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Glass Transition Dynamics in a Compatible Blend by Two-Dimensional Solid-State NMR

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ABSTRACT: Chain motion at the glass transition of one component in a compatible blend was observed by two-dimensional solid-state NMR spectroscopy. A blend of polystyrene and carbon-13-labeled poly(2,6-dimethylphenylene oxide) at two concentrations was studied by carbon-13 spectroscopy as a function of temperature and mixing time in the vicinity of the thermal glass transition. Chain motion of the labeled polymer on a millisecond time scale commenced at temperature of approximately 10 °C below the thermal glass transition in contrast to a single-component polymeric glasses which only show such motion at temperatures above the glass transition. The motion exhibited the characteristics of rotational Brownian diffusion with an associated broad distribution of exponential correlation times. Again in contrast to single-component polymeric glasses, the distribution is considerably broader and can only be simulated by bimodal or trimodal distribution of correlation times. Each of the modes involves a distribution of exponential correlation times, and that given by a stretched exponential correlation function was employed. The relative weighting of the modes corresponded to local concentration fluctuations; calculated from a lattice model. The dynamic heterogeneity associated with these concentration fluctuations exceeds the heterogeneity generally encountered in single-component polymeric glasses.

Introduction

Blends of poly(2,6-dimethylphenylene oxide) (PXE) and polystyrene (PS) constitute one of the better characterized blend systems of significant technological importance. Thermal,$^{1-7}$ mechanical,^{1,3,8} and dielectric^{9} studies all indicate a single glass transition though there are indications of a broader transition^{2,7} relative to the those of the constituent components, with the breadth of the transition being attributed to microheterogeneities associated with concentration gradients.^{9,10}

Solid-state NMR through carbon-13 spin diffusion measurements indicates mixing at a repeat unit level, though the associated interpretation allowed for local concentration fluctuations based on random statistics.^{11} The spin diffusion data along with molecular modeling is also consistent with a preferential location of the methyl groups of the PXE near the phenyl groups of the PS. This preferential relative position of one polymer with respect to the other may reflect the source of the favorable molecular level interaction which leads to compatibility over the whole composition range. Small angle neutron scattering data also shows PS to be a good solvent for PXE.^{10,12}

Solid-state NMR has recently yielded a powerful approach to the characterization of the dynamics of the glass transition, namely two-dimensional spectroscopy.^{13,14} These experiments reveal the glass transition to be segmental motion resulting from reorientational Brownian diffusion with an associated distribution of correlation times which is about 3 orders of magnitude wide just above the differential scanning calorimeter glass transition temperature. The two-dimensional experiment has a characteristic time in the millisecond to second range which allows NMR to probe local dynamics on a scale very close, if not coincident, to that of the more traditional mechanical and dielectric experiments. This coincidence of time scales precludes the need for any significant time–temperature extrapolation when comparing the results of these experiments. This important feature of the two-dimensional NMR experiment has been exploited to follow the reorientational motion of a diluent molecule in a multicomponent glass.^{15} As a result the reorientation of a fraction of the diluent molecules on a time scale of 1 s coincided in temperature with a mechanical loss peak measured at a frequency of 1 Hz. The coincidence of the bulk mechanical response and the molecular spectroscopic information clearly identifies the role of diluent motion.

It is the purpose of this contribution to utilize two-dimensional NMR to characterize the repeat unit level dynamics in a compatible blend which is expected to be well mixed at the repeat until level. The large glass transition temperature gap between PXE (T_g = 210 °C) and PS (T_g = 100 °C) indicates a significant difference in the intrinsic mobility of the individual components of the blend. To what degree, if any, is this difference preserved in the dynamics of the two chains near the DSC T_g of the blend? Is there extensive cooperativity between the motion of the two types of chains in the blend or does each component retain certain aspects of the intrinsic mobility indicated by their respective glass transition temperatures as pure polymers? From a theoretical point of view, the heterogeneity in a glass arises from a distribution of energy barriers.^{16} Defect diffusion over such a barrier distribution has been shown to lead to the stretched exponential correlation function, and this functional form will be used to simulate the observed pattern. Mechanical,^{17,18} dielectric,$^{19-21}$ and spin relaxation$^{22-24}$ data have all been analyzed using the stretched exponential correlation function. The distribution of energy barriers provides a conceptual framework for considering relaxation processes in glasses. An important example is the glass transition itself. In a multicomponent blend, the structure of the glass which leads to the distribution of barriers and subsequently to complex relaxation behavior could be fundamentally altered. Does the component with the low glass transition represent a source of defects or a region of low barriers which can in turn induce motion in the

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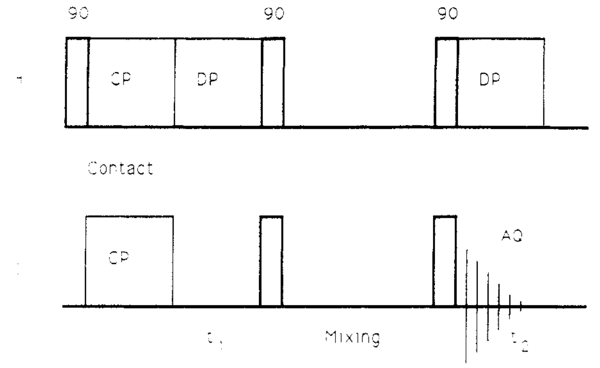

Figure 1. Two-dimensional cross polarization pulse sequence. Cross polarization is indicated by CP, dipolar decoupling by DP, $\pi/2$ pulses by 90, and data acquisition by AQ. The two time dimensions are t_1 and t_2.

higher glass transition component? If so, does the glass transition have the same significance? To address these questions, carbon-13-labeled PXE was blended with perdeuterio-PS, and the motion of the PXE is studied by two-dimensional carbon-13 solid-state line shape exchange patterns as a function of temperature and mixing time.

Experimental Section

The synthesis of the carbon-13-labeled PXE (one methyl group per repeat unit) and the preparation of the blends are as described in an earlier spin diffusion study.[15] However in the case at hand the PS is replaced by perdeuterio-PS obtained from Cambridge isotopes. DSC analyses were performed on the PXE/PS-d_8 blends using a Perkin-Elmer DSC-2C. Each sample was scanned twice at 20 deg/min from 20 to 200 °C, with a quench cool between scans. T_g's at 128 and 149 °C were obtained for the 25:75 and the 50:50 blends, respectively. These values are within experimental agreement with those reported by Yee[1] for the nondeuterated blends. The shape of the DSC traces are featureless though broad again in agreement with those presented by Yee.

A Bruker MSL 300 spectrometer was used to obtain the two-dimensional spectra. The two-dimensional pulse sequence[13-15,25] employed is shown in Figure 1 and is based on the creation of carbon magnetization by cross polarization from protons with a proton rf field of 10 G. Perdeuteriopolystyrene is employed to minimize signals from other carbons so the methyl PXE carbon powder pattern dominates the two-dimensional spectrum. A sweep width of 50 kHz with 128 data points in t_1 and 256 data points in t_2 was used to obtain the two-dimensional patterns. The narrow methyl carbon tensor minimized phase twist problems which can also be dealt with by acquiring separate real and imaginary patterns to be combined later during signal processing. Frequently with such narrow patterns, a cosine data acquisition alone with sufficient frequency offset produces an acceptable pattern. The phase cycling used to acquire either the real or the imaginary patterns follows that presented by Spiess.[13,14,25]

Results

A room temperature pattern for a 50:50 blend of PS and PXE with a mixing time of 1 s is shown in Figure 2b. The presence of considerable off diagonal intensity reflecting the occurrence of orientational exchange is evident. Such orientational exchange can arise from either molecular motion or spin exchange. Molecular motion typically has an appreciable activation energy and therefore a strongly temperature dependent pattern. Spin exchange or spin diffusion has a weak temperature dependence and therefore can be distinguished from molecular motion. At −70 °C, for the same blend and mixing time, a pattern which is identical to the room temperature pattern is obtained as shown in Figure 2a. This is strong evidence for orientational exchange by spin diffusion. If the mixing time is reduced to 50 ms at room temperature, a pattern is obtained with intensity only along the diagonal (Figure 2c). Thus no orientational exchange occurs by either mechanism under these conditions. However if the temperature is now raised to 156 °C while keeping the mixing time at 50 ms, off diagonal intensity appears (Figure 2d). This temperature is near the glass transition, and the pattern is strongly temperature dependent so the exchange mechanism occurring under these conditions is now identified as molecular motion. If two-dimensional patterns are acquired at mixing times of 50 ms or less, spin diffusion will make minimal contributions to the off diagonal intensity and molecular motion can be studied.

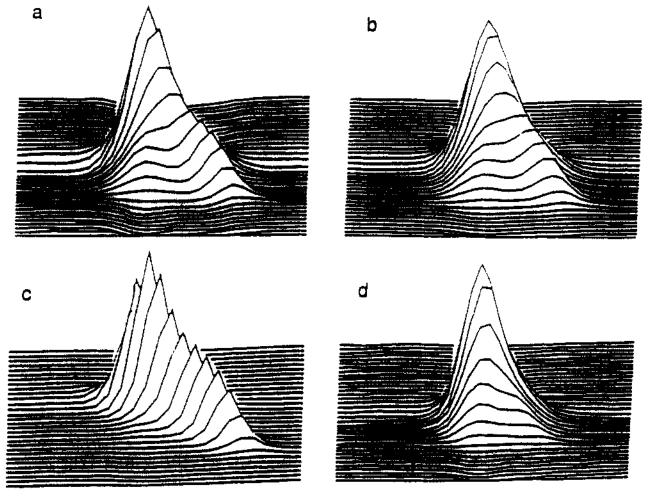

Figure 2. Two-dimensional patterns for the 50:50 blend: (a) $t_m = 1$ s and $T = -70$ °C; (b) $t_m = 1$ s and $T = 25$ °C; (c) $t_m = 50$ ms and $T = 27$ °C; (d) $t_m = 50$ ms and $T = 156$ °C. The comparison of pattern a with pattern b shows a temperature-independent orientational exchange which is characteristic of spin diffusion. The comparison of pattern c with pattern d shows a strongly temperature dependent pattern indicative of motional exchange at the shorter mixing time and higher temperature.

In a similar fashion the range over which spin diffusion contributes must also be determined for the other blend under consideration, 25% PXE and 75% PS. At the lower concentration of methyl label, spin diffusion from one methyl group to another of different orientation is slower and molecular motion can easily be monitored during mixing times of 100 ms or less.

It should be noted that at all the temperatures considered thus far, the methyl group is undergoing rapid rotation about the associated 3-fold axis and the off diagonal intensity noted in Figure 2d is from an additional motion. The time scale of methyl group rotation is so short relative to the mixing times that we will always be considering motion other than rotation about the symmetry axis. For the 50:50 blend, no off diagonal intensity is observed from −70 to about +145 °C for mixing times shorter than 50 ms. There are no mechanical loss peaks in this range either,[1] so both the NMR and mechanical experiments indicate the absence of significant chain motion. The DSC glass transition temperature[1] is about 160 °C, and as this temperature is approached off diagonal intensity is observed. The dynamic mechanical loss peak associated with the glass transition is present at these temperatures,[1] so there is a clear link between the mechanical, thermal, and two-dimensional NMR data which are all acquired on common time scales. For the 25:75 blend, a similar situation is observed. No off diagonal intensity is observed from molecular motion until the blend glass transition temperature (about 125 °C[1]) is approached.

Once the temperature regime over which molecular motion produces off diagonal intensity is established, a data grid of patterns as a function of temperature and

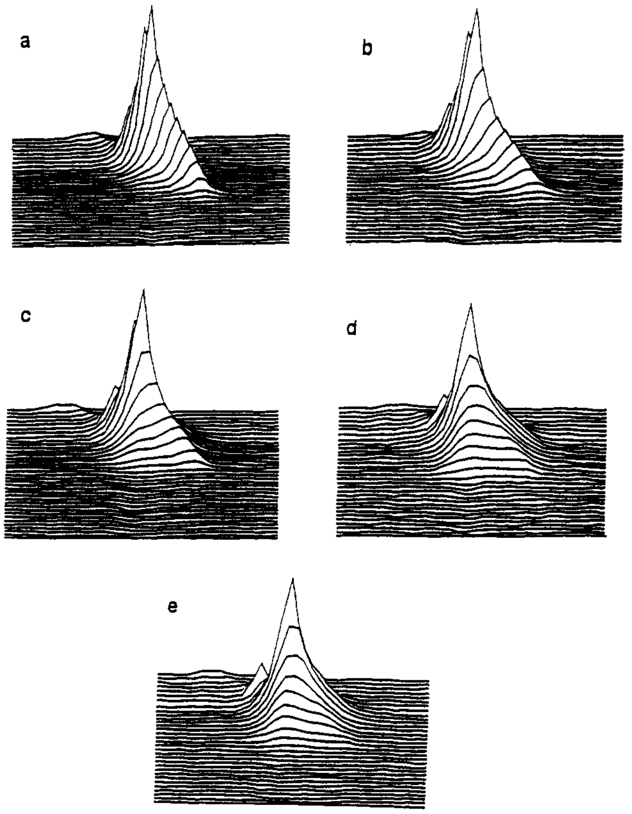

Figure 3. Two-dimensional patterns for the 25:75 blend as a function of temperature at fixed mixing time of 50 ms: (a) 90, (b) 110, (c) 115, (d) 120, and (e) 128 °C. At 90 °C, no motion is present and all intensity is along the diagonal. As temperature is raised the pattern gradually spreads over the entire available frequency range, and this behavior is indicative of Brownian rotational diffusion.

mixing time is developed. For the 25:75 blend, a series of two-dimensional patterns is shown in Figure 3 for temperatures ranging from 90 to 128 °C and a mixing time of 50 ms. This temperature span covers the change from entirely a diagonal pattern to an off diagonal pattern which completely covers all possible frequency areas. Further data sets are acquired at fixed temperatures of 115, 120, and 128 °C and a set of variable mixing times. Figure 4 contains a representative selection of these patterns at 115 °C.

For the 50:50 blend a similar set of data at 150 and 157 °C are acquired and representative patterns are presented in Figure 5.

Interpretation

Qualitatively, certain features of previous two-dimensional studies[13-15] of dynamics near the glass transition are retained in these blends. As either temperature is raised or mixing time is lengthened, off diagonal intensity gradually spreads over the whole range of accessible frequencies. This type of pattern development is characteristic of rotational Brownian diffusion and indicates that this type of motion appears to represent the nature of segmental motion in this polymer blend as it does in amorphous polymeric glasses made up of a single constituent.

There are, however, noticeable differences between the blends and pure PS. At a temperature of 115 °C there is significant off diagonal intensity at longer mixing times (>20 ms) in the 25:75 blend. This indicates the presence of backbone reorientation of the PXE at a temperature which is 10 °C below the thermal glass transition. In pure PS, there is no backbone reorientation on the millisecond to second time scale until a temperature is reached which is several degrees above the glass transition. Also there is still significant pattern evolution over the millisecond time scale at the highest temperature, 128 °C. This indicates that the breadth of the rate of motions in temperature or equivalently in time is quite broad, even broader than that observed for pure PS.

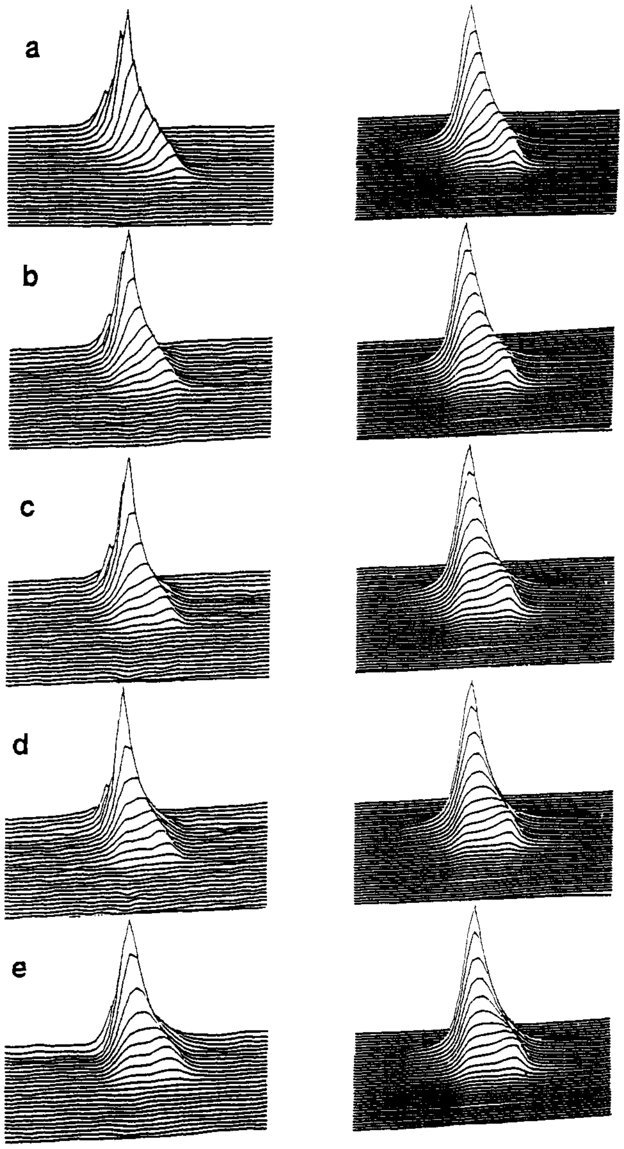

Figure 4. Two-dimensional patterns for the 25:75 blend as a function of mixing time: (a) 1, (b) 20, (c) 50, (d) 70, and (e) 100 ms, in the vicinity of the glass transition (115 °C). Experimental patterns on the left are compared with simulated patterns on the right.

Why might the glass transition be broadened? A rationale based on concentration fluctuations[9,10] appears a most likely candidate and will be considered here. It should be kept in mind that all these two-dimensional patterns are observing dynamics of the PXE so that the onset of motion well below T_g cannot be simply ascribed to some region which contains only PS. The early onset of motion with temperature must occur in a region which is rich in PS but still contains PXE units since this is the most mobile region that could be observed with a label in the PXE chain. This is a rationale which parallels that formulated for a diluent in a multicomponent glass.[15,17] There the diluent appeared to undergo rotational diffusion at a lower temperature when in contact with another diluent and a higher temperature when in contact with a polymer.

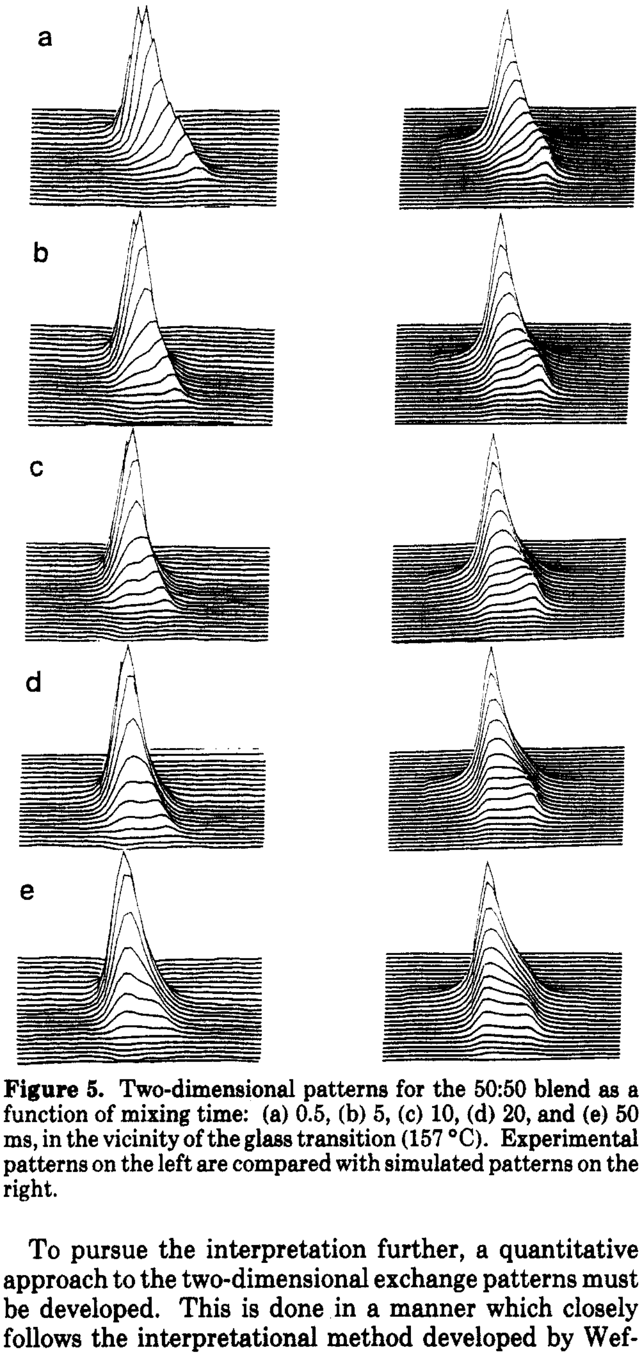

Figure 5. Two-dimensional patterns for the 50:50 blend as a function of mixing time: (a) 0.5, (b) 5, (c) 10, (d) 20, and (e) 50 ms, in the vicinity of the glass transition (157 °C). Experimental patterns on the left are compared with simulated patterns on the right.

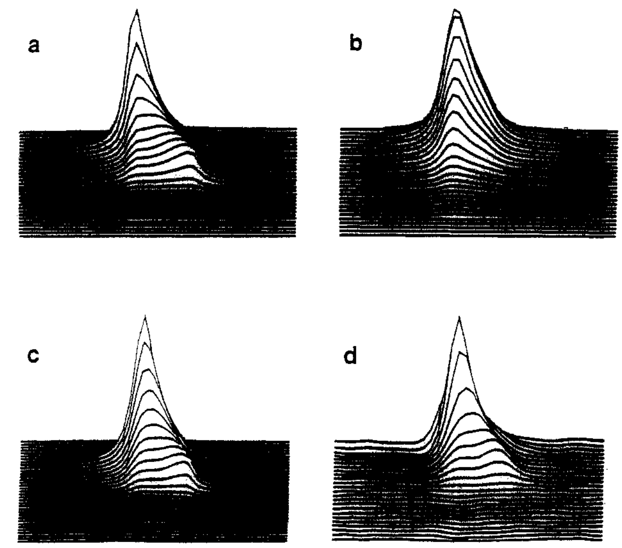

Figure 6. The two-dimensional pattern for the 25:75 blend at 100 ms and 115 °C. (a) The simulated pattern for the slow-moving component with a monomodal distribution based on the stretched exponential correlation function. (b) The simulated pattern for the fast component. The pattern (c) obtained from combining the slow and fast moving components with relative weighting of 75% and 25% is compared with experiment (d). The parameters are given in the text. Note: the fast-moving component must be added to raise the off diagonal intensity. (The off diagonal intensity is in the vertical direction on the diagram.)

To pursue the interpretation further, a quantitative approach to the two-dimensional exchange patterns must be developed. This is done in a manner which closely follows the interpretational method developed by Wefing, Kaufmann, and Spiess[13b] except the pattern intensity is calculated in the frequency domain. As is the case for PS, the simulation requires a distribution of correlation times; the distribution choice is one which corresponds to the stretched exponential. This correlation function is typically written as

$$\phi(t) = \exp(-(t/\tau_p)^\alpha) \qquad (1)$$

where the fractional exponent α controls the breadth of the distribution and the characteristic time τ_p controls the time scale. From the interpretation of dielectric and mechanical response,[17-21] a stretched exponential with an exponent in the range of 0.5–0.9 is likely. This corresponds to a distribution of exponential correlation times which spans several decades, and the weighting factors in the distribution have been the subject of considerable analysis. Three points are used to span a decade of time and the exponential correlation time corresponding to each point is taken to be a Brownian diffusion correlation time. A pattern is calculated for each correlation time with the pattern for the distribution calculated by combining the patterns for each time in the distribution with the appropriate weighting which corresponds to the stretched exponential correlation function.

It should be noted that in our simulations we employ the "slow motion limit" based on the assumption that frequency changes only occur during the mixing time.[13] In our case where there is a distribution of correlation times, it is likely that some population corresponding to the rapid wings of the distribution is moving on the time scale of the evolution time. However, it has been shown[13] that if such reorientations significantly contribute to the 2D pattern they produce strong asymmetric features and a significant decrease in spectral intensity evidenced by the reduction factor. No such features or effects are present in our data, suggesting that such effects are not influencing the overall interpretation.

Simulations for the 25:75 blend at a temperature of 115 °C and a mixing time of 100 ms are presented separately in Figure 6. The first simulation attempt involves a stretched exponential with a characteristic time, $\tau_p = 0.07$ s, and a fractional exponent of 0.6. This produces the pattern in Figure 6a which resembles the experimental result but has too much intensity along the diagonal, suggesting the need for more mobile components. Shifts in the characteristic time of the stretched exponential or the fractional exponent are unable to produce a pattern resembling the experimental result. Considerable effort was expended in attempting to do this, and one must bear in mind that while only one mixing time is being considered at the moment, the choice of parameters for the simulation must match all mixing times at 115 °C. To obtain a good match, it is necessary to add a component with a faster characteristic time (figure 6b) to the stretched exponential now being considered. A fairly close simulation of the experimental result is obtained with a composite pattern (Figure 6c) made up of 75% of the $\tau_p = 0.40$ s and $\alpha = 0.6$ pattern plus 25% of a $\tau_p = 0.35$ ms and $\alpha = 0.9$. This combined distribution of correlation times plotted in Figure 7 leads to a reasonable simulation of all mixing times at 115 °C as shown in Figure 4 along with the

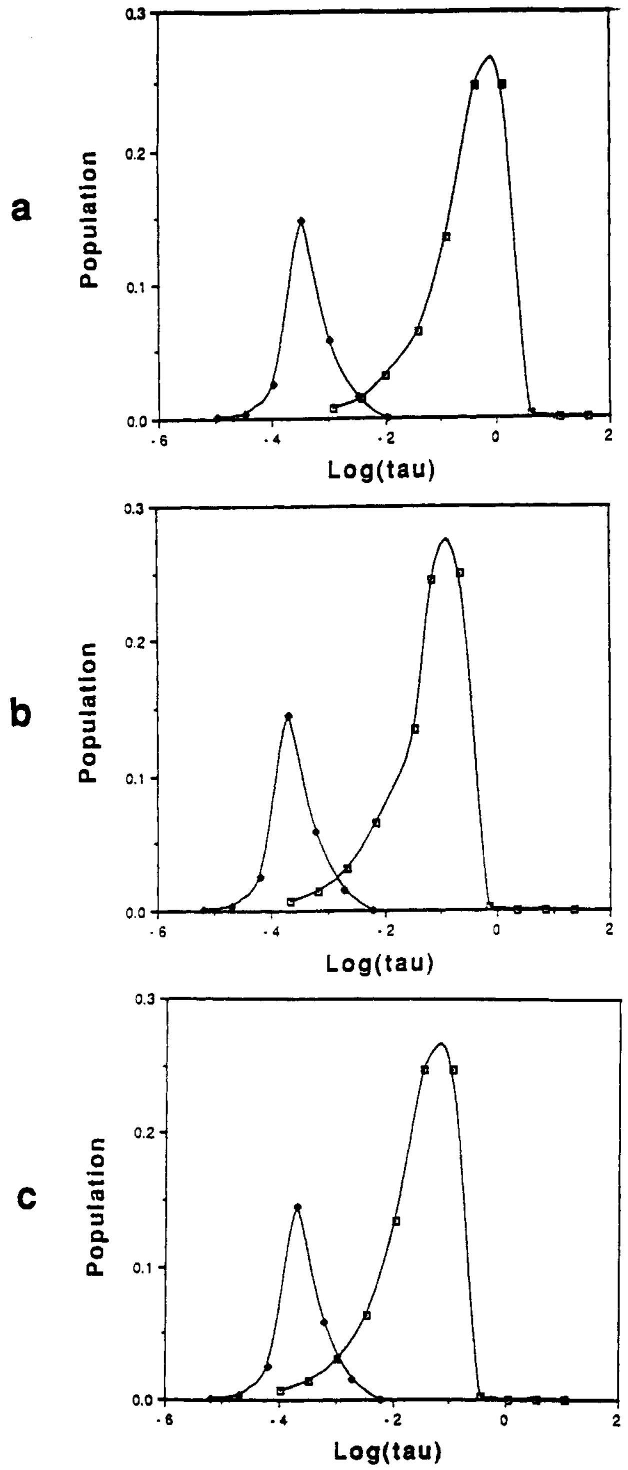

Figure 7. The distributions of exponential correlation times used to simulate the 25:75 blends at temperatures of (a) 115, (b) 120, and (c) 128 °C. One distribution simulates all mixing times at a given temperature. The distributions correspond to the combination of two stretched exponential correlation functions. The characteristic times and fractional exponents are given in the text.

experimental patterns. The same general simulation approach yielded satisfactory results for 120 and 128 °C. At each of the three temperatures the composite pattern resulted from combining 75% of a stretched exponential correlation function having a slow characteristic time with 25% of a stretched exponential correlation function with a fast characteristic correlation time. For 120 °C, the slow $\tau_p = 0.07$ s with $\alpha = 0.6$ and the fast $\tau_p = 0.20$ ms with $\alpha = 0.9$; while for 128 °C, slow $\tau_p = 0.035$ s with $\alpha = 0.6$ and the fast $\tau_p = 0.20$ ms with $\alpha = 0.9$. The associated distributions of exponential correlation times are given in Figure 7.

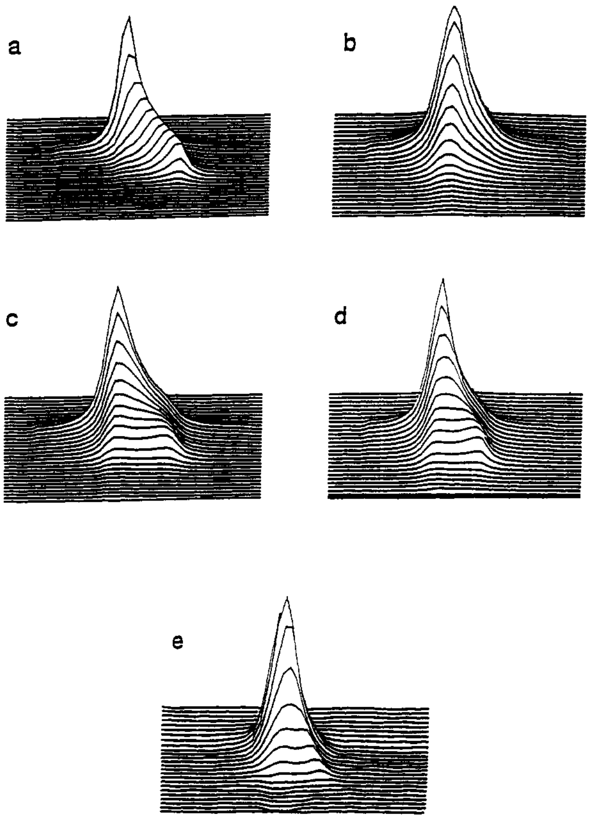

Figure 8. The two-dimensional pattern for the 50:50 blend at a temperature of 157 °C and a mixing time of 20 ms. The simulated pattern is a combination of a rigid component (a), a fast component (b), and a slow-moving component (c). The resulting trimodal distribution (d) is compared to the experimental pattern (e). The parameters are given in the text.

If the 50:50 data is now considered, a similar approach is required for the simulation but with some modification of the motional description. For a temperature of 157 °C and a mixing time of 50 ms (Figure 8), the predominant component again has a weighting of 75% but a somewhat broader distribution, $\alpha = 0.5$, works best. This component has a characteristic time $\tau_p = 0.025$ s, shown in Figure 8c. Again to develop a simulation with patterns close to the experimental results, additional stretched exponential components were required. First a two-component distribution was attempted paralleling the 25:75 simulations. However in the 50:50 simulations, the next most important contributer was found to be a slow component with a weight of 15% rather than a fast component. This slow component is so slow that it leads to no off diagonal intensity in the range of mixing times used so an arbitrarily slow characteristic time of 1s is chosen (Figure 8a). In addition, a third, small, fast component (Figure 8b) is required to produce sufficient intensity at the edges of the two-dimensional pattern. The weighting of this component is 10%, $\tau_p = 0.2$ ms and $\alpha = 0.8$. The combination of these three components is shown in Figure 8d and the corresponding experimental pattern in Figure 8e. The simulations of the 50:50 data at both 150 and 157 °C and all mixing times are done in this fashion and the patterns are compared to the experimental results in Figure 5. The overall distribution of exponential correlation times is shown in Figure 9. The actual amount of fast population ($\sim$10%) at either 150 or 150 °C is subject to a fair uncertainty (±5%), but it is required for an adequate simulation at all mix times.

The bimodal distribution used to simulate the 25:75 data is not unprecedented in the sense that such a distribution has been invoked to characterize dynamics of diluent and polymer in multicomponent glasses[15,27,28]

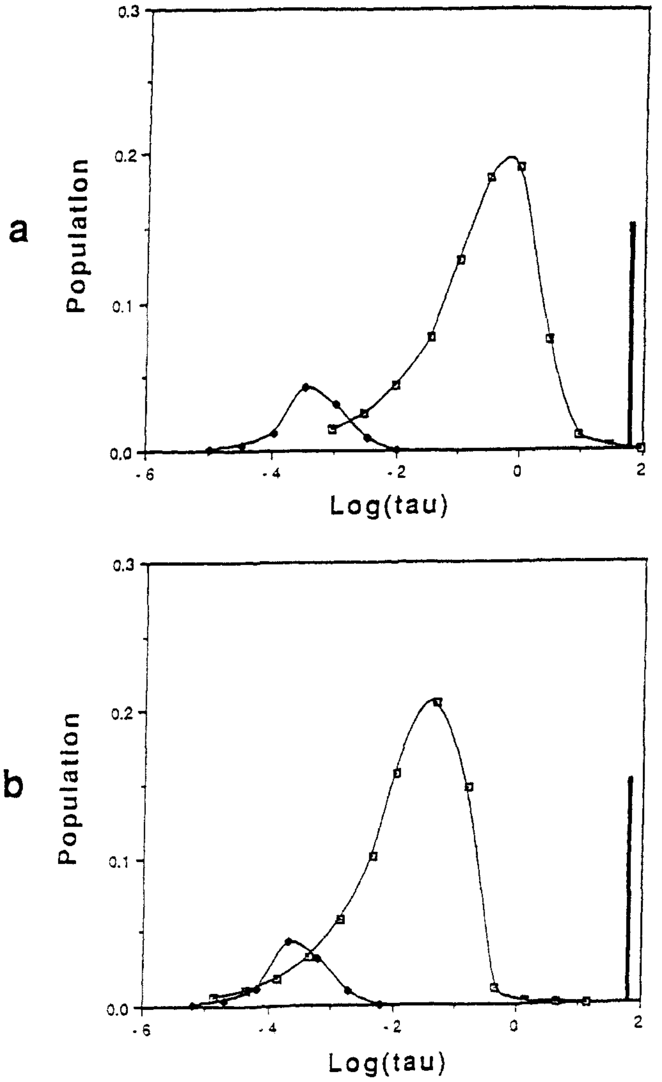

Figure 9. The distribution of correlation times used to simulate the 50:50 blend at (a) 150 and (b) 157 °C. One distribution simulates all mixing times at a given temperature. The distributions correspond to the combination of three stretched exponential correlation functions. The characteristic times and fractional exponents are given in the text. Note that the rigid component correlation time is indicated by a bar.

where the diluent and polymer have substantially different intrinsic glass transition temperatures. The trimodal distribution used in the 50:50 data represents a new level of complexity which is initially disconcerting but became plausible after attempting a quantitative description of concentration fluctuations. In the polymer diluent systems, a lattice model was developed to consider the nearest neighbor environment to either a polymer repeat unit or a diluent molecule.[27,28] The various types of environments are categorized according to the number of diluent nearest neighbors, and the populations of the various local environments correspond to the weightings of the populations of relaxing units in the bimodal distribution.

A similar strategy is adopted here to attempt to correlate nearest neighbor environments based on random concentration fluctuations at a local level with the various components of the distribution of correlation times. This strategy has been applied to the PXE–PS blend before to interpret carbon-13 spin diffusion which is again a very short range effect which correlates with the nearest neighbor environment.[11] For the problem at hand, the environment of the PXE chain is of interest since that is the location of the spectroscopic probe. To set up a lattice the relative dimensions of PXE and PS must be considered. A molecular modeling calculation[11] reveals that PXE is a longer and thinner segment than PS, so that each presents a different surface to the surroundings. Because PXE is slightly more dense than PS, the different molar masses are almost cancelled, and the volume and weight fractions are about the same. In fact even the total surface areas are nearly the same. The chief difference is the lateral surface, or the surface facing outward from the polymer chain. Fractionally this is larger for PXE because of its greater segment length. An estimation of the lateral surface area (LS) for PXE and PS repeat units gives $LS_{PXE} = 87.4$ Å^2 and $LS_{PS} = 57.7$ Å^2. On this basis a PXE chain segment of 2 repeat units is equivalent to a PS chain segment of 3 repeat units. Since we are considering glass transition dynamics it is appropriate to view the lattice unit as a short chain segment as opposed to a single repeat unit with a segment length ratio of 2:3 PXE:PS (for example, a lattice consisting of chain segments comprising 8 PXE repeat units and 12 PS repeat units).

To calculate the fractional population of PXE units with varying numbers of PS units as nearest neighbors, simple formulae often used in percolation treatments can be adopted.[27,28] Let F_i denote the fraction of PXE units which have i nearest neighbor PS units. Furthermore, p is the fraction of lattice sites which are occupied by PXE units and equals 0.3 for the 25:75 blend. Similarly, d is the fraction of sites which are occupied by PS units and equals 0.7. This leads to

$$F_0 = p^4 = 0.008$$

$$F_1 = 4p^3d = 0.076$$

$$F_2 = 6p^2d^2 = 0.265$$

$$F_3 = 4pd^3 = 0.412$$

$$F_4 = d^4 = 0.240 \qquad (2)$$

The most mobile component is F_4 which equals 24% for the 25:75 blend. F_4 is very close to the population of the fast component obtained from the fitting of the two-dimensional patterns. If all other components which contain at least some PXE units as nearest neighbors are lumped together, they account for the slow component of the fitting. Note that F_0 is a negligible contributor with a value less than 1%.

Such a lattice model interpretation is tested by changing component concentrations. This is done here by comparing model predictions with actual fitting results for the 50:50 composition. The most mobile component associated with only pure polystyrene neighbors (F_4) drops in the lattice model to about 4% while the data fitting dropped the fastest component to 10%. The fitting required the presence of a slow component with a weighting of about 15%. From the view of the lattice model, the least mobile component would be a PXE unit surrounded by other PXE units (F_0) which has a value of 10%. This is the component which is negligible for the 25:75 blend from the lattice estimate, which would account for its absence in the data fitting of that composition. The principal component which is associated with a mixed PS–PXE environment is estimated to be 86% from the lattice model to be compared with the fitting result of 75%. While not exact, the lattice model weightings compare reasonably with those derived from experiment.

Another way of viewing the two-dimensional patterns is to look at the probability, $P(\theta)$, of finding the molecule

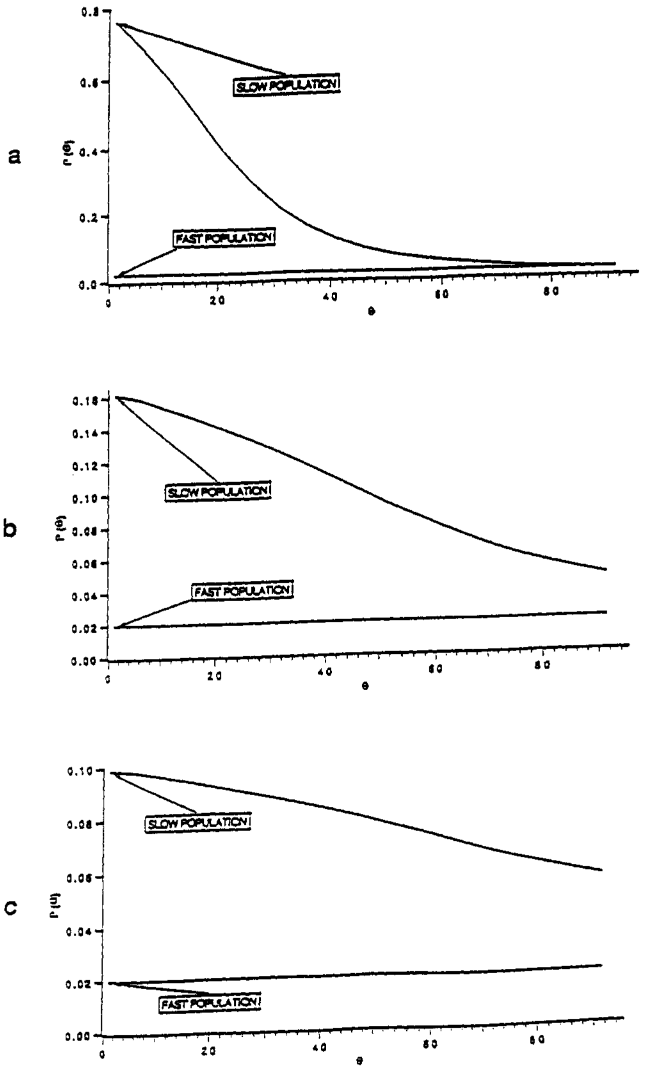

Figure 10. The probability of finding an orientation as a function of orientational angle θ based on the simulations of the 25:75 blend patterns at a mixing time of 50 ms and at three temperatures: (a) 115, (b) 120, and (c) 128 °C. The slow and fast components of the pattern are plotted separately. The slow component gradually spreads out over the angular range as temperature is raised while the fast component is equally probability at every orientational angle for the three temperatures studied.

at an orientation θ at a given mixing time and temperature given that, at time zero, θ equals zero. This approach has been used by Spiess[13,14] to assist in developing an understanding of the evolution of the two-dimensional patterns. For the 25:75 blend these plots are shown for three temperatures at a mixing time of 50 ms in Figure 10. The fast and slow components of the pattern are graphed separately. At all three temperatures, the fast component contributes equal probability at all orientations. The slow component is weighted toward low values of θ, but the weighting shifts toward higher angles as temperature is increased. Similar plots presented in Figure 11 for the 50:50 blend interpretation show comparable behavior for the fast and intermediate components relative to the fast and slow components of the 25:75 blend. The slow component for the 50:50 composition remains relatively localized near θ equals 0 for all temperatures and mixing times.

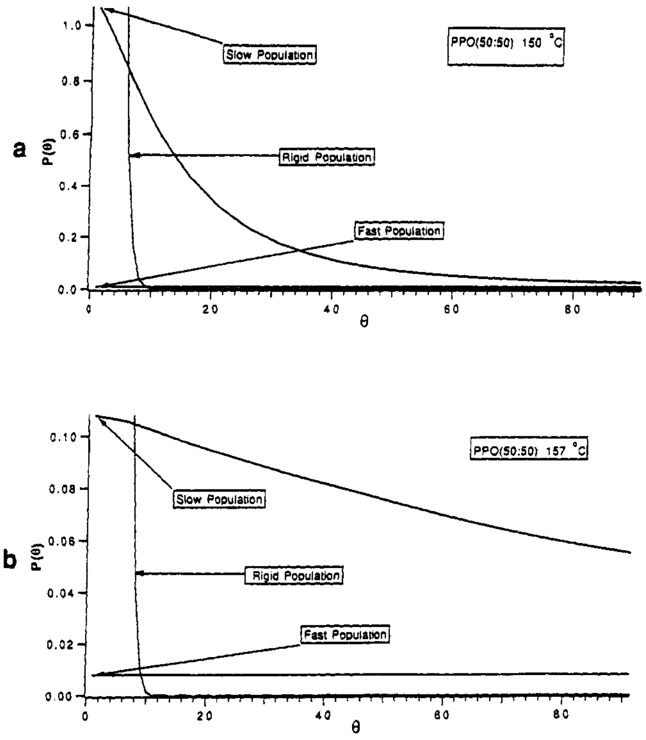

Figure 11. The same as Figure 10 but for the 50:50 blend: (a) 150 °C and (b) 157 °C.

Discussion

As in a single-component polymeric glass, the glass transition region corresponds to the onset of segmental reorientation best described as Brownian diffusion. The distinction between the single-component glass and the blends lies in the presence of a multimodal distribution of correlation times. The relative weighting of the components of the distribution can be correlated roughly with local concentration fluctuations calculated purely on the basis of random statistics. The lattice model used for this calculation is not exact but appears to agree with the pattern of the multimodal distribution invoked to simulate the two-dimensional patterns. The lattice model calculations were performed after the simulations, and, for instance, the change from a bimodal to a trimodal distribution in going from the 25:75 blend to the 50:50 blend was made to match the patterns and only later was the connection to the lattice picture developed. An uncertainty in the population of the various components of about 5–10% is likely either from the standpoint of data simulation or from the development of a lattice description. Similarly, the fractional exponent which controls the width of the various components is determined no better than to the nearest tenth, and there is a correlation between the fractional exponent choice and the weightings of the various components which contributes to the stated uncertainty in each factor. In the lattice model development, the relative dimensions of the PS units versus the PXE units is a source of uncertainty. Also if there is a favoring of PS–PXE contacts because of a negative χ parameter, the basis of purely random statistics would be altered.

NMR is generally most sensitive to very short range factors, and it is not reasonable to expect that these concentration fluctuations extend much beyond a few repeat units in size. As mentioned, spin diffusion measurements[11] show mixing on an angstrom level; this data was also considered through the lattice model allowing for local concentration fluctuations. The actual dimensions of these fluctuations is not quantitatively established beyond the qualitative characterization as local.

This examination of the glass transition shows that blending does introduce a heterogeneity which goes beyond that associated with the intrinsic structure of a glass. If a stretched exponential correlation function is used to characterize dynamics at the glass transition, an exponent of 0.5–0.8 is likely.[17-21] In the current work it is found that the various components of the multimodal distribution have exponents in this range. Though the components of the distribution are somewhat resolved in either time or temperature, they mostly appear to lie in the vicinity of the thermal glass transition. Therefore there must be still a significant amount of cooperativity of motion between chains even if the local environment is responsible for shifts among the components. Stated in another fashion, the shifts of the components are considerably smaller than the difference between the glass transition temperatures of the constituent polymers. This type of heterogeneity is no doubt linked to the broadening of the thermal or mechanical determinations of the glass transition; however, to quantitatively correlate the local motion determined by NMR with the bulk thermal or mechanical properties requires a knowledge of the amplitude or strength of the motional contribution to the bulk property which is not necessarily the same for each component of the distribution. Furthermore, only the PXE dynamics have been tracked. Thus additional experiments on the PS dynamics would be required to relate molecular level motion to overall thermal or mechanical properties. Complimentary two-dimensional experiments on the PS component using deuterium NMR are underway and will hopefully provide additional information on the glass transition in blends.

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References and Notes

(1) Yee, A. F. *Polym. Eng. Sci.* **1977**, *17*, 213.
(2) Stoelting, J.; Karasz, F. E.; MacKnight, W. J. *Polym. Eng. Sci.* **1970**, *10*, 133.
(3) Tucker, P. S.; Barlow, J. W.; Paul, D. R. *Macromolecules* **1988**, *21*, 1678.
(4) Shultz, A. R.; Gendron, B. M. *J. Appl. Polym. Sci.* **1972**, *16*, 461.
(5) Jacques, C. H. M.; Hopfenberg, H. B.; Stannett, V. *Polym. Eng. Sci.* **1973**, *13*, 81.
(6) Prest, W. M.; Porter, R. S. *J. Polym. Sci. Polym. Phys. Ed.* **1972**, *10*, 1639.
(7) Wang, L. H.; Porter, R. S. *J. Polym. Sci. Polym. Phys. Ed.* **1983**, *21*, 907.
(8) Shultz, A. R.; Beach, B. M. *Macromolecules* **1974**, *7*, 902.
(9) MacKnight, W. J.; Stoelting, J.; Karasz, F. E. *Adv. Chem. Ser.* **1971**, *99*, 29.
(10) Keskkula, H.; Paul, D. R.; Young, P.; Stein, R. S. *J. Appl. Polym. Sci.* **1987**, *34*, 1861.
(11) Wang, P.; Jones, A. A.; Inglefield, P. T.; White, D. M.; Bendler, J. T. *New Polmeric Mater.* **1990**, *2*, 221.
(12) Maconnachie, A.; Kambour, R. P.; White, D. M.; Rostami, S.; Walsh, D. J. *Macromoelcules* **1987**, *17*, 2645.
(13) (a) Wefing, S.; Spiess, H. W. *J. Chem. Phys.* **1988**, *89*, 1219. (b) Wefing, S.; Kaufmann, S.; Spiess, H. W. *J. Chem. Phys.* **1988**, *89*, 1234. (c) Kaufmann, S.; Wefing, S.; Schaefer, D.; Spiess, H. W. *J. Chem. Phys.* **1990**, *93*, 197.
(14) Schaefer, D.; Spiess, H. W.; Suter, U. W.; Fleming, W. W. *Macromolecules* **1990**, *23*, 3431.
(15) Zhang, C.; Wang, P.; Jones, A. A.; Inglefield, P. T. *Macromolecules* **1991**, *24*, 338.
(16) Bendler, J. T.; Shlesinger, M. F. *Macromolecules* **1985**, *18*, 591.
(17) Bendler, J. T.; Ngai, K. L. *Macromolecules* **1984**, *17*, 1174.
(18) Bendler, J. T. *J. Stat. Phys.* **1984**, *5/6*, 597.
(19) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.
(20) Weiss, G. H.; Bendler, J. T.; Dishon, M. *J. Chem. Phys.* **1985**, *83*, 1424.
(21) Montroll, E. W.; Bendler, J. T. *J. Stat. Phys.* **1984**, *34*, 129.
(22) Jones, A. A.; O'Gara, J. F.; Inglefield, P. T.; Bendler, J. T.; Yee, A. F.; Ngai, K. L. *Macromolecules* **1983**, *16*, 1552.
(23) Connolly, J. J.; Inglefield, P. T.; Jones, A. A. *J. Chem. Phys.* **1986**, *86*, 6602.
(24) Chung, S. H.; Jeffrey, K. R.; Stevens, J. R.; Borjesson, L. *Phys. Rev. B.* **1990**, *41*, 6154.
(25) Schmidt, C.; Blumich, B.; Spiess, H. W. *J. Magn. Reson.* **1988**, *79*, 269.
(26) Dishon, M.; Bendler, J. T.; Weiss, G. H. *J. Res. Natl. Inst. Stand. Technol.* **1990**, *95*, 433.
(27) Cauley, B. J.; Cipriana, C.; Ellis, K.; Roy, A. K.; Jones, A. A.; Inglefield, P. T.; McKinley, B. J.; Kambour, R. P. *Macromolecules* **1991**, *24*, 403.
(28) Liu, Y.; Roy, A. K.; Jones, A. A.; Inglefield, P. T.; Ogden, P. *Macromolecules* **1990**, *23*, 968.

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