Macromolecules **2003,** *36,* 10087−10094

What Length Scales Control the Dynamics of Miscible Polymer Blends?

Rama Kant and Sanat K. Kumar*

Isermann Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180

Ralph H. Colby

Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

Received May 30, 2003; Revised Manuscript Received September 30, 2003

ABSTRACT: The segmental dynamics of miscible polymer blends have been the focus of much recent research since the two constituents typically appear to experience different average dynamic environments. It has been suggested that these results can be attributed to concentration fluctuations coupled to chain connectivity effects. However, the relative importance of these two factors in determining chain dynamics is unresolved. Here we assess the importance of concentration fluctuations and also the magnitude of self-concentrations experienced by a test segment by analyzing literature values of the mean segmental relaxation times of the components of several miscible polymer blends and a disordered tetrablock copolymer. The self-composition derived in this manner is used to estimate the cooperative length scale which controls segmental dynamics, a quantity for which no first principles theory exists. Using a Taylor series expansion, we show that concentration fluctuations can strongly affect the mean relaxation time of the blend constituents in the immediate vicinity of the blend glass transition temperature, with this effect being significant even 50 K higher. We then consider the size scale of cooperative motion. For the blend component with the lower glass transition, the self-concentration is apparently independent of temperature and blend composition and consistent with a cooperative length scale of the order of one Kuhn length. This result is in good agreement with the recent conjecture of Lodge and McLeish. The results for the other blend component are quite different. At high temperatures, apparently above the glass transition of this component, the Kuhn length is still the controlling length scale for dynamics. However, the size of the cooperative volume is found to increase monotonically with decreasing temperature, in qualitative accord with the previous work of Donth.

1. Introduction

The viscoelastic properties of miscible polymer blends have been the focus of extensive research in the past 15 years.[1−10] It is now well accepted that, although these blends are thermodynamically miscible, the component dynamics often are heterogeneous. This heterogeneous behavior manifests itself as a different temperature dependence of the mean segmental relaxation time of the two components (thermorheological complexity), suggesting that the two components encounter different average dynamic environments. Experimentally, it has been found that thermorheological complexity is only important when the two components have different glass transition temperatures, T_g, i.e., for $\Delta T_g \equiv |T_{g,1} - T_{g,2}| > 20$ K.[11] Further, this effect is relatively insensitive to system thermodynamics, in that dynamic behavior does not change dramatically if one approaches the critical point for phase separation.[12] However, thermodynamics do become important when one considers strongly miscible systems, where thermorheological simplicity results.[1]

The consensus at this time is that local concentration variations, created by concentration fluctuations (driven by the thermodynamics of the blends)[13,14] and by chain connectivity effects (i.e., that a certain fraction of monomers in a control volume are intramolecular contacts),[3,4,14,15] are responsible for dynamic heterogeneity. However, the relative importance of these effects and the relevant volumes over which they need to be considered to quantitatively model blend dynamics are unresolved.

The role of concentration fluctuations is controversial, even though simulations unequivocally assert that their magnitude increases with decreasing cooperative volume size.[16] Lodge and McLeish[15] have developed a mean-field model that ignores concentration fluctuations when they estimate the mean segmental relaxation times of the two different blend components. Instead, they assume that the intermolecular environment surrounding a given monomer is the mean blend composition. In contrast, Fischer et al.[13] and Kumar et al.[14,17] explicitly account for the role of concentration fluctuations even in the enumeration of average system properties. While all workers agree that concentration fluctuations are necessary to capture the width of the relaxation time spectrum, their role in determining mean segmental relaxation times is unresolved.

Another crucial unresolved question is the appropriate size of the cooperative volume, i.e., the size of the local neighborhood of a segment which controls its dynamics.[18−20] Since there is no first-principles theory for this key quantity, several different models have been postulated for its temperature and composition dependence, as we summarize below:

a. Kornfield and co-workers[3,4,21] suggested that cooperative sizes of ≈5 nm were necessary to simultaneously capture the mean relaxation time and the width of the relaxation time distribution for the dynamics of the two components of the PI/PVE blend.

b. Fischer and co-workers[13] and Kumar et al.[14,17] have utilized a temperature-dependent cooperative volume, one suggested either by Donth[22] or by a dynamic scaling

10.1021/ma0347215 CCC: $25.00

model.[23] In this prescription, the size of the cooperative volume increases monotonically with decreasing temperature and diverges at a characteristic temperature below T_g, i.e., the Vogel temperature in the case of the Donth model.

c. Lodge and McLeish[15] have employed cooperative volumes whose lateral sizes are equal to the Kuhn segment length of the chains. Thus, each component has a cooperative volume of different size, but the volume is temperature and composition independent.

These different estimates of cooperative volume size, in conjunction with various approximations for the role of chain connectivity and concentration fluctuations, explain dynamic heterogeneity with varying degree of success. However, the relative importance of these factors remains debated at this time. The goal of this paper is to estimate (a) the relative importance of concentration fluctuations and connectivity effects and (b) the size of the cooperative volume and its temperature and composition dependence. To make statements about these issues, we utilize experimental segmental relaxation times of the two components of several miscible blends and a tetrablock copolymer and assess the regions of parameter space where concentration fluctuations are expected to be important. We also use these data to estimate the self-compositions experienced by a test segment. This information can be converted to a size scale of cooperativity through purely geometric arguments. With this knowledge we critically comment on different theoretical approaches for predicting the segmental dynamics of miscible polymer blends.

2. Importance of Concentration Fluctuations

The role of concentration fluctuations in determining the mean properties of the system, such as the segmental relaxation time of a blend component, $\langle \log \tau \rangle$, is considered here. We first perform a Taylor expansion of the mean logarithmic segmental relaxation time of a blend component:

$$\langle \log \tau(\phi) \rangle = \log \tau(\langle \phi \rangle) + \frac{1}{2}\langle (\delta\phi)^2 \rangle \frac{d^2 \log \tau}{d\phi^2}\Big|_{\phi=\langle\phi\rangle} + ... \quad (1)$$

$\langle \phi \rangle$ is the mean composition experienced by the test segment, which can be readily decomposed into mean intrachain (or self) and interchain contributions:[4,15]

$$\langle \phi \rangle = \phi_{self} + (1 - \phi_{self})\bar{\phi} \quad (2)$$

Here $\bar{\phi}$ is the mean blend composition, and ϕ_{self} is the mean value of the self-concentration. It thus follows that the first term on the right side of eq 1 explicitly accounts for the mean contribution of chain connectivity effects and the mean value of the intermolecular composition, while the second term in eq 1 is the leading contribution from thermally driven concentration fluctuations.

$\langle (\delta\phi)^2 \rangle$, the mean-squared concentration fluctuation (e.g., $\delta\phi = \phi - \langle \phi \rangle$), is typically of order 0.1 for cooperative volumes of the size of a Kuhn length for a polymer blend with weak interactions between dissimilar monomers, as suggested by previous simulation work.[16] An analytical form for $\langle (\delta\phi)^2 \rangle$ in the case where the cooperative size is smaller than a Kuhn length is presented in the Appendix. While this number will become smaller for increased cooperative sizes, our discussion below will show that the relevant cooperative sizes are equal to or smaller than a Kuhn length over much of the parameter space of interest. To evaluate the second-order derivative, $[d^2 \log \tau/d\phi^2]_{\phi=\langle\phi\rangle}$, we employ the WLF model to describe the temperature dependence of relaxation times[24] and utilize the Fox equation for describing the composition dependence of the glass transition temperature.[25] [An explicit expression is presented in the Appendix.] In Figure 1, we plot the temperature-dependent contributions from the first and second terms of eq 1 for the PI component in a 50/50 PI/PVE blend (we use $\phi_{self} = 0.45$, the value suggested by Lodge and McLeish[15] for PI). More details of these calculations, including specific values of the parameters employed, are discussed in the Appendix. The two terms in eq 1 are comparable at the blend glass transition, since the first term is typically of order 1−2 in this temperature range, while the second term is typically in the range 0−1. At T_g + 10 K, the second term is roughly a factor of 4 smaller than the first term in eq 1, while it is a factor of 10 smaller at T_g + 40 K. Thus, for all temperatures within roughly 50 K of the blend glass transition, ignoring the role of concentration fluctuations can result in 10% (or more) error in the determined value of the mean of the logarithm of the segmental relaxation time of each blend component. Obviously, concentration fluctuations always play an important role in determining the *width* of the relaxation time distributions.

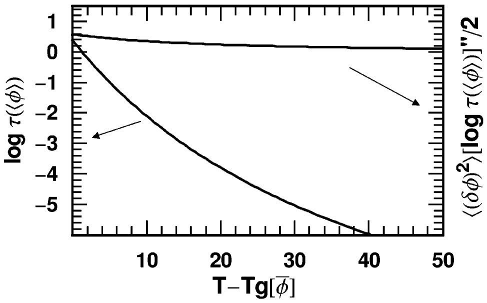

Figure 1. Plot of the first and the second terms of eq 1 as a function of $T - T_g$, where T_g is the blend glass transition temperature. Curves are plotted for the PI component in a PI/PVE blend with $\bar{\phi} = 0.5$ and $\phi_{self} = 0.45$.[15]

Note also that the derivative $[d^2 \log \tau/d\phi^2]_{\phi=\langle\phi\rangle}$ depends explicitly on the glass transition contrast between the two polymers. For the case where $\Delta T_g \equiv 0$ and all WLF parameters are matched, this term will be equal to zero everywhere. This result is in agreement with intuition since there will be no dynamic contrast in these situations.[26] In contrast, this derivative will become larger as we consider blends with larger values of ΔT_g, especially as one approaches the glass transition temperature of the blend.

For the sake of simplicity, in the rest of the paper we shall only consider the mean value of relaxation times and utilize the approximation

$$\langle \log \tau(\phi) \rangle = \log \tau(\langle \phi \rangle) \quad (3)$$

Ignoring concentration fluctuations is clearly an approximation in the range of interest to this work, namely in the proximity of the glass transition of the blend, but we shall discuss below that it does not qualitatively alter the conclusions we draw.

3. Obtaining ϕ_{self} and the Size of the Cooperative Volume

As noted above, we shall utilize experimental segmental relaxation times to generate the size of the

Table 1. Best Fit WLF Parameters and Monomer Level Length Scales[a]

component	b (Å)	l_p (Å)	T_g (K)	$\log(\tau_g)$	C_1	C_2 (K)	refs for the mean segmental time
PI	8.2	3.2	210	0.384	13.2	46.0	3, 4, 5, 21, 23, 27, 29, 30
PVE	14	2.8	273	−0.082	11.8	35.4	3 ,4, 21, 23, 27, 29
PVME	13	2.7	249	0.144	12.9	50.3	7
PS	18	3.9	379	1.030	13.3	50.0	7, 30
PIB	12.5	3.2	203	1.794	14.8	57.9	8, 31
hhPP	11	3.0	253	1.475	13.2	53.2	8

[a] Kuhn length and packing length from ref 28.

cooperative volume for each species in a miscible polymer blend. The specific aspects of our implementation are discussed below.

Obtaining Cooperative Sizes from Relaxation Time Data. The mean of the logarithm of the segmental relaxation time of a blend species can be converted to a mean self-composition, through the use of eqs 2 and 3, and an equation for the composition dependence of relaxation times. The relation between composition and relaxation times is provided by the WLF equation,[27] which assumes the following functional form for a blend with composition $\langle\phi\rangle$:

$$\log\left[\frac{\tau(\langle\phi\rangle)}{\tau_g}\right] = -\frac{c_1(\langle\phi\rangle)(T - T_g(\langle\phi\rangle))}{T - T_g(\langle\phi\rangle) + c_2(\langle\phi\rangle)} \qquad (4)$$

To complete this description requires that we specify the WLF parameters c_1, c_2, and τ_g and their composition dependence, but we defer this discussion to the next section. Inverting eq 4 allows for the determination of the average composition experienced by a test segment, $\langle\phi\rangle$, from its mean segmental relaxation time. The self-concentration within the cooperative volume, ϕ_{self}, is then evaluated using eq 2.

The ϕ_{self} value obtained in this manner is related to the size of a cooperative volume, r_c, through standard geometrical arguments. For cooperative sizes smaller than the Kuhn length of the chain, b, the volume occupied by chain segments at the center of the volume is $2(r_c/b)b^2l_p$. l_p is the packing length of the chain,[28] (b^2l_p) is the volume of a Kuhn segment, and the factor 2 accounts for the two walks which originate from the origin. Our definition of the volume of a Kuhn segment must be contrasted with the one utilized by Lodge and McLeish where $V = b^3$. The cooperative volume is $4\pi r_c^3/3$. From here we get

$$\phi_{self} = \frac{3bl_p}{2\pi r_c^2} \qquad r_c < b \qquad (5a)$$

When r_c becomes larger than b, it is clear that ϕ_{self} will actually be larger than that estimated following eq 5a. One can also estimate an upper bound for ϕ_{self} by calculating the number of Kuhn segments in two random walks of end-to-end distance r_c:

$$\phi_{self} = \frac{3l_p}{2\pi r_c} \qquad r_c > b \qquad (5b)$$

Equation 5b overestimates ϕ_{self} since it accounts for all walks which begin at the center of a cooperative volume and end on its surface: thus, walks with segments outside the cooperative volume are included. A more accurate value of ϕ_{self} can be obtained by calculating the mean first passage length of a Gaussian chain beginning at the origin of this cooperative volume, as we have discussed elsewhere.[16] In this paper we ignore this complication and use eq 5a to estimate r_c. The r_c values reported in this paper thus represent upper bounds to the real value of the size of the cooperative volume.

Obtaining the Pure Component and Mixture WLF Parameters. Previous efforts to obtain the three WLF parameters for a pure material, i.e., c_1, c_2, and τ_g, involve minimizing the quantity $\sum_i[\log \tau_i(\text{predicted}) - \log \tau_i(\text{experimental})]^2$. We utilize a slightly different method since we want to ensure that accurate values of T_g's are predicted by assuming the WLF model in conjunction with the best fit parameters and temperature-dependent relaxation times. To satisfy this goal, we used the WLF equation along with relaxation time information at each temperature and assumed values of c_1, c_2, and τ_g. This yields a predicted value of T_g at each temperature. The optimum values of the WLF parameters are obtained by minimizing $\sum_i[T_{g,i}(\text{predicted}) - T_g(\text{experimental})]^2$, where the summation is over the number of experimental temperatures at which relaxation time is available. $T_{g,i}$(predicted) is the predicted value of T_g using the relaxation times and the assumed values of the three WLF parameters, and T_g(experimental) is the experimental glass transition. While the quality of fits, as characterized by the value of the correlation coefficient (r^2) obtained by plotting $1/\log(\tau/\tau_g)$ vs $1/(T - T_g)$, are comparable in both fitting procedures, we find that the T_g values predicted by the temperature-dependent relaxation times and our results for the WLF parameters are much more accurate, ±3 K in our case versus ±7 K in the case of the traditionally determined WLF parameters. Table 1 reports our estimates of the WLF parameters as obtained from this analysis.

It is important to note that eq 4, in combination with eq 2, can yield negative self-concentrations if the WLF parameters are obtained by only employing data over a narrow range of temperature. We avoid this problem by using pure component relaxation time data over the broadest possible temperature range, sometimes by combining data from various sources, some of which are for materials with drastically different molecular weights, and hence glass transition temperatures. In these cases care has to be taken in evaluating the sum $\sum_i[T_{g,i}(\text{predicted}) - T_g(\text{experimental})]^2$, where the proper experimental T_g has to be used for each specimen.

A more careful examination of Table 1 shows that the τ_g vary by almost 2 orders of magnitude across the different pure polymers in question, a result that is not consistent with the notion that most materials have comparable dynamics at T_g. Since the reported values of T_g themselves have some uncertainty, we have performed a sensitivity analysis of our results in the case of one material, PVE. Specifically, we changed T_g from 273 to 266 K and reoptimized the WLF parameters. While the best fit value of $\log \tau_g$ now changes to

2.23, more in line with the other materials, and the c_1 and c_2 values change, our analysis of blend data as discussed below is not qualitatively affected by these changes.

For each blend we have assumed that c_1 and c_2 are either linear functions of composition or constants equal to their respective pure component values. The results obtained using both protocols were qualitatively similar, and hence we only report results for the case where c_1 and c_2 are treated as composition-dependent quantities. Recent experimental[32] work has suggested that the dynamics of infinite dilution blends are unusual in that the matrix determines the relaxation time of the dilute blend component. This result, which is supported by simulation evidence in some limits,[33] does not imply that self-concentration effects disappear at infinite dilution, but rather that segmental dynamics (as represented by the WLF parameters, c_1 and c_2) are strongly affected by blending. Such facts are ignored in the simple mixing laws that are assumed for the composition dependence of these WLF parameters in this work. There is also the issue that, for all the blends we shall discuss below, i.e., PI/PVE, PS/PVME, hhPP/PIB, and for the one tetrablock copolymer (SISI) the temperature ranges of interest will, in general, be below the T_g of the higher glass transition blend component but above the T_g of the blend. It is reasonable to ask whether WLF parameters, which are derived from information above the T_g of the pure material, can be employed in this range. This issue is addressed in the Discussion section.

4. Results

The mean segmental relaxation times are used to obtain the mean self-composition and the size of the cooperative volume for each constituent of three different blends and one disordered tetrablock copolymer. The system for which the most extensive segmental relaxation data exists, PI/PVE, is examined first. Next, we examine the disordered SISI tetrablock for which segmental relaxation times for both blocks exist. For all other blends, typically, there are only extensive segmental relaxation data for a single blend component. Thus, the conclusions drawn from these other systems are secondary to those from the PI/PVE blends and the SISI tetrablocks. Nevertheless, the data analyzed in composite support a unifying picture which we shall elucidate below.

PI/PVE Blends. The segmental dynamics of the *cis*-polyisoprene (PI)/poly(vinylethylene) (PVE) blend have been extensively studied with NMR and dielectric spectroscopy.[3-5,34] Further, segmental relaxation results from blends and disordered block copolymers are similar, suggesting that both sets of data can be viewed in the same framework.[34] This blend is miscible over a broad range of temperatures and concentrations and has a slightly negative Flory interaction parameter.[9] We use the protocol discussed above to determine the temperature dependence of the self-composition and cooperative size of PI (Figure 2) for a range of temperatures and compositions (25%, 50%, and 75% PI). In particular, we use the mean logarithmic relaxation time, in conjunction with eq 4, to obtain the effective glass transition temperature experienced by each type of species as a function of temperature. Note that we assumed that the WLF c_1 and c_2 parameters are linear functions of composition. The resulting T_g values are converted to an effective composition experienced by a segment through the use of the Fox equation, and this information further is converted to the mean self-composition using eq 2. Finally, the self-composition is converted to a size of cooperativity through the use of eq 5a.

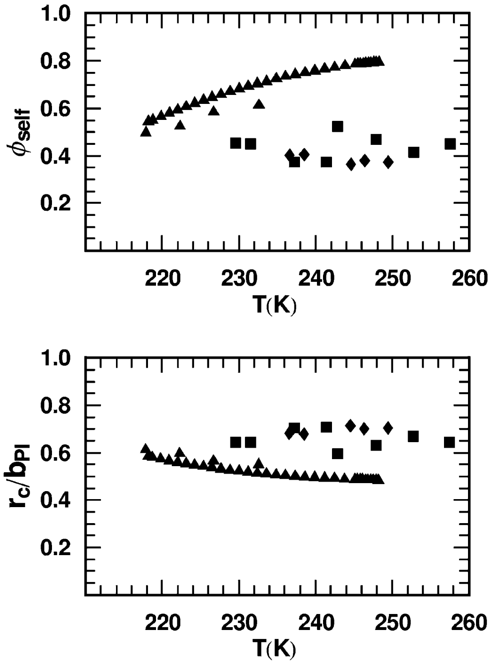

Figure 2. (a) Self-concentrations for the PI component in a PI/PVE blend as a function of temperature at a variety of compositions. (b) Corresponding plots of r_c derived following eq 5a. (◆) correspond to blends with a mean PI composition of $\bar{\phi} = 0.25$, (■) 0.5, and (▲) 0.75. Most of the data used in our analysis were obtained from NMR,[3,4] but for $\bar{\phi} = 0.75$ we have utilized both NMR and dielectric spectroscopy results.[5]

For this low-T_g blend component, the self-composition is practically independent of temperature and composition and is consistent with a cooperative size whose diameter is comparable to the Kuhn segment length of PI (see Table 1). This conclusion, and also the mean value of the self-composition ($\phi_{self} \approx 0.55$), are close to the predictions of Lodge and McLeish ($\phi_{self} = 0.45$).[15]

To further stress the fidelity with which the Lodge–McLeish model[15] describes the experimental results for the low-T_g component, we compare the mean segmental relaxation times, calculated following eq 3 (assuming that $\phi_{self} = 0.45$ independent of temperature and composition), with experimental data (Figure 3). It is clear from this figure that this mean-field approach quantitatively describes the mean relaxation time of the PI component in this blend over the relatively broad parameter space considered.

Examination of the corresponding predictions for the PVE component following eq 3 and assuming that the diameter of the cooperative volume is equal to the Kuhn segment are also shown in Figure 3. A significantly less satisfactory description of the experimental data is obtained, suggesting that the high-T_g component's behavior is quite different. This fact is emphasized by our calculation of the mean self-composition and corresponding estimates of the cooperative length for PVE, as shown in Figure 4. Unlike the low-T_g component, these plots show a strong dependence of ϕ_{self} and r_c on temperature. At high temperatures, above the glass transition temperature of the pure PVE, we find that the diameter of the cooperative volume is independent of temperature, in general agreement with the results

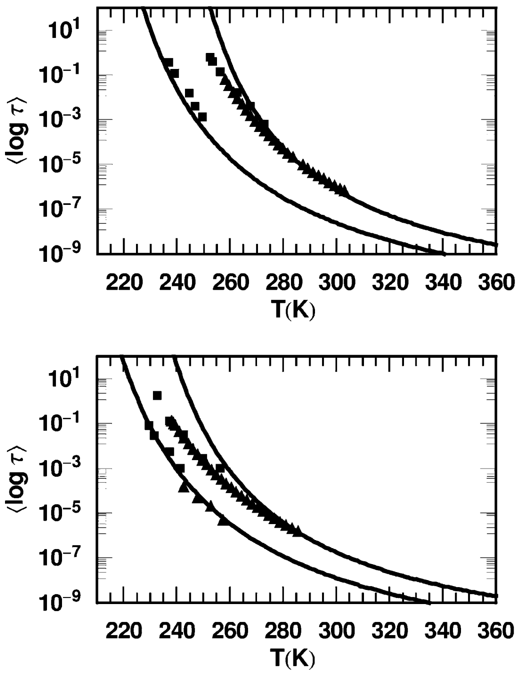

Figure 3. Plots of the mean segmental relaxation times for the PI and PVE components as a function of temperature. The symbols are experimental data as discussed below while lines are predictions of the Lodge−McLeish approach using ϕ_{self}(PI) = 0.45 and ϕ_{self}(PVE) = 0.25. The lower sets of points correspond to PI relaxation times data while upper sets of points are PVE data. (■) is from NMR,[3,4] and (▲) is from dielectric spectroscopy.[5] Part a is for a blend with 25% PI, and part b is for a blend with 50% PI.

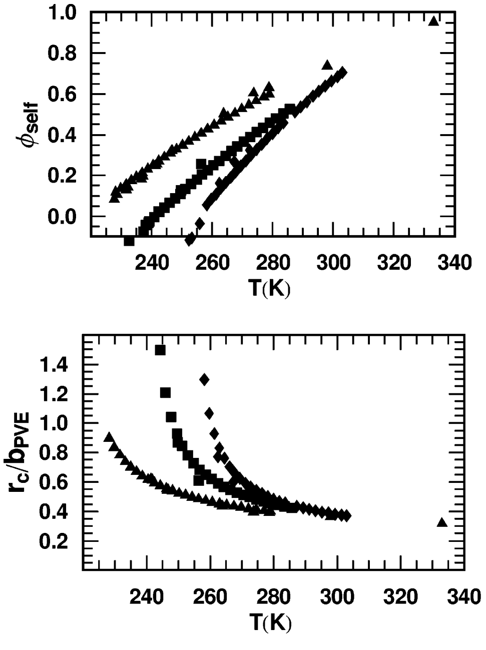

Figure 4. (a) Self-concentrations for the PVE component in PI/PVE blends as function of temperature at a variety of compositions. (b) Corresponding plots of r_c derived following eq 5a. (◆) correspond to blends with mean PI composition $\bar{\phi}$ = 0.25, (■) = 0.5, and (▲) = 0.75. The data were obtained from analysis of NMR[3,4] and dielectric spectroscopy[5] relaxation time data.

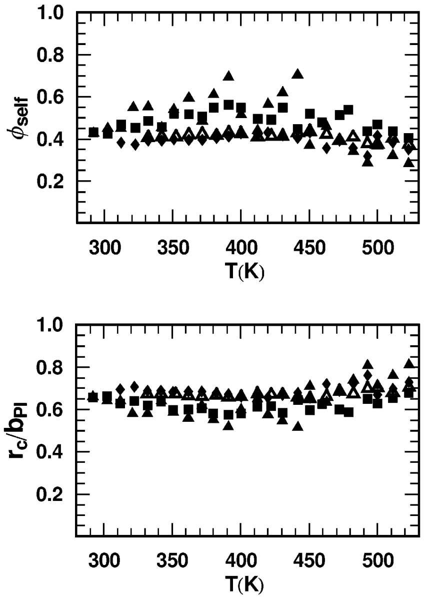

Figure 5. (a) Self-concentrations for the PI component in a SISI tetrablock as a function of temperature.[30,35] (b) Corresponding plots of r_c derived following eq 5a. The overall compositions are 23% (▲), 42% (■, 60% (◆), and 80% (△) styrene.

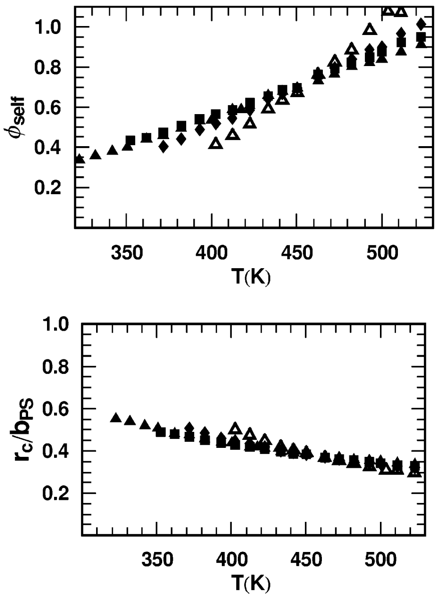

Figure 6. (a) Self-concentrations for the PS component in a SISI tetrablock as a function of temperature.[30,35] (b) Corresponding plots of r_c derived following eq 5a. The overall compositions are 23% (▲), 42% (■), 60% (◆), and 80% (△) styrene.

obtained from the PI dynamics. However, with decreasing temperature the self-concentration decreases toward *zero*, implying that the size of the cooperative volume increases strongly with decreasing temperature. Over this temperature range, r_c increases by a factor of 3, i.e., to about 1.5*b*. Here, it is no longer reasonable to use eq 5a to relate the self-concentration to r_c, and a more accurate approach would be based on the idea of the first passage of a Gaussian chain from the surface of a sphere.[16] This yields slightly different values for r_c, but the qualitative trends persist.

SISI Tetrablock Copolymers. SISI tetrablocks of degree of polymerization ∼120 with overall compositions of 23%, 42%, 60%, and 80% styrene are considered in Figures 5 and 6. In this case only the low-T_g component (isoprene) is dielectrically active,[35] and hence NMR has to be employed to determine the relaxation times of the two components.[30] We find over a very broad temperature range that the self-composition of PI is effectively

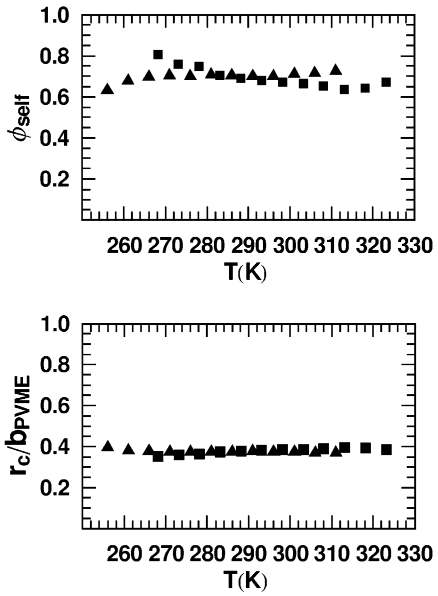

Figure 7. (a) Self-concentrations for the PVME component in a PVME/PS blend as a function of temperature at a variety of compositions. (b) Corresponding plots of r_c derived following eq 5a. (▲) and (■) correspond to blends with 70% and 50% PVME, respectively.[7]

constant. The r_c values are also relatively small, comparable to what was found for PI in the case of the PI/PVE blends. In contrast, the self-composition of the PS block decreases monotonically with decreasing temperature, leading to an increase in the r_c values in the same range. While we do not account for the connectivity of the blocks in this analysis as suggested by Ediger and co-workers,[30] it is clear that the results obtained are qualitatively consistent with the results from the PI/PVE blend.

PVME/PS Blends. Miscible blends of poly(vinyl methyl ether) (PVME) and polystyrene (PS) have a weakly negative Flory interaction parameter and display lower critical solution behavior at relatively high temperatures.[7] The glass transition temperatures for PVME and PS are 249 and 379 K, respectively.[27] The segmental dynamics of this system have only been studied through dielectric spectroscopy, and the dielectric response is dominated by the PVME. Hence, experimental segmental relaxation time data are exclusively for the PVME component. Figure 7 shows the temperature dependence of the self-composition and r_c of PVME using our inversion procedure. Consistent with the PI/PVE blends, this system conclusively shows that the low-T_g component has an essentially temperature independent self-concentration, i.e., $\phi_{self} \approx 0.75$. While this value of ϕ_{self} is not in agreement with the predictions of the Lodge−McLeish approach which suggests that $\phi_{self} \approx 0.25$,[15] nevertheless newer estimates by Lodge and Ediger are more consistent, i.e., $\phi_{self} \approx 0.8$.[36] In contrast, the diameter of the cooperative volume, $2r_c \approx 0.8b$, is in reasonable agreement with the Lodge−McLeish approach.

PIB/hhPP Blends. Next we consider a hydrocarbon blend system where only the high-T_g component is dielectrically active.[8] This is the blend hhPP/PIB where the T_g of the PIB is 203 K, while that of hhPP is 253 K. Data are available for two different compositions of hhPP/PIB blend, and in Figure 8 we plot the self-compositions of the hhPP component.[8] Again, the ϕ_{self} of the high-T_g component is temperature dependent, exactly as reported for the two systems examined above. Similarly, r_c increases with decreasing temperature.

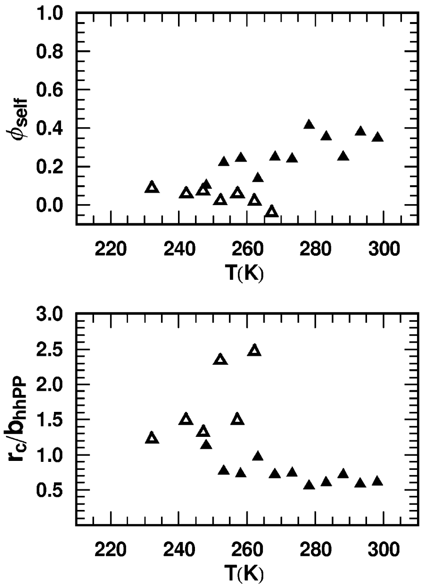

Figure 8. (a) Self-concentrations for the hhPP component in hhPP/PIB blends as a function of temperature. The overall compositions are 30% (▲) PIB-10K and 70% (△) PIB-410K. (b) Corresponding plots of r_c derived following eq 5a. The data were obtained from analysis of dielectric spectroscopy results.[8]

5. Discussion

Our results clearly imply that the self-composition of the high-T_g and the low-T_g blend components are quite different. For temperatures above the T_g of both pure components, it appears that the self-compositions of both constituents can be explained by cooperative sizes that are comparable to the Kuhn lengths of the chains in question. This conclusion bolsters the utility of the model of Lodge and McLeish at high temperatures.[15] Since concentration fluctuations play a minor role in determining the mean segmental relaxation times of the blend components at high temperatures, we conclude that chain connectivity effects will provide a good description of the mean segmental dynamics in this range. Concentration fluctuations, however, have to be introduced if the width of the relaxation time spectrum needs to be modeled. For lower temperatures, especially below the T_g of the pure high-T_g component, but above the blend T_g, the self-concentration of the high-T_g component is observed to decrease monotonically. In conjunction with the independent fact that concentration fluctuations become important at low temperatures, even for predicting mean properties, we suggest that system dynamics become complicated in this regime. Our conclusions on the behavior of the self-concentration (and hence the r_c) of the high-T_g component in this range are not in agreement with the Lodge−McLeish approach,[15] but rather point to the importance of other approaches such as that proposed earlier by Fischer and co-workers[13] and developed by us further.[14] It should be clear that our conclusions are based on a modeling approach that incorporates a variety of assumptions. Below we discuss these different assumptions and their consequences on our conclusions: however, we stress that relaxing these approximations will only cause quantitative changes to our predictions, without qualitatively altering our findings.

In the analysis of the relaxation times of the high-T_g component, we have assumed that the WLF parameters c_1, c_2, and τ_g are temperature-independent and are relevant to materials below their T_g. It is reasonable to question how applicable this approximation might be. We point to the work of Kornfield et al.,[4] who took an alternative route and fit the temperature-dependent segmental relaxation times of the two components of the PI/PVE blend to a standard WLF form where the c_1 and τ_g were assigned to the pure material values while the c_2 was a composition-dependent fit parameter. Blend T_g values were estimated by looking for a temperature where the mean segmental relaxation time assumed a prespecified value. For the PI component, the c_2 values in all of the blends considered were found to be roughly equal to their pure component values. However, for all three blends considered, the c_2 value for PVE is about 20 K larger than for the corresponding pure PVE value. This means that the PVE relaxation times in the blends have a much weaker temperature dependence than in the pure material. In this paper, we do not treat c_2 as a fit parameter since we hypothesize that it is a material specific constant as found in the case of the low-T_g component. Rather, we describe this weaker temperature dependence of the relaxation time of the high-T_g component by hypothesizing that its self-composition decreases with decreasing temperature. The resulting increase of cooperative volume then follows.

In our modeling to this point, we have assumed that the Kuhn length and the packing lengths were independent of temperature, while in fact these quantities do change weakly with temperature. A simple analysis of the definition of the packing length suggests that the product b^2l_p varies inversely with the density of the fluid.[28] While b^2l_p is expected to decrease with decreasing temperature and can indeed lead to a decreasing self-concentration, we do not believe this effect to be the primary cause of our results since the low-T_g component does not show any temperature dependence to its self-composition. Any change in packing or Kuhn length with temperature must affect both components in a similar manner.

While we have ignored concentration fluctuations by using eq 3 to obtain estimates of ϕ_{self} and r_c, we shall show here that the results derived are not qualitatively affected by this approximation. To understand the consequence of this approximation, consider eq 1, which includes the leading contribution from concentration fluctuations. In all cases this leading concentration fluctuation term will be positive. Thus, eq 3 should really be replaced by the inequality

$$\langle \log \tau(\phi) \rangle \geq \log \tau(\langle \phi \rangle) \tag{6}$$

This equation suggests that the “real” $\langle \phi \rangle$ encountered by a blend segment would actually be more enriched in the low-T_g component than that suggested by the application of eq 3. We illustrate our point with the PI/PVE system. Application of eq 6 for the PI component would suggest that $\phi_{\mathrm{self}} \geq 0.55$; i.e., the real self-composition would be richer in PI than that derived from eq 2. Similarly, the self-concentration of PVE would be even more depleted in PVE than in Figure 3. Thus, the real variation of the self-concentration of PVE with temperature should be even stronger than that represented in Figure 3. We conclude that ignoring concentration fluctuations does not yield qualitatively incorrect conclusions, but a quantitative reanalysis of this situation would require that concentration fluctuations are dealt with properly. This is an issue we are currently working on and will report in future work.

We now consider other experimental results that are consistent with our notion of a growing length scale of cooperative motion for the high-T_g component, especially below its glass transition temperature. Sy and Mijovic[37] conducted a seminal dielectric relaxation study of the segmental dynamics of the miscible PVDF/PMMA blend as a function of composition and temperature. These workers suggest that, well above the T_g of the two components, the cooperative size scales of the two components are small. As one approaches the T_g of the blend (i.e., below the T_g of pure PMMA), the cooperative length scale of the PMMA segments grows larger. In contrast, the cooperative size for the PVDF remains small. At the blend T_g, the system is globally vitrified. The segmental motions of the PMMA segments, which are associated with a large cooperative length scale, are exceedingly slow at the blend T_g. In contrast, PVDF segments continue to have a small cooperative length scale. The cooperative length scale associated with PVDF segments grows as temperature goes below the blend T_g and eventually diverges. It is clear that these workers suggest that the behaviors of the high-T_g and low-T_g blend components are very different, in line with our interpretation. However, these past workers do not offer any quantitative measure of r_c.

Previously, Lodge and McLeish[15] had suggested that the mean segmental relaxation times of the constituents of a polymer blend can be derived by using eq 3 with cooperative volume sizes equal to the Kuhn lengths of the chains. Our results strongly suggest that these conjectures are only valid at temperatures above the glass transition temperature of the high-T_g blend component. For lower temperatures, it is clear that eq 3 is no longer appropriate, since concentration fluctuations contribute significantly to the mean segmental times. Further, the cooperative length scale for the high-T_g component increases monotonically with decreasing temperature in a manner that is more in accord with the work of Donth,[22] utilized by Fischer and co-workers[13] and by us in our previous work.[14] Nevertheless, we stress the strong relevance of the Lodge−McLeish approach[15] since it provides a robust means of at least qualitatively predicting the segmental relaxation times of miscible polymer blends over a large range of parameter space.

Many ideas about the glass transition[20,22,23,38] invoke a temperature-dependent length scale for cooperative motion. These ideas expect the length scale to emerge below the temperature at which caging starts.[39−41] Our observation that the length scale only shows substantial temperature dependence for the high-T_g component is surprising. The fact that this temperature dependence appears to start at the T_g of the pure high-T_g component is potentially very important for our understanding of the glass transition. Clearly, more experimental data on miscible blends are needed to see whether this observation is universal.

Acknowledgment. We thank the National Science Foundation (DMR-9977928) for funding and Mark Ediger, M. Muthukumar, and Tim Lodge for many useful comments on this work.

Appendix

For cooperative sizes smaller than a Kuhn length, i.e., for $2r_c \leq b$, the variance of concentration fluctuations is easy to evaluate. This is because the self-concentration is determined exactly following eq 5a. In this case the variance of composition is

$$\langle(\delta\phi)^2\rangle = \left(\frac{\partial\phi}{\partial\phi_m}\right)^2 \langle(\delta\phi_m)^2\rangle = (1-\phi_{\mathrm{self}})^2\langle(\delta\phi_m)^2\rangle \qquad (A.1)$$

where ϕ_m is the intermolecular volume fraction, while ϕ is the net composition including both intra- and intermolecular contributions. Since the interpolymer distribution for small cooperative sizes is broad, it can be approximated as a uniform distribution, effectively independent of the blend composition. This is expected to breakdown in the limit where one considers infinitely dilute blends. The variance of intermolecular composition for a uniform distribution is $\langle(\delta\phi_m)^2\rangle = 1/12$. For this case eq A.1 simplifies to

$$\langle(\delta\phi)^2\rangle = \frac{(1-\phi_{\mathrm{self}})^2}{12} \qquad (A.2)$$

For the case where the relaxation time is described by the WLF model, the T_g is described by the Fox equation, and where c_1 and c_2 are linear functions of composition we can evaluate the second derivative of eq 4. The resulting expression is

$$\frac{\partial^2}{\partial\phi^2}\log\left[\frac{\tau(\phi)}{\tau_g}\right] = 2\delta C_1\left(\frac{(T-T_g(\phi))(\delta C_2 - T_g'(\phi))}{(T+C_2(\phi)-T_g(\phi))^2} + \frac{T_g'(\phi)}{T+C_2(\phi)-T_g(\phi)}\right) - C_1(\phi)\left(\frac{2(\delta C_2 - T_g'(\phi))T_g'(\phi)}{(T+C_2(\phi)-T_g(\phi))^2} + (T-T_g(\phi))\left(\frac{2(\delta C_2 - T_g'(\phi))^2}{(T+C_2(\phi)-T_g(\phi))^3}\right) - \frac{T_g''(\phi)}{T+C_2(\phi)-T_g(\phi)}\right) \qquad (A.3)$$

where $T_g'(\phi)$ and $T_g''(\phi)$ are the first and second derivatives of $T_g(\phi)$, $\delta C_1 = C_1^A - C_1^B$, and $\delta C_2 = C_2^A - C_2^B$. All of these quantities, i.e., $T_g'(\phi)$, $T_g''(\phi)$, $\delta C_1 = C_1^A - C_1^B$, and $\delta C_2 = C_2^A - C_2^B$ vanish if both components have matched WLF parameters. To calculate the derivative in eq A.3, we need to know the WLF parameters (listed in Table 1), the mean self-composition, and the blend composition.

References and Notes

(1) Prest, W. M.; Porter, R. S. *J. Polym. Sci., Part B: Polym. Phys.* **1972**, *10*, 1639.
(2) Colby, R. H. *Polymer* **1989**, *30*, 1275.
(3) Chung, G.-C.; Kornfield, J. A.; Smith, S. D. *Macromolecules* **1994**, *27*, 964.
(4) Chung, G.-C.; Kornfield, J. A.; Smith, S. D. *Macromolecules* **1994**, *27*, 5729.
(5) Alegria, A.; Colmenero, J.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1994**, *27*, 4486.
(6) Alvarez, F.; Alegria, A.; Colmenero, J. *Macromolecules* **1997**, *30*, 597.
(7) Pathak, J. A.; Colby, R. H.; Floudas, G.; Jerome, R. *Macromolecules* **1999**, *32*, 2553.
(8) Pathak, J. A. Miscible Polymer Blend Dynamics. Ph.D. Thesis, The Pennsylvania State University, University Park, PA, 2001.
(9) Tomlin, D. W.; Roland, C. M. *Macromolecules* **1992**, *25*, 2994.
(10) Roovers, J.; Toporowski, P. M. *Macromolecules* **1992**, *25*, 3454.
(11) Pathak, J. A.; Colby, R. H.; Kamath, S. Y.; Kumar, S. K.; Stadler, R. *Macromolecules* **1998**, *31*, 8988.
(12) Wagler, T.; Rinaldi, P. L.; Han, C. D.; Chun, H. *Macromolecules* **2000**, *33*, 1778.
(13) Zetsche, A.; Fischer, E. W. *Acta Polym.* **1994**, *45*, 168.
(14) Kumar, S. K.; Colby, R. H.; Anastasiadis, S. H.; Fytas, G. *J. Chem. Phys.* **1996**, *105*, 3777.
(15) Lodge, T. P.; McLeish, T. C. B. *Macromolecules* **2000**, *33*, 5278.
(16) Salaniwal, S.; Kant, R.; Colby, R. H.; Kumar, S. K. *Macromolecules* **2002**, *35*, 9211.
(17) Kamath, S.; Colby, R. H.; Kumar, S. K.; Karatasos, K.; Floudas, G.; Fytas, G.; Roovers, J. E. L. *J. Chem. Phys.* **1999**, *111*, 6121.
(18) Tracht, U.; Wilhelm, M.; Heuer, A.; Feng, H.; Schmidt-Rohr, K.; Spiess, H. W. *Phys. Rev. Lett.* **1998**, *81*, 2727.
(19) Arndt, M.; Stannarius, R.; Groothues, H.; Hempel, E.; Kremer, F. *Phys. Rev. Lett.* **1997**, *79*, 2077.
(20) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.
(21) Saxena, S.; Cizmeciyan, D.; Kornfield, J. A. *Solid State Nucl. Magn. Reson.* **1998**, *12*, 165.
(22) Donth, E. *Polym. Commun.* **1990**, *31*, 139.
(23) Colby, R. H. *Phys. Rev. E* **2000**, *61*, 1783.
(24) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(25) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *2*, 123.
(26) Gomez, D.; Alegria, A.; Arbe, A.; Colmenero, J. *Macromolecules* **2001**, *34*, 503.
(27) Mark, J. E., Ed.; *Physical Properties of Polymers Handbook*; AIP Press: Berlin, 1996.
(28) Fetters, L. J.; Lohse, D. J.; Graessley, W. W. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1023.
(29) Min, B.; Qiu, X.; Ediger, M. D.; Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* **2001**, *34*, 4466.
(30) He, Y.; Lutz, T. R.; Ediger, M. D.; Lodge, T. P. *Macromolecules* **2003**, *36*, 1724.
(31) Richter, D.; Arbe, A.; Colmenero, J. H.; Monkenbusch, M.; Farago, B.; Faust, R. *Macromolecules* **1998**, *31*, 1133.
(32) Adams, S.; Adolf, D. B. *Macromolecules* **1999**, *32*, 3136.
(33) Kamath, S. K.; Colby, R. H.; Kumar, S. K. *Phys. Rev. E* **2003**, *67*, 010801.
(34) Alig, I.; Kremer, F.; Fytas, G.; Roovers, J. *Macromolecules* **1992**, *25*, 5277.
(35) Doxastakis, M.; et al. *J. Chem. Phys.* **2002**, *116*, 4707.
(36) Ediger, M.; Lodge, T. P. Personal communication.
(37) Sy, J. W.; Mijovic, J. *Macromolecules* **2000**, *33*, 933.
(38) Donth, E.-J. *The Glass Transition: Relaxation Dynamics in Liquids and Disordered Materials*; Springer-Verlag: Berlin, 2001.
(39) Sastry, S. *Phys. Chem. Commun.* **2000**, *14*.
(40) Kamath, S.; Colby, R. H.; Kumar, S. K.; Baschnagel, J. *J. Chem. Phys.* **2002**, *116*, 865.
(41) Erwin, B. M.; Colby, R. H. *J. Non-Cryst. Solids* **2002**, *307–310*, 225.

MA0347215