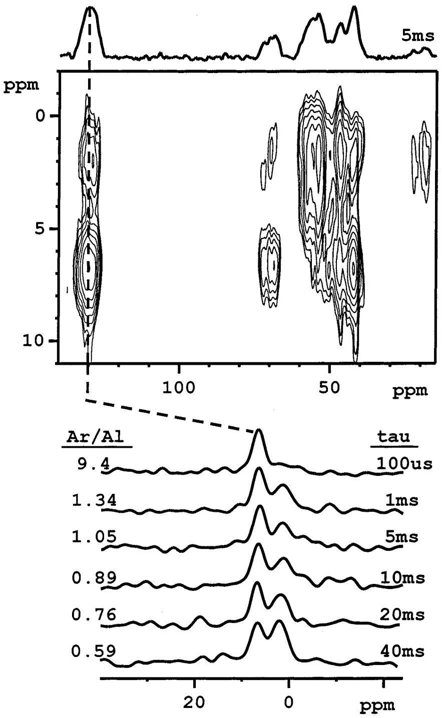

Figure 8. (top) Two-dimensional $^1H-^{13}C$ Hetcor spectrum for a monodisperse PS-*b*-PMMA diblock copolymer obtained using a 5 ms spin-diffusion time, with the summed cross-peak projection for the ^{13}C dimension shown on the top of the plot. (bottom) Selected ^1H slices through the 128 ppm PS peak as a function of spin-diffusion time tau; the ratio ($I_{aromatic}/I_{aliphatic}$) in the ^1H slice is indicated for each slice. The dashed line on the contour plot indicates the slice position.

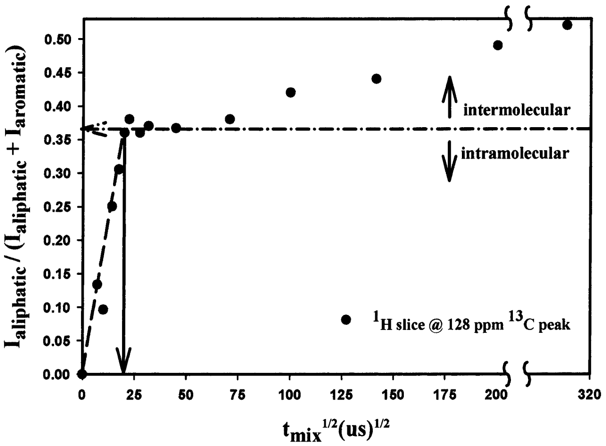

Figure 9. Complete spin-diffusion curves for the PS-*b*-PMMA in which ($I_{aliphatic}/I_{aromatic} + I_{aliphatic}$) is plotted vs the square root of the mixing time for the 128 ppm peak. Intramolecular spin diffusion leads to the short time equilibration with the PS chains, followed by a longer intermolecular polarization transfer between the PS and PMMA blocks. A clear plateau is observed following intramolecular polarization equilibration within the PS units, but prior to significant interdomain polarization transfer.

b-PMMA results, one observes that the aliphatic region from 30 to 60 ppm contains many overlapping peaks from both polymer constituents. However, the PS protonated aromatic carbons at 128 ppm are well-resolved, and quantitative analysis of their ^1H slices as a function of mixing times indicates the time scale required for *both* intramolecular *and* intermolecular spin-diffusion equilibration. On the basis of the results reported above for PC and PPO, stoichiometric slice intensities are generally observed at spin-diffusion equilibrium for any homopolymer. From the detailed data in Figure 9, we observe that the monomeric stoichiometry for PS ($I_{aliphatic}/I_{aromatic} + I_{aliphatic}$) = 0.375 is achieved in less than 400 us. Indeed, a well-defined plateu region is observed after intramolecular equilibration, but prior to significant intermolecular spin diffusion. If the block polymers were completely phase-separated, with no spin diffusion between the blocks, then the slice ratio for the 128 ppm peak would not increase above the 0.375 value. However, we see from Figure 9 that as the mixing time increases, spin diffusion continues such that by 40 ms additional aliphatic magnetization has been transferred into the PS domains as indicated by the increasing ($I_{aliphatic}/I_{aromatic} + I_{aliphatic}$) ratio = 0.50. This proves that intermolecular spin diffusion takes place between the two blocks on a time scale significantly longer than spin diffusion within the individual polymers and that, on the time scale of 40 ms, there is nearly complete spin diffusion between all protons of each block (as would be indicated by an intensity ratio of 0.68). The last data point in Figure 9 corresponds to 100 ms, and although the intensity ratio of 0.55 indicates the system is approaching the expected intermolecular equilibrium value of 0.68, spin–lattice relaxation effects should be considered at these longer mixing times. Even so, this is extremely useful information for this polymer system, since the $T_{1\rho H}$ values are not the same for the two blocks,[22] but the T_{1H} values are equal (1.0 ± 0.1 s for all protons in the copolymer). This is a common situation for nanoscale phase morphology in polymers, and on the basis of these experiments, we can define the length scale of mixing quantitatively, instead of defining only possible upper and lower limits based on $T_{1\rho H}$ and T_{1H}.

A complete analysis of these results begins by measuring intramolecular spin-diffusion equilibration to determine the values of D for the PS and PMMA blocks. From Figure 9, $(\tau_{eq})^{1/2}$ for PS = 18.75 $\mu s^{1/2}$. This result, combined with the calculated monomer dimension for PS of 0.55 nm, yields $D_{PS} = 6.9 \times 10^{-12}$ cm^2 s^{-1} using eq 2. For the PMMA block, a similar analysis of slice ratios through the $-OCH_3$ carbon at 53 ppm and the $-CH_3$ carbon at 18 ppm indicated intramolecular equilibration at $(\tau_{eq})^{1/2} = 20$ $\mu s^{1/2}$. Since their ^1H chemical shifts were well-resolved at zero mixing time, and these regions had little or no overlap with other PS peaks in the ^{13}C dimension, one can easily follow the convergence of line shape/^1H chemical shift as methyl, methylene, and methoxyl polarization equilibrates within the PMMA units. *No aromatic intensity was observed in PMMA slices for mixing times less than 1 ms.* These data, along with calculated monomer dimensions for PMMA (0.50 nm), yield $D_{PMMA} = 5.0 \times 10^{-12}$ cm^2 s^{-1}. Solving eq 1 for τ_{eq} = 100 ms, and neglecting relaxation effects, the length scale of mixing x for the individual PS and PMMA domains in the diblock copolymer system is 18 nm. Clearly, this is in agreement with the possible limits from the $T_{1\rho H}$ and T_{1H} data (obtained by solving the diffusion equation for time limits of 15 ms[22] and 1 s, respectively) and exemplifies the utility of experiments that simultaneously provide *resolved* intramolecular and intermolecular spin-diffusion information.

We also note that the form of the spin-diffusion "curves" in Figure 9 are reminiscent of structure factor curves from scattering experiments, in which short-range "order" from the monomer structure, as well as long-range "order" from the domain structure, is visibly obvious from the data. Of course, the relative length scale of the domain sizes, and morphology, will influence this shape. We are currently examining more rigorous analytical models, of the type reported by Schmidt-Rohr and Spiess,[11] to see whether they will accurately model data of this type.

In this study, the values obtained from the independent NMR data for the polymers investigated (PC, PPO, PS, PMMA) are in agreement with literature values for these and similar glassy polymers ($(5-8) \times 10^{-12}$ cm^2 s^{-1}). However, a previous study for PIB, a low-T_g amorphous polymer, in which intramolecular spin-diffusion was measured provided much smaller values of D (4.4×10^{-14} cm^2 s^{-1}).[12] This demonstrates that the strategy is sensitive to differential dynamics, and therefore generally applicable to all polymers, assuming a ^{1}H magnetization gradient exists within the monomer prior to any spin diffusion.

4. Conclusions

The analysis of spin diffusion in the context of polarization transfer within monomer units has been shown to provide quantitative spin-diffusion coefficients D, which are in agreement with those published in the literature. The fact that the monomer structure extracted from individual polymer chains, which are easily simulated using commercially available software, defines the basic ^{1}H "polarization stoichiometry" in homopolymers provides the necessary control experiment for calculating spin-diffusion coefficients. Further, the fact that ^{1}H static line width or relaxation methods can be used to get good estimates for D based on the fairly large amount of data in the literature on model systems, such experiments usually cannot address the changes in D that may occur when a blend or copolymer is formed. In the absence of well-characterized model polymers, and other forms of scattering data, the method described in this paper provides quantitative results. While any NMR experiment that allows one to generate an initial ^{1}H magnetization gradient in the pure polymer can potentially reveal simultaneous intramolecular and intermolecular spin-diffusion processes, the 2D Hetcor experiment is particularly attractive since only one resolved peak in the ^{13}C spectrum is required for measuring spin diffusion, and often the intrachain and interchain events may be separately measured and quantitative limits on miscibility established. Further, since all ^{1}H polarization is preserved for the initial condition, the results are more representative of the bulk morphology than those obtained with initial conditions generated by motional filters.

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