Prediction of Segmental and Global Dynamics in Disordered Styrene−Isoprene Tetrablock Copolymers

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ABSTRACT: The Lodge/McLeish model successfully fits the temperature and composition dependences of the segmental dynamics for both components in disordered styrene−isoprene tetrablock copolymers (SISI). The fitted parameters ϕ_{self} are in good agreement with the values anticipated in the Lodge/McLeish model after accounting for the junction effect. A geometric mean mixing rule was used to average the segmental dynamics of the two components in order to describe tracer diffusion in the SISI matrices. This mixing rule accurately reproduces previously reported experimental results for polyisoprene, polystyrene, and styrene−isoprene diblock tracers. The unusual homogeneity of these matrices, as inferred from tracer diffusion measurements, is discussed in terms of thermodynamic barriers to diffusion.

Introduction

The dynamic properties of miscible polymer mixtures are a topic of great current interest. Because of the limited number of homopolymers available in practice, mixing these homopolymers is one way to produce inexpensive materials with a much broader range of properties than the homopolymers alone exhibit. It would be an important advance to be able to predict the viscoelastic and transport properties of such mixtures from the composition, component molecular weights, and architectures. We imagine that this should be possible by dividing the problem into two parts. First, the segmental dynamics of each component in the mixture need to be accurately predicted. Then, with knowledge of the component segmental dynamics, it should be possible to predict the longer length scale dynamics which are most relevant for rheology. Unfortunately, there is no consensus about how to do either of these steps. Progress is further hampered by a lack of complete data sets for the global and segmental dynamics of both components in miscible mixtures.

There has been considerable effort focused on understanding segmental dynamics in miscible blends. A large number of data sets are available for at least one component in miscible polymer mixtures.[1−16] Several theoretical approaches have been proposed attempting to explain these data.[17−23] Factors that are included in these different models include the intrinsic mobility difference between the two homopolymers, the self-concentration effect, thermal concentration fluctuations, and coupling between neighboring chains (especially for those blends with strong interactions). Several recent publications[23−25] have highlighted the success of the Lodge/McLeish model,[23] which takes into account the first two factors.

To our knowledge, there are only two miscible polymer mixtures for which segmental and global relaxation have been separately measured for all components: polyisoprene/polyvinylethylene (PI/PVE) blends and styrene−isoprene tetrablock copolymers (SISI). In a recent publication we discussed PI/PVE,[25] and here we focus on SISI tetrablocks. Lodge and co-workers have thoroughly investigated the SISI systems by small-angle neutron scattering (SANS), shear viscosity, and tracer diffusion measurements.[26,27] Remarkably, they reported that polyisoprene (PI) and polystyrene (PS) tracers of similar molecular weight have similar diffusion coefficients in SISI matrices. This result is surprising given the large ΔT_g between homopolymers PS and PI, which leads to the expectation that the component dynamics should be quite distinct in these tetrablocks. Recent work[28,29] confirms that the *segmental* dynamics of styrene and isoprene segments in SISI tetrablocks typically differ by orders of magnitude. These new results allow us to test the predictions of existing models for segmental dynamics and, in combination with the tracer diffusion data, allow a test of mixing rules for global dynamics.

In this paper we test the ability of the Lodge/McLeish model to predict the isoprene and styrene segmental dynamics of SISI. We have used the model with the Fox equation to predict the mixture T_g and modified the model for block copolymers by accounting for the altered dynamics of segments very near a junction point. The Lodge/McLeish model quantitatively fits the segmental dynamics of both components in SISI over a wide temperature and composition range with fitted parameters ϕ_{self} that are identical to the predicted values.[23] The unusual homogeneous global dynamics of SISI matrices can be reproduced by using a geometric mean mixing rule to average the component segmental relaxation times of the matrices.

Lodge/McLeish Model

In this section we explain our implementation of the Lodge/McLeish model.[23] The model assumes that chain segments in a mixture have an average relaxation time that depends only on the average composition of a small volume centered on the segments of interest. In a binary

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blend of homopolymers A and B, the local volume V centered on a segment of A affects the segmental dynamics of the A unit. In this local volume, there will be on average an excess of A units relative to the bulk average concentration due to chain connectivity (the "self-concentration" effect). The effective local concentration is given by

$$\phi_{\text{eff}} = \phi_{\text{self}} + (1 - \phi_{\text{self}})\phi \tag{1}$$

Here ϕ_{self} is the self-concentration and ϕ is the overall concentration.

The Lodge/McLeish model assumes that the length scale relevant for the segmental dynamics should be of the same order as the Kuhn segment length l_k. ϕ_{self} is determined from the volume fraction occupied by a Kuhn length of repeat units inside a volume equal to l_k^3:

$$\phi_{\text{self}} = \frac{C_\infty M_0}{k\rho N_{\text{av}} V} \tag{2}$$

Here M_0 is the molar mass of the repeat unit, N_{av} is the Avogadro constant, k is the number of backbone bonds per repeat unit, ρ is the bulk density, and C_∞ is the characteristic ratio. In our analysis we treat ϕ_{self} as a fit parameter.

To test their model, Lodge and McLeish proposed to calculate the effective glass transition temperature $T_{\text{g,eff}}(\phi)$ for each component from the calorimetric glass transition temperature $T_g(\phi)$ using the following equation:

$$T_{\text{g,eff}}(\phi) = T_g(\phi_{\text{eff}}) \tag{3}$$

In other words, the effective T_g for component A is determined from the macroscopic $T_g(\phi)$ but evaluated at ϕ_{eff} rather than ϕ.

As described previously,[25] we use the Fox equation to calculate the blend T_g.

$$\frac{1}{T_g(\phi)} = \frac{\phi}{T_g^A} + \frac{1-\phi}{T_g^B} \tag{4}$$

This approach has the benefit of only using homopolymer properties to describe blend dynamics. For SISI tetrablock copolymers, a DSC T_g could not be readily measured.[27]

For quantitative prediction of the segmental dynamics over a wide temperature and composition range, two additional assumptions are proposed:[25] (1) The segmental relaxation times of each component in a binary system have the same Vogel−Tammann−Fulcher (VTF) temperature dependence as the corresponding homopolymer; only the Vogel temperature T_0 varies with composition:

$$\tau_{\text{seg},i}(\phi,T) = \tau_{\infty,i} \exp\left[\frac{B_i}{T - T_{0,i}(\phi)}\right] \tag{5}$$

Here "i" represents component A or B. $\tau_{\infty,i}$ and B_i are the VTF parameters that describe the temperature dependence of segmental relaxation times for pure homopolymer A or B. (2) For each component in the blend, the variation of T_0 with composition completely follows that of effective glass transition $T_{\text{g,eff}}$.

$$T_{0,i}(\phi) = T_{0,i} + [T^i_{\text{g,eff}}(\phi) - T^i_g] \tag{6}$$

Here $T_{0,i}$ is the Vogel temperature for pure homopolymer A or B, and $T_{0,i}(\phi)$ is the Vogel temperature for component i in the blend.

For multiblock copolymers with short chains, such as SISI, one additional modification is necessary. Pure homopolymers PI and PS have very different segmental dynamics at a given temperature. Therefore, in SISI tetrablock copolymers, there are a few isoprene and styrene units at each side of a styrene−isoprene junction point whose dynamics are strongly influenced by the other component. This "junction effect" is likely much stronger than the influence of neighboring chains in the case of simple mixing. To account for this, we replace eq 6 with

$$T_{0,i}(\phi) = T_{0,i} + (1 - \phi_{\text{junc}})[T^i_{\text{g,eff}}(\phi) - T^i_g] + \phi_{\text{junc}}[\overline{T_{\text{g,eff}}}(\phi) - T^i_g] \tag{7}$$

ϕ_{junc} is the fraction of repeat units in each block whose segmental dynamics are strongly affected by the junction point and show average dynamics characterized by

$$\overline{T_{\text{g,eff}}}(\phi) = \frac{1}{2}[T^A_{\text{g,eff}}(\phi) + T^B_{\text{g,eff}}(\phi)] \tag{8}$$

We assume that there are four repeat units near each side of a junction point that have the average dynamics of the two components; thus, the largest value of ϕ_{junc} used here is 0.37 for the isoprene component in SISI80. Although no direct experiment has been done on this issue, the use of four repeat units here is not completely arbitrary. MD simulations[30,31] suggest it is likely to be 3−5 units based upon the assumption that the junction effect in block copolymers is similar to the chain end effect in homopolymers. In addition, a recent experiment[29] on a blend of PI (5%) and SISI60 (95%) showed that there is a 9 K temperature shift between the segmental dynamics of the PI tracer and the segemental dynamics of the isoprene segments in the SISI60 matrix. The assumed junction effect (using four repeat units) produces a 7 K temperature shift, in reasonable agreement.

As mentioned in the Introduction and supported by the experimental results on PI/PVE blends[7] and SISI tetrablock copolymers,[29] the intrinsic mobility difference between the two components is a significant contribution to distinct component dynamics, especially at high temperatures. This effect is implicitly present in eq 5, where the VTF parameters $\tau_{\infty,i}$ and B_i for the two components in mixtures are the same as their corresponding homopolymers. This indicates that the components in the multicomponent system still retain some intrinsic character of their homopolymer motion, such as their relaxation time in the high-temperature limit τ_∞.

We note that the Lodge/McLeish model assumes that the relevant local volume is fairly small as compared to some other approaches. This is qualitatively consistent with recent solid-state NMR experiments. The 4D3CP experiment allows the length scale of spatially heterogeneous dynamics to be measured in a homopolymer.[32,33] This heterogeneity length should be an upper bound for the size of the local volume which determines the local relaxation time. In one polymer (poly(vinyl acetate)) at T_g + 10 K, a heterogeneity length of 3.7 nm

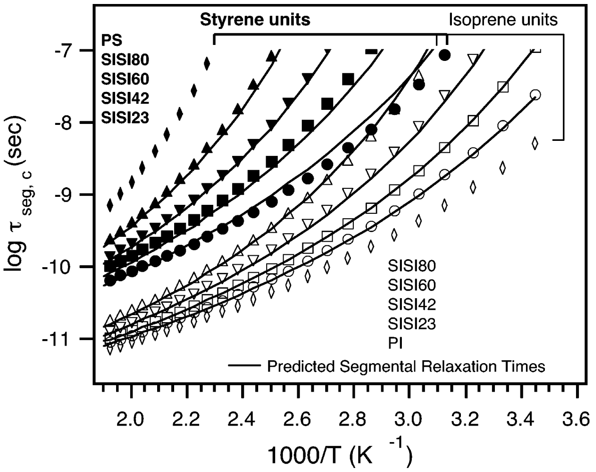

Figure 1. Segmental relaxation times (calculated from the fit parameters to NMR data[29] and shown as symbols) for both components in SISI and comparison with the fits to the Lodge/McLeish model. The fit parameters are ϕ_{self}(PI) = 0.45 and ϕ_{self}(PS) = 0.27. A junction effect on four repeat units at each side of each junction point is included, as described in the text.

has been determined.[32−34] Other liquids, such as glycerol,[34,36] D-sorbitol,[35] and *o*-terphenyl,[34] also gave similar length scales.

The current application of the Lodge/McLeish model to tetrablocks implicitly assumes that the local composition field in a tetrablock and in a blend of the same composition are identical. This is completely consistent with mean-field calculations of the structure factor $S(q)$, which show that $S(q)$ is essentially indistinguishable for a blend and a tetrablock of the same composition (and independent of χ), on length scales corresponding to several Kuhn lengths and below. For these tetrablocks, which are far above any order−disorder transition temperature, scattering experiments also support this assumption (see Figure 1 of ref 27).

Results and Discussion

Prediction of Segmental Dynamics. In a recent paper,[29] we reported ^{13}C and ^{2}H NMR relaxation time measurements on four linear SISI tetrablock copolymers of overall molecular weight about 12 000 g/mol in order to characterize the segmental dynamics of both components. A wide temperature range and several compositions (SISI23, SISI42, SISI60, SISI80; the suffixes denote the volume percentage of styrene units) were investigated. The two components show quite distinct segmental dynamics. At sufficiently high temperatures, the segmental dynamics of styrene segments are slower than that of isoprene segments by about 1 decade. The dynamic difference between the two components becomes larger at lower temperatures. The points shown in Figure 1 are not directly measured relaxation times but are calculated from fits to the experimental data.[29] The uncertainty of those fits is ±0.1 decade at high temperatures and ±0.2 decade at low temperatures. Only for the styrene component in SISI23, at the lowest temperature, is there a larger uncertainty (0.3 decade).

Figure 1 shows the comparison between the experimental results and the Lodge/McLeish model, with fit parameters ϕ_{self}(PI) = 0.45 and ϕ_{self}(PS) = 0.27 (Table 1). For each component, the ϕ_{self} value and the homopolymer relaxation curve generate the four curves shown for that component. The uncertainty for ϕ_{self} is ±0.05, as estimated by the point where the deviation from the fitting is comparable to the experimental uncertainty. The Lodge/McLeish model successfully describes changes in segmental dynamics with composition and temperature for both components in SISI. The ϕ_{self} values obtained in our fitting are identical to the predictions of Lodge and McLeish (eq 2).[23] This excellent agreement should be tempered with the recognition that the choice of the relevant averaging length scale as exactly equal to the Kuhn length is possibly fortuitous; modest changes in the choice of length scale would weaken the agreement.

Table 1. Parameters Used in Fits to the Lodge/McLeish Model

	τ_∞ (ps)[a]	T_0 (K)	B (K)	ϕ_{self}[b]	T_g (K)[c]
PI	0.23	168	1220	0.45	208
PS	0.68	317	1414	0.27	367

[a] τ_∞ for the segmental relaxation. [b] ϕ_{self} is a fit parameter, obtained by assuming that four repeat units at each side of a junction point have dynamics which are strongly modified (eqs 7 and 8). [c] DSC T_g from ref 27.

While all the predicted curves in Figure 1 agree with the experimental results within experimental uncertainties, there is a slight mismatch between the predictions and the data for the styrene component at lower temperatures. This suggests that the styrene component (the high T_g component) would be better fit with a temperature-dependent ϕ_{self}, consistent with recent findings of Kumar and co-workers.[54] The largest deviations, for the segmental dynamics of the styrene component in SISI23, might be partly due to the molecular weight dependence of the fragility in PS homopolymers. Roland and co-workers reported a systematic and significant increase in fragility of short PS chains (M_w < 10 kg/mol) with increasing molecular weight.[37] Unlike binary polymer blends, the chain length of the styrene segments in SISI changes as the overall composition is varied.

If we fit the experimental results without considering the junction effect (i.e., using eq 6 rather than eq 7), we obtain slightly smaller self-concentration values: ϕ_{self}(PI) = 0.37 and ϕ_{self}(PS) = 0.24. The quality of fitting (not shown) in this case is somewhat inferior to that shown in Figure 1.

Relationship between Segmental and Global Dynamics. Lodge and co-workers[26] have studied the tracer diffusion of a PS homopolymer, a PI homopolymer, and a SI diblock copolymer in SISI tetrablock matrices as a function of temperature and matrix composition. The Rouse model was used to extract the monomeric friction factors ζ for the unentangled tracers from the measured tracer diffusion coefficient, D:

$$\zeta = \frac{kT}{ND} \tag{9}$$

where N is the degree of polymerization based on the styrene monomer volume. Remarkably, the friction factors of PS, PI, and SI tracers are almost indistinguishable and are equal to the friction factors of the matrix from self-diffusion. How might these friction factors characterizing the global dynamics be predicted?

Previous investigators have used various mixing rules to predict the terminal dynamics in polymer mixtures from the terminal dynamics of the pure homopolymers.[27,38,39] We take a different approach here, attempting to predict the global dynamics from the segmental dynamics.

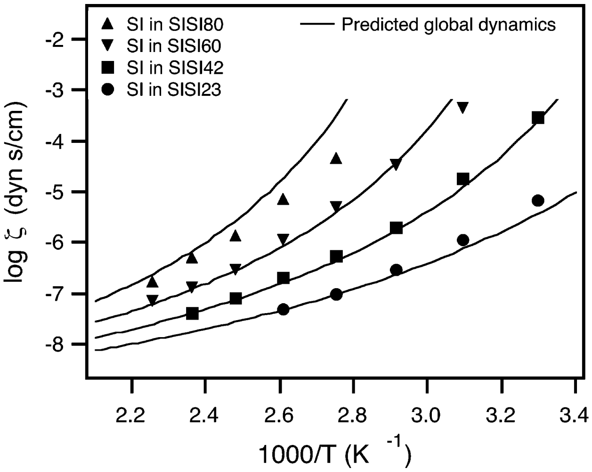

Figure 2. Comparison of the monomeric friction coefficients ζ for SI diblock tracer diffusion in SISI matrices (from ref 26) with the geometric mean prediction based on the experimentally measured segmental relaxation times of the two matrix components.

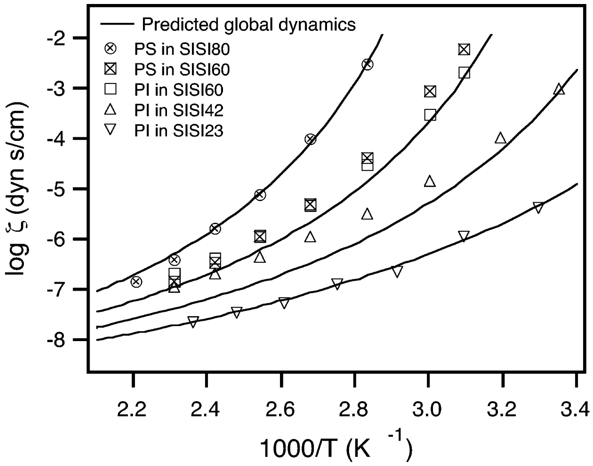

Figure 3. Comparison of the monomeric friction coefficients ζ for PS and PI tracer diffusion in SISI matrices (from ref 26) with the geometric mean prediction based on the experimentally measured segmental dynamics of the two matrix components.

The tracer diffusion results discussed above suggest that global dynamics of tracers in the SISI tetrablocks sense some sort of average segmental dynamics. We find the following volume fraction-weighted geometric mean mixing rule to be quite successful in reproducing the experiments:

$$\log \frac{\zeta_{\text{tracer}}(\phi)}{T} = [\phi \log \tau_{\text{seg,PS}}(\phi) + (1-\phi) \log \tau_{\text{seg,PI}}(\phi)] + \left[\phi\left(\log \frac{\zeta^0_{\text{PS}}}{T} - \log \tau^0_{\text{seg,PS}}\right) + (1-\phi)\left(\log \frac{\zeta^0_{\text{PI}}}{T} - \log \tau^0_{\text{seg,PI}}\right)\right] \tag{10}$$

Here ϕ is the volume fraction of styrene units in the matrix material, $\tau_{\text{seg,PS}}$ and $\tau_{\text{seg,PI}}$ are the segmental correlation times of isoprene and styrene components in SISI matrix, and ζ_{tracer} is the monomeric friction factor for a tracer chain. All superscripts “0” indicate pure homopolymer values. The second term in eq 10 accounts for the slightly different relationship between the segmental correlation times and the monomeric friction coefficients of the two pure homopolymers. The necessity of this correction (no more than 0.4 decade change with composition) can be seen by considering the limit of self-diffusion in the two homopolymers.

Figure 2 shows a plot of the monomeric friction factors of diblock SI tracers diffusing in SISI matrices compared to the geometric mean prediction, using experimentally obtained segmental dynamics data as input to eq 10.[26,29] Except for the SISI80 matrix at low temperatures, the geometric mean expression is nearly perfect. This agreement may not be surprising since the SI diblock is almost a 50/50 copolymer and reasonably senses a completely averaged dynamic environment. The geometric mean expression also matches friction coefficients derived from diffusion and viscosity measurements on the tetrablock matrices (not shown here). Furthermore, the geometric mean expression also describes the temperature dependence of self-diffusion[51] for a SI diblock just above the order−disorder transition (also not shown here).

Figure 3 shows a similar comparison for PS and PI tracers in the tetrablock matrices. The geometric mean expression catches the main features of dynamic variation with temperature and composition here. The deviations between the friction coefficients from tracer diffusion and eq 10 are less than half a decade while the data extend over more than 5 decades. With close inspection, it is found that PS tracers have a slightly stronger temperature dependence than the geometric mean prediction while PI tracers have slightly weaker temperature dependence than the prediction. This difference may imply that both PI and PS tracers retain their intrinsic properties (temperature dependence) to a small extent while they mainly sense the average dynamic environment at a given temperature.

From Figures 2 and 3, we conclude that the geometric mean mixing rule, applied to the segmental dynamics, successfully describes the global dynamics of tracer diffusion in SISI. To predict all the tracer diffusion data, we extrapolated our segmental relaxation times to somewhat lower temperatures than we have measurements. Nevertheless, the prediction remains very good.[40]

Why Is Tracer Diffusion in SISI Tetrablocks Different Than in Miscible Blends? It has been shown in a number of miscible blend studies[39,41−49] that the two polymer components have distinct friction coefficients in the blend and also that the friction coefficients have distinct temperature dependences. With this in mind, it is quite interesting that PI and PS tracers in SISI tetrablocks have similar friction coefficients. We illustrate this comparison in the following two paragraphs.

We can explore quantitatively the comparison between miscible blends and tetrablock matrices by making reference to particular blend system, PI/PVE. For PI/PVE, the global dynamics of each component in a given blend are observed to have essentially the same temperature and composition dependence as the segmental dynamics of that component; i.e., the terminal dynamics are apparently slaved to the segmental dynamics.[1,25] This empirical relationship can be simply represented by

$$\left.\frac{\tau_{\text{term}}}{\tau_{\text{seg}}}\right|_{\text{blend}} = \left.\frac{\tau_{\text{term}}}{\tau_{\text{seg}}}\right|_{\text{melt}} \tag{11}$$

Figure 4 shows the global dynamics of three kinds of

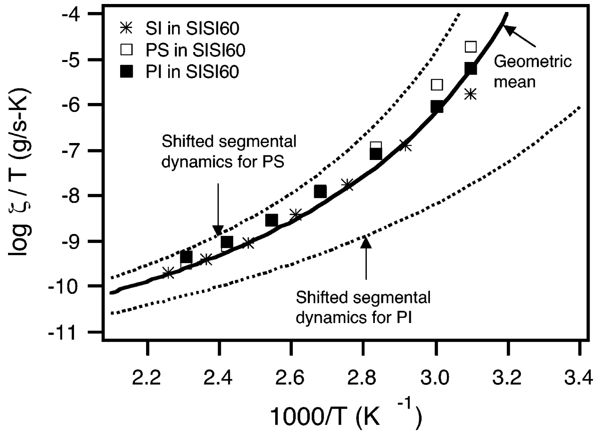

Figure 4. Comparison of the monomeric friction coefficients for SI, PS, and PI tracer diffusions in the common matrix SISI60 to the geometric mean prediction and the shifted segmental dynamics of both matrix components.

tracers (PS, PI, and diblock copolymer SI) in the common matrix SISI60 along with the geometric mean prediction (eq 10). Also shown are two dotted lines which represent the friction coefficients for PI and PS tracers which would have been expected if tracers in the tetrablock matrix followed the same rule observed for the PI/PVE system (eq 11);[50] clearly tracers in the tetrablock do not follow eq 11. In making this comparison, we are treating the mixture of the tracer and tetrablock as a two-component polymer blend and then applying eq 11 to the tracer component. This comparison assumes that the segmental dynamics of a tracer chain are identical to the segmental dynamics of the corresponding segments in the tetrablock. This assumption was validated for the isoprene component in a recent paper[29] where we found that the segmental dynamics of a 5% PI tracer (^{13}C labeled with a molecular weight of either 11 000 or 900 g/mol) are almost identical to that of the isoprene segments in SISI tetrablock copolymers.

There is a second way to compare tracer diffusion in tetrablock and miscible blend matrices. Figure 3 shows that the global dynamics of a PI tracer are controlled by the average segmental dynamics of the matrix for styrene compositions up to 60%. If this trend continues up to 100% styrene, the prediction would be that the PI tracer friction coefficient would match the styrene friction coefficient. While this conclusion may be intuitively appealing, it contradicts results from other miscible blend systems. For example, in polystyrene/tetramethylpolycarbonate (PS/TMPC), the friction coefficients of PS chains in a matrix which is 95% TMPC are 2−3 orders of magnitude smaller than for the TMPC chains.[47]

Why does a PI chain in an SISI matrix, with its very fast segmental dynamics, "lose its advantage" and translate globally with the same friction coefficient as the matrix chains or a PS tracer? We propose that something on a length scale intermediate between that of the segmental dynamics (roughly 1 nm) and that of the diffusion measurements (roughly 1 μm) intervenes to slow down the PI chains. The structure factor $S(q)$ for the tetrablock matrix contains a peak[27] associated with the block structure which is completely missing in miscible blends. Qualitatively, this peak signifies a segregation of styrene and isoprene units on the length scale of the chain radius of gyration (ca. 4 nm) that we imagine would pose a significant thermodynamic barrier to the diffusion of either a styrene or isoprene homopolymer tracer. If these barriers are sufficiently high, then the tracer chains will be trapped in free energy minima until fluctuations in the tetrablock structure allow them to move to a neighboring region. In other words, the tracer mobility would be matched to the collective dynamics of the matrix. This could account for the essentially identical friction coefficients of the PI tracer, the PS tracer, and the SISI matrix chains.

The idea that fluctuations in block copolymer matrices influence the diffusion of homopolymer or block copolymer tracers has been previously explored by Tang and Schweizer[52] and by Leibig and Fredrickson.[53] These groups developed theories that predict significant suppression of diffusion in fluctuating block copolymer matrices above but near the order−disorder transition. Quantitative comparison of results for diffusion in SISI tetrablocks is complicated due to the tetrablock architecture and especially the very large asymmetry in pure component friction coefficients, neither of which are accounted for in the theories.

Our hypothesis that thermodynamic barriers control the motion of tracer chains in tetrablocks, even considerably above the order−disorder transition, could be tested in a number of interesting ways. In tetrablocks (or possibly diblocks) of isoprene and vinylethylene, we would predict that PI and PVE tracers would have distinct friction coefficients since χ is very close to zero, and thus no thermodynamic barriers should be relevant for tracer diffusion. We would predict that the diffusion of lower molecular weight PI and PS tracers in the SISI tetrablocks studied here would have friction coefficients that approach the dotted lines in Figure 4. The thermodynamic barriers imposed by concentration variations in the matrix should decrease linearly with the tracer chain degree of polymerization. Tracer diffusion in block copolymer matrices composed of styrene and vinylpyridine, because the pure component friction coefficients are similar, would more nearly conform to the assumptions invoked in refs 52 and 53 and as such would provide a way to isolate the influence of thermodynamics in block copolymer systems.

Conclusion

Using the Fox equation to predict the copolymer T_g, and accounting for the junction effect, the modified Lodge/McLeish model is able to quantitatively fit the segmental relaxation times of both components in tetrablock SISI copolymers. The fit parameters ϕ_{self} are in good agreement with the values anticipated in the original model. This suggests that the relevant length scale for composition variations is roughly the Kuhn segment length and that the self-concentration is the dominant factor leading to the very heterogeneous segmental dynamics in these tetrablocks. Monomeric friction coefficients of tracer chains in SISI matrices can be accurately reproduced using a geometric mean mixing rule to average the component segmental dynamics of the matrices. The similarity of monomeric friction coefficients for PI and PS tracers in SISI tetrablocks can be reconciled by the proposition that thermodynamic barriers to tracer transport are so substantial that the mobilities of both types of tracers are determined by the dynamics of matrix chain fluctuations.

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