Proton Spin Diffusion Studies of Polymer Blends Having Modest Monomer Size: 1. Polystyrene/Poly(xylylene ether), a Miscible Blend

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ABSTRACT: Proton spin diffusion experiments, utilizing multiple-pulse methods, have been conducted on three samples of a 50/50 blend of polystyrene (PS) and poly(xylylene ether) (PXE) as well as on the PS and PXE homopolymers. The PS/PXE blend is considered miscible on a molecular scale; this was verified by demonstrating the strength of the early-time spin diffusion between the PS and PXE protons. An attempt was made to estimate the average number of dissimilar monomers surrounding a repeat unit of a given type, and for this discussion a model of a simple cubic lattice was adopted. This exercise involved several other assumptions and was semiquantitative. It was judged that, allowing for chain continuity, the number of dissimilar nearest neighbors surrounding any given repeat unit is close to or greater than that dictated by the relative abundances of the respective monomer units. A second motivation for this study is that it provides a base line for other spin diffusion studies on glassy, phase-separated blends of similar monomer size. In the general case, spin diffusion data from such blends involves three kinds of spin equilibration, namely, homopolymer, intraphase heteropolymer (assuming phases of mixed composition), and interphase heteropolymer, where only the latter process is considered interesting. The PS/PXE data and the homopolymer data relate to the appropriate modeling of the first two kinds of equilibration. Homopolymer equilibration is seen to be better than 99% complete after 1 ms of spin diffusion, while intraphase heteropolymer equilibration has an initial fast component followed by a rather long tail, extending past 10 ms of spin diffusion, owing mostly to the statistics of mixing or the fluctuations in average composition over small volumes.

Introduction

Solid-state proton NMR techniques[1–3] which make use of magic angle spinning[4] (MAS) and proton multiple-pulse[5] (MP) techniques are now available for characterizing glassy polymer blends both in terms of domain size (2–60-nm range) and, to a less precise extent, in terms of the stoichiometries[6] of the individual phases in a phase-separated blend morphology. These techniques rely on proton spin diffusion,[7] a term which describes the movement of proton polarization (per spin) in response to the imposition of a nonequilibrium distribution of spin polarization. These experiments can be thought of as microcalorimetry experiments in which local temperature gradients, dependent on proton chemical composition for the experiments reported herein, are suddenly set up both within monomeric repeat units and between dissimilar repeat units. After a very short time internal thermal (spin) equilibrium, distinct from Boltzmann equilibrium, is reestablished within each monomer, and over a longer period of time internal thermal reequilibration is established between the dissimilar polymers. The time required for this latter, slower process will indicate the length of the most efficient path (a measure of domain size) for producing heteropolymer internal thermal equilibrium, supposing that we know the thermal conductivity (spin diffusion constant).

Combining the techniques of MAS and MP allows one to observe CRAMPS[8] (combined rotation and multiple pulse spectroscopy) proton spectra having modest resolution of isotropic chemical shifts. This combination of techniques has sharply increased the power of proton spectroscopy for investigating polymer blends for two reasons: First, polarization (temperature) gradients may be generated based on more detailed differences in proton spectra or in chemical structure. Second, resolution improvement allows us to separate better the signals from each polymer, thus enabling us to monitor the return to spin equilibrium more accurately for each component.

This lead paper in our series on polymer blends deals with a 50/50 polystyrene/poly(xylylene ether) (PS/PXE) blend (see Figure 1 for chemical structures of the repeat units) which is believed to be thermodynamically miscible and thus is expected to be mixed on a molecular level. Miscibility is indicated by such considerations as single T_g's in DSC measurements,[9,10] a negative enthalpy of mixing,[11] a negative volume change upon blending,[10] determination[12] of a negative Flory–Huggins χ_{12} interaction parameter, IR and UV spectral shifts upon blending, ^{13}C NMR spectral shifts along with strongly-coupled proton rotating-frame relaxation for protons located on both PS and PXE chains,[14] ^{13}C–^{13}C spin exchange between carbon sites on dissimilar chains,[15] and multimodal, broad distributions of PXE methyl-group reorientation times, as judged by ^{13}C NMR and explained in terms of statistical variations in the number of dissimilar nearest-neighbor chains.[16]

In studying this blend, we were motivated by two considerations. First, we wished to see whether the proton spin diffusion data would corroborate this view of intimate mixing, and, more particularly, whether there could be some estimate of the average number of nearest dissimilar neighbors. Direct measurements of this number have not been made; however, inferences have been drawn,[16] via models, that this number is close to statistical, i.e., relates only to the relative numbers of each kind of repeat unit. Second, in the NMR spin diffusion data on other phase-separated blends in this series, there are three spin-diffusion time scales which are important, two of which must be understood well before information about domain sizes and stoichiometries can be extracted. These latter two time scales relate to achieving internal spin equilibrium within each monomer and to achieving internal spin

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equilibrium within each phase, supposing that each phase has, in the general case, mixed, rather than pure homopolymer composition. We refer to these processes, respectively, as homopolymer spin equilibration (HmSE) and intraphase heteropolymer spin equilibration (HtSE). While these latter two time scales are both expected to be quite short, owing to the relatively short proton–proton distances within each monomer and the similarly short distances of closest approach between protons on neighboring chains, the statistics of chain mixing will influence the latter process and not the former. Hence, it is important to measure the time required for internal spin equilibration in an intimately mixed system. We use the PS/PXE blend as an experimental model for estimating the time required for intraphase HtSE.

Comments about the NMR Method

Since the NMR method has been described in detail elsewhere,[2] a few salient points will be noted about the method.

We use a 1D variation of the 2D spin diffusion experiment first utilized by Caravatti et al.,[1] and we designate this variation to be a chemical-shift-based spin diffusion experiment. The name derives from the feature that the initially generated polarization (per average proton spin) is a sinusoidal function of the apparent chemical shifts in a MP spectrum. The period and the phase of the sinusoid are tailored experimentally to fulfill two criteria, namely, that the initial average polarizations for each of the two homopolymers of the blend are opposite in sign and similar, but not equal, in magnitude. When these conditions are satisfied, the integrals of the spin diffusion spectra are small, relative to integrals of Boltzmann-equilibrium signals; however, the line shape is a very sensitive function of the progress of spin equilibration, the process we are interested in monitoring.

There are four periods associated with the spin diffusion experiments we employed. They are (a) the generation of the initial spin polarization gradient using MP irradiation, (b) a period of varying length, t_{sd}, during which spin diffusion proceeds toward equilibrium, (c) a monitoring period where a MP spectrum is taken and subsequently analyzed for the polarization levels of each polymer, and (d) a waiting period for the restoration of Boltzmann polarization levels. Since spin diffusion is arrested during MP irradiation, the interpretation of this experiment is simplified by the absence of spin diffusion during periods 1 and 3 and by our corresponding ability to generate initial polarization gradients which are as spatially sharp as the chemical composition gradients. For any particular blend, one faces the challenges of how to produce the most appropriate gradient and how to analyze the spin diffusion spectra in terms of the individual polarization levels. The choice of gradient and the method of analysis will be different for each blend in this series; the particulars for the PX/PXE blend will be summarized in the Data Analysis section. We have already mentioned criteria for selecting the gradient. It is helpful to bear in mind three things in order to appreciate the methods for analysis. First, spin diffusion is adiabatic in the sense that there is no implied change in net proton polarization, i.e., no change in the total signal integral. Changes in the total integral relate only to longitudinal proton relaxation (T_1) processes. Second, as the initial nonequilibrium polarization moves toward internal spin equilibrium via spin diffusion, the spin diffusion line shape evolves toward the Boltzmann-equilibrium line shape which we shall call the M_0 line shape. This line shape is characteristic of a uniform polarization per spin throughout the entire sample; thus, when internal spin equilibrium is reached, the line *shape*, but not the total intensity, will match that of the Boltzmann signal. Third, we must take account of T_1 processes. We make the assumption (good for many blends with small domain sizes and certainly good for the PS/PXE blend) that T_1 is uniform in all phases. Then it follows that one can correct for T_1 effects with a simple multiplication factor. This assumption gets better as T_1 gets longer and as domain sizes get smaller.

The mathematical modeling of spin diffusion utilizes diffusion equations. A general characteristic of diffusion is that the root-mean-square (rms) distance, x, that polarization travels in a time t is given by the relation:[17]

$$x = (kDt)^{1/2} \tag{1}$$

where k is a constant which depends on the dimensionality of the diffusion and on the boundary conditions. For a spatially-sharp initial polarization gradient at the boundaries of an idealized lamellar morphology (a 1D diffusion problem), k will be[18] $^4/_3$. The $t^{1/2}$ dependence is general; therefore, all of the spin diffusion data will be plotted against $t_{sd}^{1/2}$.

For the data analysis, we use quantities which are not, at least to first order, sensitive to the slight instrumental instabilities which can create, say, noticeable changes in the spin diffusion integrals and line shapes. Thus, we invariably plot a difference quantity, ΔM_s, defined in detail later, which is determined from a comparison of both the spin diffusion line shape at each t_{sd} and the corresponding M_0 line shape scaled to a total integral identical to that of the spin diffusion line shape (this scaled M_0 line shape represents the internal-equilibrium line shape that the particular spin diffusion integral should progress toward).

The final comment about these spin diffusion experiments will help explain why we take care in determining, or deducing, the spin diffusion behavior of a physical mixture, having the identical stoichiometry as the blend considered and exposed to the identical polarization preparation that we use for the mixed blend. Following the preparation of the initial polarization gradient in a physical mixture, only HmSE happens. When this HmSE is complete (after ≈1 ms as will be seen), one achieves what we will call the physical-mixture spin equilibration (PMSE) condition. When one looks at data corresponding to miscible or small-domain blends, the PMSE condition is not obvious since HmSE and HtSE occur simultaneously and on similar time scales when the phases have mixed composition. Therefore, the PMSE condition must be determined via separate experiments. Understanding where the PMSE point is in our data presentations allows us to do two things. First, it allows us to determine whether or not the phases, in a phase-separated morphology, are pure homopolymer phases or are mixtures. Second, it allows us to compare curves which stem from very different kinds of data analyses because each data presentation can be scaled to that interval which brackets the conditions of no HtSE and sample-wide internal spin equilibrium. This is the interval of interest since we set out to examine the mixing of dissimilar chains. Thus we will use the convention that the quantity ΔM_s, plotted on the ordinate of our spin diffusion plots, will be scaled and will be defined so that $\Delta M_s = 1$ corresponds to the PMSE asymptotic condition and $\Delta M_s = 0$ represents sample-wide spin equilibration.

Experimental Section

Materials. Three research samples of additive-free 50/50 blends of PS/PXE were provided by Drs. E. R. Williams, K. P.

McAlea, and R. P. Kambour of General Electric. Two samples were in the form of pellets, and another was in the form of a molded plate. Spin diffusion experiments were run on each of these samples in order to check whether there was any dependence on sample preparation. A sample of additive-free PXE was also obtained from General Electric. The PS homopolymer used for the characterization of HmSE was an NIST standard reference material, SRM 706 (atactic, $M_n = 1.36 \times 10^5$, $M_w = 2.7 \times 10^5$).

Instrumentation. Proton NMR experiments were conducted at 4.7 T on a Bruker CXP200 spectrometer[19] equipped with a Doty Scientific, Inc., probe. All experiments were conducted at ambient temperature, i.e., 22 °C. The details of the pulse sequence have been outlined elsewhere.[2] Briefly, the pulse sequence for the spin diffusion experiment is as follows: the preparation period involves the application of n MREV-8 MP cycles (1.5-μs 90° pulses, 38.4-μs cycle time) bracketed by initial and final 90° pulses whose respective roles are (a) to generate a strong projection of the magnetization in the plane of precession in the toggling frame and (b) to restore the magnetization alternately parallel and antiparallel to the static field. No pulses are applied during the spin diffusion period. In the readout period, an MREV-8 spectrum is acquired. Data are accumulated by alternatively adding and subtracting into computer memory. MAS frequencies are set so that the preparation period is an integral number of rotor periods; this eliminates certain undesirable artifacts in the spin diffusion spectra. T_1's were determined from the zero-crossing times[20] in an inversion–recovery sequence assuming exponential relaxation and a perfect 180° inversion pulse.

Data Analysis. Here we describe the approach used to prepare gradients and analyze data for each blend. In describing the data analysis we will be interested in extracting from our data some quantity which relates to the departure from spin equilibrium of the average PXE or PS polarization. Owing to PS and PXE spectral overlap, the spectral observables, i.e., the intensities of the aromatic or aliphatic spectral regions, represent combined contributions from PXE and PS; hence, other arguments must be invoked before we may claim to extract the polarization of either the PS or the PXE protons from these observables. In addition, we discuss exactly how ΔM_s should be scaled in order to be most meaningful in terms of HtSE. We must pay careful attention to this scaling because one of the questions we seek to answer concerns the distribution of nearest neighbors in this blend and proper scaling allows us to estimate the short-time HtSE profile, which, in turn, is related to the number of nearest neighbors.

Figure 1 shows MREV-8 spectra of the blend and of the homopolymers along with representative spin diffusion spectra. In the homopolymer spectra, one differentiates aromatic (5–9 ppm) from aliphatic (0–4 ppm) resonances. In PS, five of eight protons are aromatic, and in PXE, two of eight are aromatic. There is severe spectral overlap of these resonances; i.e., in the blend spectrum one cannot easily determine what the fractional contribution from each polymer is in either band without some further assumptions. At least at the early spin diffusion times, one cannot make the assumption that spin diffusion line shapes are weighted sums of undistorted PS and PXE line-shape contributions. Only when internal equilibrium is established within the monomers will this condition be fulfilled. Hence, any attempt to separate HmSE and HtSE at the earliest times cannot depend on line-shape arguments alone.

Since PXE and PS have CRAMPS spectra which are approximately mirror images of one another, it makes sense that an initial polarization profile having the aromatic resonances strongly positive and the aliphatic resonances strongly negative (or vice versa) would satisfy the conditions of a strong initial gradient between PXE and PS (with average polarizations of opposite signs for PXE and PS) and would result in a total integral which was small. Thus, the sinusoidal period for the initially imposed polarization gradient is chosen ($n = 24$) to be 10.9 ppm, i.e., about twice the separation between the aromatic and aliphatic maxima. Once n is chosen, then the rotor frequency (3255 Hz) is set so that the n MP cycles is an integral number (=3) of rotor periods. The rf frequency is then chosen to obtain the proper phase of the sinusoidal pattern with respect to the chemical shift axis. The initial polarization profile is reflected in Figure 1 by the spin diffusion line shape having a t_{sd} of 25 μs. Spin diffusion line shapes are also shown for $t_{sd} = 1$, 6.5, and 25 ms. As spin diffusion proceeds (at constant total integral) between aliphatic and aromatic protons, negative and positive intensities cancel one another with the result that, at 1, 6.5, and 25 ms, the aliphatic and aromatic signals have much smaller amplitudes compared with that at 25 μs; in Figure 1 relative amplitudes of all the blend spectra are indicated by the vertical amplification factors. The total signal intensity in these spectra is about 1.2% of the Boltzmann signal intensity, $I(M_0)$. We also conducted the spin diffusion experiment (spectra not shown) on samples of pure PS and PXE using the same choices of n and rotor frequency.

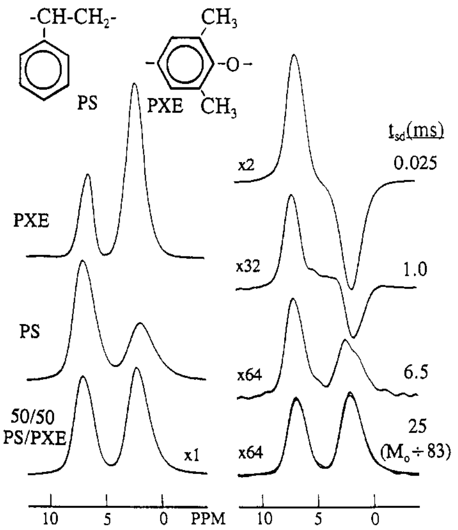

Figure 1. 200-MHz CRAMPS spectra relating to spin diffusion experiments on the 50/50 blend of PS and PXE (chemical structures given). The left-hand column shows M_0 spectra of the indicated pure homopolymers and the blend. The right-hand column contains spin diffusion spectra associated with the indicated spin diffusion times; the 25-ms spectrum is superposed on an M_0 spectrum which has been scaled down by a factor of 83. The agreement between these latter two spectra indicates that internal spin equilibrium has been achieved at 25 ms. All blend spectra have a vertical amplification factor shown; the sensitivity of the line shapes to the progress of spin diffusion is a result of the small total intensity of the spin diffusion spectra relative to the M_0 spectrum.

The fact that the aromatic and aliphatic resonances are almost fully resolved in these spectra helps us decide how we can perform our analysis. In each spin diffusion spectrum and in the M_0 spectrum, we integrate a consistently-defined aromatic region from the saddlepoint in the M_0 spectrum to a convenient baseline point downfield. The *ratio* of this integral in each spin diffusion spectrum to the identically described integral in the Boltzmann-equilibrium spectrum we define to be the aromatic integral, I_R. For the PS/PXE blend, the quantity $\Delta M_s(t_{sd})$ is defined as

$$\Delta M_s(t_{sd}) = [(I_R(t_{sd}) - I_R')/(I_R(\mathrm{PMSE}) - I_R')] \exp(t_{sd}/T_1) \quad (2)$$

where $I_R(t_{sd})$ is the aromatic integral of the spin diffusion spectrum associated with spin diffusion time, t_{sd}. I_R', in actuality, is $I_{tot}(t_{sd})/I_{tot}(M_0)$, the total spin diffusion integral divided by the total integral of the Boltzmann-equilibrium spectrum but, in concept, is the aromatic integral of an M_0 line shape whose total integral is scaled to the same value as the total integral of the spin diffusion spectrum for t_{sd}; I_R(PMSE) is the equilibrium value of the aromatic integral for a physical blend of the identical stoichiometry in the absence of T_1 effects.

All terms in eq 2, except I_R(PMSE), can be evaluated by measuring T_1 (=0.90 s) for the blend along with integrals over the aromatic region and total integrals for each spin diffusion spectrum as well as the M_0 spectrum. The quantity I_R(PMSE) can either be obtained from direct measurements on a physical mixture of identical stoichiometry or, as we did in this case, from measurements of the quantity $S = [I_{tot}(t_{sd})/I_{tot}(M_0)] \exp(t_{sd}/T_1)$ for each of the pure homopolymers. If the latter approach is taken, then

$$I_R(\text{PMSE}) = [f_A f_R(\text{A})\, S(\text{A}) + (1 - f_A) f_R(\text{B})\, S(\text{B})]/f_R(\text{blend}) \quad (3)$$

where f_A is the proton fraction in the blend associated with polymer A, and $S(x)$ is the value of S associated with polymer x, x = A, B. Likewise, $f_R(y)$ is the measured fraction of the total proton intensity residing in the aromatic region in the M_0 spectrum of y, y = A or B or a blend. Since the monomeric structures and the blend stoichiometry are known, f_A can be calculated; thus, all quantities on the right side of eq 3 are known. The validity of eq 3 depends on there being a negligible change in the line shape of each component of the blend relative to the respective line shape of the pure homopolymers. In the case of the PS/PXE blend, this assumption seems to be borne out insofar as the blend line shape is reproduced quite well by summing the homopolymer line shapes, appropriately weighted according to stoichiometry and chemical formulas.

The quantity $\Delta M_s(t_{sd})$ defined in eq 2 has the following simple interpretation: $\Delta M_s(t_{sd})$ is a T_1-corrected, normalized, average departure from equilibrium, in polarization per spin, at a time t_{sd}, for all of the aromatic protons. Again, the normalization constant is chosen such that $\Delta M_s(t_{sd})$ will go to unity if only HmSE goes to completion, and $\Delta M_s(t_{sd})$ will go to zero if both HmSE and HtSE processes are completed. Changes in $\Delta M_s(t_{sd})$ caused by HmSE dominate in this PS/PXE blend; i.e., they account for about 85% of the observed change in $\Delta M_s(t_{sd})$. Since the focus of this investigation is to follow HtSe, we note that $\Delta M_s(t_{sd})$ truly reflects HtSE (i.e, $|\Delta M_s(t_{sd})|$ is proportional to the absolute value of the departure from sample-wide spin equilibrium for he average polarization of either the PS or PXE protons) only for those t_{sd}'s longer than the time required for equilibration within the homopolymers (i.e., when line shapes are truly linear combinations of undistorted homopolymer line shape contributions). For shorter times, changes reflect a combination of both HmSE and HtSE. This ambiguity of interpretation is avoidable because of strong band-shape overlap in the homopolymer spectra. In spite of these ambiguities $\Delta M_s(t_{sd})$ has two useful properties, namely, (a) that all HtSE is mapped into a unit change in $\Delta M_s(t_{sd})$ and (b) at longer spin diffusion times, $\Delta M_s(t_{sd})$ is a faithful monitor of HtSE. As will be seen, semiquantitative information about HtSE at short times will be deduced from a knowledge of the PMSE asymptote and from a characterization of the time required to reach internal spin equilibrium in the homopolymers.

Results and Discussion

Figure 2 is a spin diffusion plot for the three 50/50 PS/PXE blend samples. The ordinate in the inset plot goes from 0 to 7, while the main plot of the same data covers the interval from 0 to 1. Figure 2 illustrates that over 85% of the intensity change observed is associated with HmSE. Nevertheless, there is good reproducibility to the data for the three samples, even for longer t_{sd}'s, thereby indicating that mixing in each material is not a sensitive function of the various preparations and that the method is very reproducible. Note that, at t_{sd} = 1 ms, at least 80% of the HtSE is complete because $\Delta M_s(t_{sd}) < 0.20$. There is significant "tailing" of this curve to longer times; deviations from equilibrium are still visible at t_{sd} = 6.5 ms (see also Figure 1).

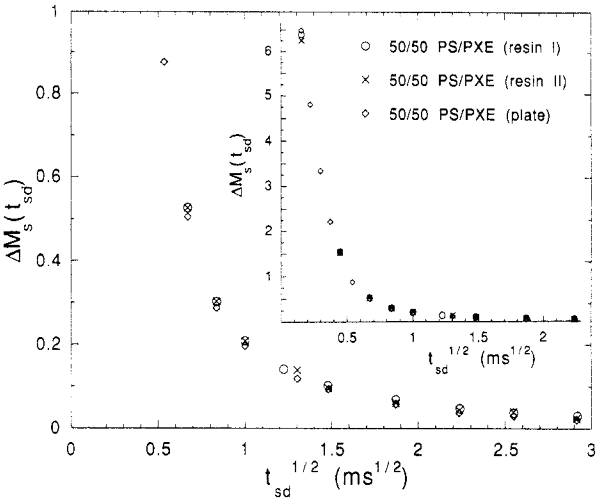

Figure 2. Plots of the scaled departure from internal spin equilibrium of the aromatic polarization (see eq 2) in the three indicated 50/50 PS/PXE blends versus $t_{sd}^{1/2}$. The inset shows the full range of the spin diffusion data, while the main plot focuses on the interval from 0 to 1, i.e., that interval whose magnitude of change is associated with heteropolymer spin diffusion. The agreement of the three sets of data indicates that the tailing out of the data to longer times is not an artifact of poor mixing; rather it probably represents the larger statistical fluctuations in mean composition on smaller distance scales.

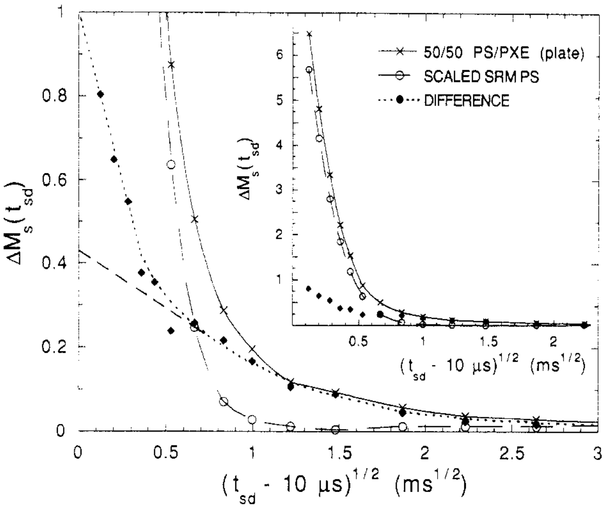

Figure 3. Spin diffusion plots, having the same format as in Figure 2, for two experimental curves (the 50/50 blend and pure PS) and a plot of the difference, designated $\delta\Delta M_s(t_{sd})$ in the text, between these curves. The PS data have been arbitrarily scaled so that $\delta\Delta M_S(0) = 1$. $\delta\Delta M_s(t_{sd})$ is an approximation to the rate of heteropolymer spin equilibration; the dotted line is drawn merely to aid the eye. The early fast decay in $\delta\Delta M_s(t_{sd})$ indicates the presence of dissimilar nearest neighbors. The variable on the abscissa has been modified slightly to account for the fact that it takes about 10 μs before spin diffusion evidences itself owing to the finite dipolar coupling which drives it; this minor modification of the very earliest data helps to justify setting $\delta\Delta M_s(0) = 1$.

Figure 3 reproduces the PS/PXE plate data of Figure 2 and illustrates how, semiquantitatively, the short-time HtSE behavior is estimated. Since we assume, and will presently support, the notion that the PS/PXE blend is a single phase of intimately mixed polymers, only HmSE and *intraphase* HtSE occur; moreover, they happen on similar time scales. If the HmSE contribution could somehow be subtracted from the overall behavior of $\Delta M_s(t_{sd})$, the difference would represent the desired HtSE. In Figure 3, we have attempted this separation by assuming that the HmSE process in the blend has the same time dependence as HmSE does in pure PS (pure PXE has spin equilibrium behavior very similar to PS). Thus, a second curve in Figure 3 represents the deviation of the aromatic polarization from internal spin equilibrium for pure PS, under the same experimental conditions used for the PS/PXE samples. The data for pure PS has been scaled so that the curve (the "dotted" curve with the solid symbols in Figure 3) generated from the difference between the PS/PXE data and this scaled data has an ordinate intercept near unity. This difference curve, which we will call $\delta\Delta M_s(t_{sd})$, is then an approximation to the HtSE profile; i.e., this is an approximation to $\Delta M_s(t_{sd})$ for the case there the initial condition is that there are no polarization gradients within the homopolymers; gradients exist only between PS and PXE chains.

That we should be able to generate $\delta\Delta M_s(t_{sd})$ by this simple subtraction method and assign it this meaning seems intuitively reasonable but is, in fact, not easy to show owing to the very complex nature of spin diffusion pathways. Nevertheless, since we will be interpreting $\delta\Delta M_s(t_{sd})$ as having a *semiquantitative* correspondence to the true HtSE profile, it is important that we argue for the validity of that correspondence. Since the nature of that argument is quite convoluted and involves further assumptions, we defer that argument to the Appendix and proceed with the interpretation of $\delta\Delta M_s(t_{sd})$ in Figure 3 as though it were a good approximation to the true HtSE profile.

First, we note that there is a rather steep decay at early times. At $t_{sd} = 250$ μs the HtSE is at least 70% complete. There is a break in slope at about 0.4 $\mathrm{ms}^{1/2}$, corresponding to $t_{sd} = 160$ μs; prior to that point the slope is not far from linear. Qualitatively, we interpret this break to correspond to the tailing off of the equilibration process between nearest neighbors and the movement of polarization to more distant spins. It seems evident that the amplitude of the initial decay due to nearest neighbors should offer semiquantitative insight into the number of nearest heteropolymer (dissimilar) neighbors; the more such neighbors, the closer the system should be to internal spin equilibrium following this nearest-neighbor spin diffusion. However, before we address the issue of the number of heteropolymer nearest neighbors, we argue that the *time scale* for this initial fast decay is qualitatively consistent with assignment to *nearest-neighbor* spin diffusion.

If we use eq 1 with $t_{sd} = 160$ μs (the time over the initial fast decay occurs), with $D = 5 \times 10^{-12}$ cm^2/s (a value obtained from the calculated D for *alkanes*,[21] scaled by the cube root of the relative proton densities[7]), and with $k = {}^4/_3$ (from the 1D diffusional model), then x, the rms distance over which polarization moves in 160 μs, is 0.34 nm. This x is approximately half the diameter of an aromatic ring, i.e., about half of the monomer size. The validity of this x, so determined, depends on whether a 1D spin diffusion model is appropriate in this case, considering that a monomer is situated in a 3D lattice and the k used in eq 1 increases as the dimensionality of the spin diffusion problem increases. For our purpose, which is to identify this time scale with nearest neighbors as opposed to, say, next nearest neighbors, we justify the use of k for the 1D model by adopting a simplistic model of the glass as being a cubic array of monomeric repeat units. Then, because of chain continuity, only four of the six nearest sites are candidates for positioning a monomer of a type different from that of the central monomer. In a 50/50 blend, approximately half of these four sites will be occupied by such a monomer if packing is purely "statistical", i.e., if the site occupation probabilities for these four sites depend only on the relative abundance of each type of repeat unit. This we refer to as the "statistical model". From the point of view of any given monomer in this model, only two of six possible boundaries involve dissimilar neighbors; these are the boundaries across which initial heteropolymer polarization diffuses. In a 1D (lamellar) morphology heteropolymer spin diffusion also occurs from two sides of each domain. Moreover, in keeping with that analogy, the thickness of the domain in a 50/50 blend having a lamellar morphology is about $2x$, which, for our case, would be 0.68 nm or very close to the diameter of an aromatic ring. Hence, we conclude that the initial fast decay can rightly be ascribed to nearest-neighbor spin diffusion. We turn now to the more complicated issue of trying to extract an average number of nearest neighbors from the amplitude of the initial fast decay.

In Figure 3, a linear dashed line appears whose intercept is 0.43, and this line is linearly extended toward the $\delta\Delta M_s(t_{sd})$, so as to be tangential to it. By this means we are roughly estimating the amplitude of that portion of the decay which will be associated with nearest-neighbor spin diffusion assuming that the early-time behavior of each process is linear as is the case[17] for diffusion between domains, given spatially sharp interfaces and sharp initial gradients. The claims for linear behavior in this case are rather coarse approximations, but in order to estimate the number of nearest neighbors, we need some estimate of the change, ΔM_{nn}, in $\delta\Delta M_s(t_{sd})$ which can be ascribed to the initial, fast, nearest-neighbor spin diffusion. The difference in intercepts between $\delta\Delta M_s(t_{sd})$ and the dashed line in Figure 3 suggests a ΔM_{nn} of 0.57, and we will proceed with the semiquantitative interpretation of this fast decay using the assumption that $\Delta M_{nn} = 0.55$, which is to say that we believe $\delta\Delta M_s(t_{sd})$ indicates that $0.50 < \Delta M_{nn} < 0.60$.

If we adopt the value $\Delta M_{nn} = 0.55$, we can ask the following simple question: On average, how many PXE (PS) spins must *fully* equilibrate with each PS (PXE) spin in order to achieve this value? The answer, taking into account relative molar abundances, is easily computed for this 50/50 blend. When PS is the central monomer, 0.34 PXE protons are required for every PS proton, and when PXE is the central monomer, 0.42 PS protons are required for each PXE proton. Corresponding numbers for achieving full equilibrium are respectively 0.87 PXE protons and 1.15 PS protons. The simple interpretation for $M_{nn} = 0.55$ is that, in the first 160 μs, any given spin equilibrates with about 35–40% of the number of dissimilar-monomer spins needed to achieve full equilibrium. Unfortunately, this result does not directly imply that 35–40% of the nearest neighbors should be dissimilar. We seek a mathematical definition which can be applied to all monomer positions *and* which has an associated natural time scale.

As a model with a more intuitive cutoff for marking the end of the fast decay, we first thought that this fast process should correspond to the full equilibration of the initial spin polarization on each monomer with the initial polarizations on each of its six nearest neighbors in this idealized cubic lattice. This works as a concept for the central monomer; in fact, if we consider a collection of such central monomers, surrounded by repeat units whose occupation probabilities are purely statistical at the four available sites and if we average initial polarizations over all of the seven monomers, we predict the $\Delta M_{nn} = 0.57$. This result prompted the drawing of the dashed line in Figure 3. However, it is easily recognized that one cannot independently claim full equilibration within all such seven-monomer clusters without concluding that all spins in the sample are at spin equilibrium ($\Delta M_s(t_{sd}) = 0$ and $\Delta M_{nn} = 1$). Thus, this definition of spin equilibration does not correspond to the fast decay; it corresponds to the *entire* HtSE process. Clearly we cannot insist that nearest-neighbor spin diffusion involves *all* of the protons on each monomer *and* results in *full equilibration* of the spin polarizations involved. So we look for another definition of nearest-neighbor spin diffusion which will be physically meaningful and be applicable to all of the monomers.

There is a mathematical definition (we call this the "$^1/_6$ model") of nearest-neighbor spin equilibration which avoids the implication that sample-wide equilibrium is also achieved. The corresponding physical picture is that every pair of nearest neighbors at all cubic lattice sites equilibrates the polarization from the most proximate $^1/_6$ of its protons. Thus, after such nearest-neighbor spin equilibration, the average polarization of any central monomer on the cubic lattice is influenced equally by the initial polarizations on each of the six nearest neighbors albeit in such a way that each of these neighbors also experiences a similar equilibration process, determined by its nearest neighbors. This $^1/_6$ model leads to a ΔM_{nn}'s of 0.33 or 0.65 respectively for the cases where the distributions of neighbors are (a) statistical or (b) correspond to the maximum occupancy of monomers dissimilar to the central monomer. The dashed line in Figure 3, which has a ΔM_{nn} of 0.57, implies an active interleaving of PS and PXE, rather than just a statistical occupancy if this model of nearest-neighbor spin diffusion is adopted. To be specific, if the experimental ΔM_{nn} is 0.55, this $^1/_6$ model predicts that, of the four available cubic sites around a PS (PXE) central monomer, an average of 3.06 (3.54) sites are occupied by PXE (PS) repeat units, compared to 1.86 (2.14) sites so occupied as predicted from a statistical distribution.

The problem with the foregoing analysis is that equilibration with only $^1/_6$ of the neighboring protons seems artifically restrictive. To the degree that, during the initial fast decay, a more extensive equilibration takes place both within and between nearest neighbors, the corresponding modified distribution which will be consistent with a given ΔM_{nn} will require a reduced interleaving.

Relative to the earlier calculation offered, it is clearly too ambitious a claim that *full* equilibration over a central monomer *and* its nearest neighbors occurs in 160 μs. The reasons are both experimental and theoretical. First, experimentally gradients *within* monomers are only about 80% dissipated after 160 μs in the HmSE curve of Figure 3; i.e., equilibrium has not been fully achieved even though the gradients occur over distance scales of, say, half a monomer. Second, the spatial extent of spin diffusion over 160 μs, calculated earlier, is 0.34 nm, i.e., of dimension comparable to half a monomer. So realistically, during the first 160 μs, only three or four spins at most on each monomer can be involved in polarization transport between two dissimilar nearest neighbors and, even then, they will not fully equilibrate. Given these considerations, the $^1/_6$ model probably underestimates the amount of HtSE but not by very much. If, for the statistical model, we try to take account of further HtSE (i.e., more than $^4/_3$ spins per monomer per nearest-neighbor pair) during the first 160 μs by iterating a second time on the $^1/_6$ model (apply the $^1/_6$-model calculation, derive new average polarizations for each kind of monomer, and then repeat the $^1/_6$-model calculation), then $M_{nn} = 0.55$, in good agreement with the analysis of Figure 3. By performing the calculation this way we simulate more extensive spin equilibration while maintaining the mathematical independence of averaging polarization over each central monomer. We are not suggesting a two-step process; this is only a mathematical strategy for simulating more HtSE while maintaining mathematical tractability.

This latter calculation is probably an overestimate of the amount of HtSE which occurs in 160 μs since it assumes full equilibration of the spins involved *and* assumes full equilibration within the monomers prior to the second part of the calculation. Therefore, the latter two calculations should bracket the true number of nearest neighbors. Hence, we conclude that the average number of dissimilar nearest neighbors *may be higher but is not significantly lower than is given by the statistical distribution of nearest neighbors.*

For us, an important reason for investigating this blend was that we wished to measure, for polymers whose repeat units are of modest size, the time scales for spin equilibration corresponding to the processes of HmSE and intraphase HtSE. These time scales are necessary to understand when analyzing data on phase-separated blends where information on domain size and stoichiometry depends on being able to separate the interphase HtSE from these other two kinds of spin equilibration. From the PS decay in Figure 3, about 96% of the original polarization gradient has dissipated in 0.5 ms, 99% in 0.75 ms, and 99.5% in 1 ms. Therefore, we can be quite confident that in blends of glassy polymers, whose monomer size and proton density are comparable to that of PS, HtSE should be dominant for $t_{sd} > 1$ ms.

With respect to the 50/50 PS/PXE blend serving as an experimental reference for the time scale for intraphase HtSE, the following observations pertain. While there is an early fast decay (see Figure 3) associated with spin diffusion between nearest neighbors, the tail of the decay curve extends over a considerable time period. Thus, intraphase HtSE is about 80% finished after 1 ms, 90% after 2 ms, and 96% after 4 ms, and changes can still be followed beyond 10 ms (see Figure 1). This final decay, whose length was somewhat surprising to us, tails out to significantly longer times than does the HmSE. In a very approximate way one expects that, since HtSE involves average polarization differences from monomer to monomer while HmSE in homopolymers follows gradient dissipation over length scales within monomers (length scales of about $^1/_2$ a monomer), statistics of mixing aside, the HtSE, should take about 4 times as long as the HmSE process (see eq 1). Thus, the tail of $\delta\Delta M_s(t_{sd})$, particularly as it extends beyond 4 ms, is evidence of the statistics of mixing or local departures from average blend composition although one must also factor in the role of chain continuity in biasing the statistics of nearest neighbors. In practical terms, if one wishes to isolate interphase from intraphase HtSE in a glassy, phase-separated blend, then one cannot usually afford to ignore the first 10 ms of data while intraphase HtSE is being achieved, unless domain dimensions are in excess of about 10 nm. For smaller characteristic domain dimensions, one would be better off analyzing all spin diffusion data for $t_{sd} > 1$ ms. Since, to a very good approximation, such longer-time data would represent only the HtSE profile, one could then approximate the relative amounts of interphase and intraphase HtSE (the decay profile of the latter being obtained from the PS/PXE experimental curve) by iteratively adjusting the relative amplitude of the intraphase contribution until the interphase portion of this decay acquires an initial linear portion, characteristic of spin diffusion between regions having relatively small interface widths.

Conclusions

Chemical-shift-based proton spin diffusion studies utilizing multiple-pulse techniques have been conducted on a 50/50 blend of PS/PXE as well as on the pure homopolymers. We were interested in these experiments from two points of view: first, we wished to verify that this is a blend mixed on a molecular level, and, second, we wanted to use the data from this blend to analyze data from other phase-separated glassy blends having comparable monomer size.

Proof of molecular-level mixing requires that one monitor polarization transfer between PS and PXE protons (heteropolymer spin equilibration) at very short spin diffusion times, t_{sd}. Because of spectral overlap of the PS and PXE spectra, we could not directly isolate the polarization flow between PS and PXE protons. Therefore, we used the measured rate of homopolymer spin equilibration (HmSE) to approximate, by difference, the rate of heteropolymer spin equilibration (HtSE). This inferred profile had an initial decay whose time scale and amplitude indicated substantial molecular-level mixing. We considered whether we could extract the average number of dissimilar repeat units surrounding any central monomeric repeat unit. However, we were only able to argue that this number could be larger than but could not be much less than the number predicted from a statistical distribution based on the overall number density of the repeat units. This conclusion is certainly consistent with expectations based on thermodynamic miscibility and a negative enthalpy of mixing. While we admit that this conclusion rests on the interpretation of a nonrigiously justified difference curve derived from two experimental data sets, the amplitude of this difference curve for $t_{sd} >$ 1 ms is correctly derived and interpreted. From the shape of the curve at longer times and the amount of HtSE at that time, it is clear that there is some mixing of PS and PXE on a nearest-neighbor scale. In other words, the assumptions made influence the *number* of dissimilar nearest neighbors but certainly not their existence. In principle, NMR methods[22] combining multiple-pulse proton and ^{13}C irradiation, along with special cross-polarization techniques, have the capability of sorting out the rate of HtSE in PS/PXE blends. However, the short time scales on which spin equilibration happens, the finite required times for cross-polarization, and the rigorous requirement that protons attached to ^{13}C nuclei behave exactly as their counterparts on ^{12}C nuclei make this an exceedingly demanding experiment.

In the analysis of our data we did not consider any possibilities for most-favored PS/PXE spin diffusion pathways which might be associated with specific, prevalent geometric dispositions of dissimilar monomers (see Appendix). Thus, for example, we could not test the hypothesis, suggested by some liquid-state NMR measurements[23] using small molecules with structural analogy to the PS and PXE repeat units, that the major interaction is between the PXE methyl protons and the π-orbitals of the PS rings.

Relative to the interpretation of spin diffusion results on other phase-separated glassy polymer blends having similar monomer size, the following practical points were observed: (a) Spin equilibrium within the homopolymers is achieved (residual polarization gradients are less than 1% of the initial value) after 1 ms of spin diffusion. Therefore, for glassy blends of similar monomeric size and proton density, decays beyond 1 ms may be ascribed exclusively to HtSE. Moreover, the other implication is that all spin diffusion line shapes beyond 1 ms will, to a very good approximation, consist of some linear combination of the homopolymer line-shape contributions to the blend spectrum. This latter feature generally simplifies line-shape analysis in blends where spectral overlap does not allow a clean separation of contributions from the individual homopolymers. (b) The HtSE curve covers a rather broad range of spin diffusion times. Beyond the initial rapid decay, the tail of this curve extends to times in excess of 10 ms. This tailing, to the extent that it is to significantly longer times than required for HmSE, is attributed partly to the fact that, when average polarization gradients exist between dissimilar monomers, the length scale is approximately twice the length scale associated with gradients within monomers. The remaining contribution to the tailing of the HtSE curve is attributed to the statistical mixing of chains, i.e., to the idea that the smaller the sampled volume, the greater is the rms deviation from the sample-average PS/PXE stoichiometry. Blends with three preparation histories including a modeled plate all showed the same sluggish longer-time behavior, thereby indicating that this behavior is typical of the thermodynamically equilibrated blend and not a result, say, of incomplete mixing. Therefore, spin diffusion must cover longer distances than are involved in HmSE before the last chemically-based polarization gradients disappear. The sluggish character of the tail of this decay will generally mandate some curve fitting, utilizing this PS/PXE data, if one is to extract domain sizes and domain stoichiometries in phase-separated (phases of mixed composition), glassy blends having comparable monomer sizes to those of PS and PXE and domain sizes less than about 10 nm. We will use such analyses in the next paper in this series when we examine blends of cellulose with either poly(acrylonitrile) or poly(4-vinylpyridine).

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Appendix

Our objective is to argue that $\delta\Delta M_s(t_{sd})$ in Figure 3 is a good approximation to the true heteropolymer spin equilibration (HtSE) profile; i.e., $\delta\Delta M_s(t_{sd})$ approximates the case where no initial polarization gradients exist within the protons of a given kind of residue; initial gradients only exist between protons on dissimilar residues.

We start with some general comments. First, the range of $\Delta M_s(t_{sd})$ from 0 to 1 is the proper range to be ascribed to HtSE.

Second, the initial gradients which are set up in these experiments derive from the Boltzmann populations of spin states. These latter polarizations represent excess populations of spins in one Zeeman state over another of about 3 in 10^5. Thus, the polarization gradients which are spoken of in this paper are exceedingly small; moreover, the relative fluctuations from monomer to monomer in instantaneous total polarization for the eight protons in each monomer is, in comparison, very large and of order unity. It is evident that the spin diffusion experiments only make sense as *ensemble averages* over large numbers of protons. Thus, for our experiments where polarization gradients are based on distinctions between aromatic (Ar) and aliphatic (Al) protons, the principal ideas which validate the language we employ in describing these experiments (language like "polarization gradients across monomers or between dissimilar residues") are (a) that the chemical compositions of the residues are uniform on the monomeric length scale, (b) that the spin exchange process is Zeeman-energy conserving, and (c) that there should be no net correlation spatially in the Boltzmann polarizations of the aliphatic and aromatic protons. Then the ensemble averages of polarization can be understood in terms of the *ensemble-averaged* distributions of these compositionally reproducible entities. A corollary is that *no structural details can be elucidated which are not ensemble-average structural correlations.*

Third, the process of spin equilibrium between Al and Ar protons involves *all* pathways for transporting polarization via spin exchange events. These events involve Al–Al, Al–Ar, and Ar–Ar proton pairs, which are, in turn, principally resident on the same or nearest-neighbor (NN) residues. Three statements follow: (a) Homononuclear spin equilibration (HmSE) in both homopolymers and blends is not limited to spin exchange events within each monomer nor does it depend solely on Ar–Al spin exchange events. (b) HtSE in the 50/50 blend is not dependent only on spin exchange events between PS and PXE protons. Rather, HtSE is a process defined only in terms of the *initial* polarization conditions; the process itself involves all the spin diffusion pathways. Moreover, in a miscible blend where a variation in residue identity may occur on the length scale of NN's, one must expect that small gradients could develop across monomer units during the HtSE process. Whether such gradients are detectable depends on the dominance of the packing geometries which give rise to such gradients, i.e., whether evidence of such geometries will persist after ensemble averaging. (c) If the appearance of small gradients over monomer dimensions is observable in the HtSE process, then it is not accurate to insist that the HmSE process is complete after 1 ms, at least not from the point of view that gradients across monomers have vanished after 1 ms. This points to a semantic problem in the use of the terms HtSE and HmSE since HmSE, by this definition, is complete as an initial condition for HtSE and becomes incomplete during HtSE. Rather than deal with this possibility, we will presently make a simplifying assumption about ensemble averages and whether such gradients are observable in the PS/PXE blend.

To a first approximation the blend has the same proton density as the homopolymers. Therefore, we may expect interchain dipolar interactions between protons on NN residues to be very similar for the blend and the homopolymer. (For example, the dipolar interaction between a PS proton and a methyl proton of PXE is not so much influenced by methyl rotation since rotation averages that interaction less and less as the distance to the PS proton increases.) Since spin exchange is driven by the strength of the dipolar interaction, the *number of interchain spin exchange events per unit time ought to be similar in the blend and the homopolymers*. The claim in Figure 3 that both HtSE and HmSE occur simultaneously does *not* imply that *more* spin exchange events occur; rather, by blending, more Al–Ar spin exchange events take place and fewer Al–Al and Ar–Ar events occur with the result that a larger change in relative Ar and Al polarizations happens than would have happened if the PS and PXE were just blended physically.

Given all of the foregoing remarks, the approximation which is probably most important in validating the analysis in Figure 3 takes account of NN polarizations in a kind of "mean-field" way. We assume that there is *no ensemble-averaged preference for spin exchange events between Al or Ar protons on dissimilar residues*. In other words, the average Al proton (or the average Ar proton) of PS undergoes spin exchange as readily with either the Ar or the Al protons of PXE when averaged over the whole ensemble. While this appears to contradict the notion that blending is promoted by specific geometric interactions between unlike residues, we offer the following arguments in support of this assumption, keeping in mind that the analysis of Figure 3 need only be a reasonable approximation to, and not an exact replication of, the true HtSE profile. (a) The homopolymers and the blend are all glasses; hence, there is significant variation in the interchain packing geometries. (b) The assumption is phrased in terms of *averages* over all *Al* or *Ar* protons of PS or PXE. There is less chance that an average Al or Ar proton would show a preference for a particular kind of proton on a dissimilar residue than that a single proton site would exhibit such a preference. (c) Implied in the ensemble average is averaging over all geometries of NN's. Thus, for all PS residues with, say, one PXE NN, one must average over all possible geometries for positioning that PXE NN and then ask whether there is a preference for Al–Al, Ar–Ar, or Al–Ar interactions beyond what is consistent with the corresponding numbers of such protons. (d) One expects spin exchange events between two spins to occur roughly at a rate proportional to the dipolar interaction itself, which, in turn, scales as the inverse cube of the internuclear distance, neglecting the angular term. A typical distance of closest approach for protons on different chains is about 0.3 nm. While this 0.3-nm distance may give rise to some correlation between Ar and Al protons, other protons, say, 0.5 nm away, have spin exchange rates only about 5 times slower. Therefore, the selectivity within dissimilar NN's toward one dominant dipolar pair is not high.

If we accept the foregoing assumption about the lack of correlation as valid, then what are the implications for the analysis of Figure 3? First, the ensemble-averaged gradients across PS or PXE monomers will be negligible after 1 ms of spin diffusion. Second, the HtSE process is presumed to occur without producing any net alteration in the Ar/Al polarization ratios for either PS or PXE protons. Third, the additivity of HmSE and HtSE suggested in Figure 3 is reenforced in the sense that, *averaged over the ensemble*, when an Al or Ar proton on a central monomer undergoes spin exchange with a proton on a NN, the average polarization of that latter proton is the monomer-averaged polarization. It follows from this that, if the NN in question is the same as the central monomer, such spin exchanges contribute to the equilibration process for the central monomer and so contribute to HmSE. On the other hand, if the NN is dissimilar instead of the same, the principal change is that more polarization will flow during each exchange event owing to the difference in initial monomer-averaged polarizations. Such spin exchange events between protons on dissimilar residues contribute both to HmSe and to HtSE in an additive way. (This comes from the recognition that the monomer-averaged initial polarization, P_B, on monomer B is different from that, P_A, on monomer A by an amount ΔP_{AB}. Thus, a proton on A spin-exchanging with an ensemble-averaged B proton transfers a polarization P_B to the A site. This can be thought of as the sum of a P_A and a ΔP_{AB} transfer where these transfers are respectively associated with HmSE and HtSE.) Hence, within the approximation of the foregoing paragraph, one can reasonably equate the time dependence of HmSE in the homopolymer to the time dependence of HmSE in the blend and thereby capture the time dependence of HtSE by difference. Fourth, that the ensemble averaging justifies the separation of the HmSE and HtSE processes also implies that, after 1 ms of spin diffusion, the experimental curve ought to merge with that of the true HtSE profile. This latter claim is also least likely to depend on the assumption of the foregoing paragraph since there is a property of spin equilibration curves which is as follows: the further in time one goes, the less sensitive one gets to reconstructing the initial conditions, especially those, like intramonomer gradients, whose length scale has been well covered by diffusion over the time in question.

A final qualitative comment supporting the notion that the experimental HmSE profile in PS (or PXE) ought to mimic HmSE in the blend follows from the expected relative importance of intramonomer-spin-exchange contributions to HmSE coupled with the similarity of NN environments, owing to chain connectivity. For example, in the statistical model described in the text, $^2/_3$ of the NN's, on average, are the same as the central monomer. Hence, many of the spin diffusion pathways characteristic of the homopolymer should also be present in the blend.

In summary, it is our judgment that the analysis of Figure 3, although not perfect owing to some possible ensemble-averaged correlations between Al and Ar protons on dissimilar residues, is approximately correct and that the semiquantitative interpretation of $\delta\Delta M_s(t_{sd})$ is justified.

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