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Evidence for dynamic heterogeneities in computer simulations of miscible polymer blends

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The controversial origins of the unusual dynamics of miscible polymer blends are incisively probed through computer simulations. The distribution of mobilities experienced by a probe monomer in a miscible blend of chains with disparate glass transition temperatures is found to be much broader than in the pure polymers, providing clear evidence for local concentration variations in the mixture. These concentration fluctutations yield distinctly different temperature dependences for the dynamics of the two different components, in a manner that closely mimics experiments.

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The dynamics of miscible polymer blends are unusual since, in many cases, the two components appear to maintain their own independent dynamic identities. Such behavior, termed ''thermorheological complexity,'' manifests itself in the anomalous broadening of the distribution of relaxation times of both blend components compared to the pure polymers, and in the breakdown of the empirical time-temperature superposition principle at both the segmental and chain levels [1–8]. The microscopic origins of these effects have been the subject of considerable debate in recent years [4,9–12]. One explanation for these phenomena is that the local environment in the blend is heterogeneous, with this effect being attributed to concentration fluctuations [2–5,10] and chain connectivity effects [2,3,9]. In contrast, others have argued that thermorheological complexity *only* reflects inherent differences in the local dynamics of the constituents [12].

Since the dynamics of miscible blends are of fundamental and practical relevance, it is important to resolve the molecular origins of these effects. To this end we have simulated a miscible blend comprised of materials with disparate glass transition temperatures in the framework of the bond-fluctuation model. For blends of chains of length $N=10$ we find that the dynamics of the two different components display different temperature dependences. In contrast, mixtures of chains with $N=2$ show that the two components have identical temperature dependences. We have also simulated the motion of nonselective small molecule probes in the $N=10$ systems to delineate the origins of these results. By considering the distribution of displacements in the blend and contrasting it to the corresponding behavior in the pure polymers, we show that the probe experiences a wide range of environments. These span motion as slow as the mean blend composition and as fast as regions strongly enriched in the fast polymer. These results, in conjunction, conclusively demonstrate that the origins of thermorheological complexity can be attributed to the presence of concentration variations in the blend, as has been conjectured by several groups [2–5,9,10].

In the bond fluctuation model each monomer occupies eight adjacent sites, which define a cube of side 1, on a simple cubic lattice [13]. Monomers along a chain are connected by bonds of variable length. Double occupancy of sites is prohibited and no bond crossing is allowed. The ground state is defined to be ''long'' bonds of length 3; all others are assigned an energy $\epsilon>0$. $T^*=k_BT/\epsilon$ is the reduced temperature, where k_B is the Boltzmann constant. Previous studies have demonstrated that this model can qualitatively capture the vitrification of polymers [13,14].

We have studied two chain lengths, $N=10$ and $N=2$. For the $N=10$ systems, we employ a 60^3 lattice, with periodic boundary conditions in all 3 directions. The overall lattice filling fraction is $\rho=8NM/L^3=0.8$, where $M=2160$ is the number of chains in the system and $N=10$ is the chain length. For the $N=2$ system, we employ a 10^3 lattice, with periodic boundary conditions in all 3 directions. The overall lattice filling fraction is $\rho=8NM/L^3=0.9$, where $M=3600$ is the number of dimers in the system. We model a 50/50 binary blend of two polymers where the two components have different bond stiffnesses, $\epsilon_A=1$, and $\epsilon_B=2$, respectively. Component A will thus have a lower T_g. The corresponding pure materials are also simulated. In another set of simulations we replace 10 chains in the $N=10$ system with 100 ''monomers'' to probe the motion of small molecules in these matrices while keeping the overall lattice filling fraction constant. Note that these small molecules only experience excluded volume interactions. Since the bond bending potential is the primary cause of vitrification of these models [13], a lattice of pure monomers would not possess a glass transition. Thus, these tracers are expected to be sensitive probes of the variation in local composition (and hence glass transitions) in polymer blends, without any interference from their own vitrification.

The systems were simulated using the standard metropolis Monte Carlo technique. Only local moves are employed to study system dynamics. Initially, the system was equilibrated at $T^*=\infty$. Starting configurations for lower temperatures were equilibrated configurations from the next highest temperature. To check for equilibrium, we have monitored the autocorrelation function of the end-to-end vector and the self-intermediate scattering function, both of which go to zero as $t \to \infty$, and the average mean square displacement of the center of mass, which is diffusive at long times. The system was considered to be in equilibrium if *all three criteria were simultaneously satisfied*. We have also considered

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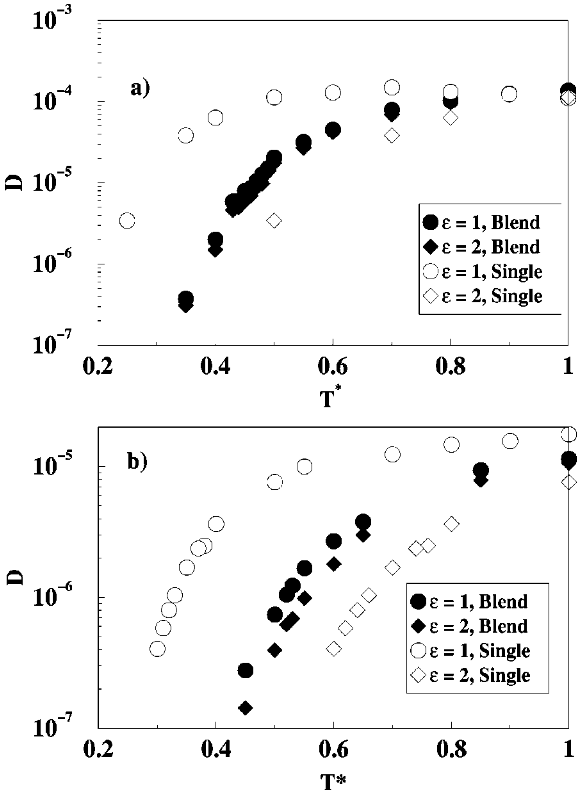

FIG. 1. Plot of the diffusion coefficients of the pure components and each component in a 50/50 blend. (a) $N=2$, (b) $N=10$.

the miscibility of these mixtures by calculating the chemical potential changes on mixing, using the chain increment method [15]. In agreement with previous work we find that $\chi\sim 0$, thus suggesting that the stiffness disparities are not large enough to induce immiscibility [16].

From the mean square displacement of the center-of-mass $\langle r^2\rangle$ for each component in the blend, the single component melt, and the tracers, we have calculated the diffusion coefficient of each component as $D=\lim_{t\to\infty}(\langle r^2\rangle/6t)$, where t is the Monte Carlo time. We first consider the systems without any tracer particles. Figure 1 demonstrates that the diffusivity data from both the pure materials and the blend show a significant slowing down with decreasing temperature, both for $N=10$ and $N=2$. Each set can be adequately fit by either the scaling form $(D\sim[T-T_c]^{-x})$ or the Vogel form $(D\sim\exp[A/(T-T_0)])$. We find, as expected, that pure chains of type B have a Vogel temperature that is twice that of pure A chains [i.e., $T_0^B=2T_0^A=0.40\pm 0.02$]. We now consider the 50/50 blends of $N=10$ [Fig. 1(b)]. The D of the two components have different temperature dependences. The Vogel temperatures of the two blend components are $T_0^A=0.30$, $T_0^B=0.34$, quantifying this fact. Qualitatively similar results are found for two other compositions studied, i.e., 25/75 and 75/25. Thus, this blend demonstrates the normal signatures of thermorheological complexity, in a manner that mimics experiment. We have also considered mixtures of dimers $[N=2]$ with the same bond length potentials. Figure 1(a) suggests that, in contrast to the longer chains, the dynamics of the dimers have identical temperature dependences in the blend, i.e., thermorheological simplicity. These results unequivocally prove that thermorheological behavior is more than a difference in the local dynamics of the two materials.

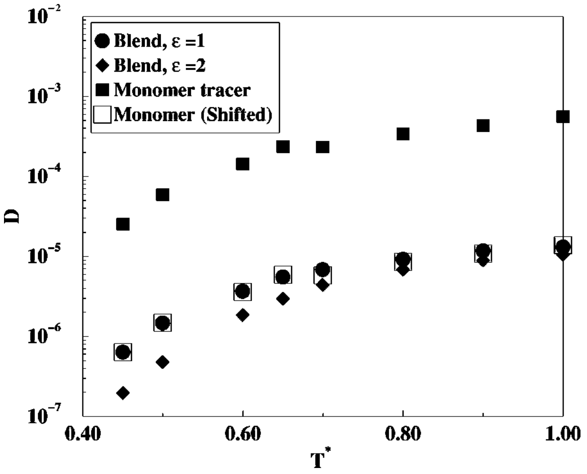

FIG. 2. Plot of the diffusion coefficients of the probe monomer and of each component in a 50/50 blend with $N=10$. The data for the monomer tracer are also divided by 40 (open squares) to compare with the flexible component data.

Thermodynamics suggests that $\langle(\Delta\phi)^2\rangle\sim S(0)$, where $S(0)$ is the zero wave vector limit of the scattering function, and $\langle(\Delta\phi)^2\rangle$ is the width of the distribution of concentration fluctuations. For a system with $\chi=0$ and $N=2$, the random phase approximation yields $S(0)=0.5$, while for $N=10$, $S(0)=2.5$. This argument suggests that the longer chain system, which shows a breakdown of time-temperature superposition, samples a much wider range of concentrations than the dimer blend. To conclusively establish that local concentration variations are the cause of disparate dynamics, we now consider the diffusion of $N=1$ tracer molecules in the 50/50 $N=10$ blend. Figure 2 shows a plot of the D values of the two blend components and also of the monomer tracer. When we divide the tracer diffusion data by 40, we find that its temperature dependence tracks that of the flexible component in the blend. This temperature dependence is distinctly different from that of the slower component. These results, therefore, suggest that the diffusion coefficient of the tracer is determined by environments that are dominated by the faster blend component.

Since diffusivity data are dominated by the fastest moving monomers, such data do not provide adequate information on the distribution of environments that a tracer particle experiences. To probe this issue further we focus on the distribution of displacements of the probe monomer in the blend as well as the single component systems. In the temperature range $0.5\leq T^*\leq 2$, the diffusion coefficient in the blend is smaller than that in the single component [low T_g] system. A comparison makes the most sense where the diffusion coefficient of the probe monomer is the same in both systems. For this reason, we compare the distribution of tracer displacements in the pure low T_g polymer at a temperature which is lower than the blend by a factor of 0.625. The mobility of each tracer monomer was tracked at these different temperatures for the blend and pure polymer as a function of time, and

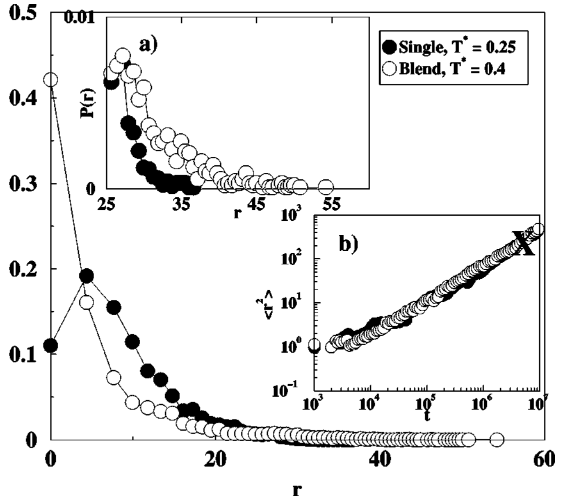

FIG. 3. Plot of the distribution of tracer displacements for both the blend and the single component melt at the point where the mean square displacement of the tracers are identical in both systems. The data correspond to a time-step of 5×10^6 Monte Carlo units and $\langle r^2\rangle=218$, indicated by the large “X” in inset (b). Inset (a) shows an expanded view of both distributions for displacements greater than 25. Inset (b) shows a plot of the mean square displacements of the tracers for both systems.

their distributions are compared at identical times, i.e., where their mean square center-of-mass displacements are identical [see inset (b) of Fig. 3]. In Fig. 3 we plot the quantity $P(r)\equiv4\pi r^2W(r)$,where $W(r)$ is the probability that a monomer has moved exactly r in the time t. Inset (a) in Fig. 3 is an expanded view of both distributions at displacements greater than 25 lattice units. It is clear that the distribution of displacements in the blend is much broader than that in the pure material. This suggests that the tracer in the blend experiences a broad range of dynamic environments. Since the diffusivity data suggest that the largest particle displacements have a temperature dependence analogous to the faster blend component, we conclude that the high displacement end of the tracer distribution corresponds to regions rich in the flexible component. To bolster this statement, we have tracked the local environment (i.e., the immediate six neighbors) around a probe monomer and averaged this quantity over the whole dynamic run. We find that monomers with lower mobilities $[\langle r^2\rangle\leqslant10]$, on average, experience a composition that is identical to the mean blend composition, while monomers with $\langle r^2\rangle\geqslant40$ (the high displacement end of the distribution) have a local environment that is richer in the flexible component $[\phi_{flex}\sim0.75]$. Thus, we have clear evidence that the local environment in the blend is heterogeneous, with composition spanning from regions close to the average blend composition to regions rich in the faster component.

A final point is to understand the difference in behavior of the $N=10$ blend, which appears thermorheologically complex, and the $N=2$ blend which is thermorheologically simple. Above we have suggested that the random-phase approximation model anticipates that the longer chain blend experiences larger concentration variations than the $N=2$ blend. To substantiate this prediction we examine the quantity $2\Delta g(r)=g_{AA}(r)+g_{BB}(r)-2g_{AB}(r)$, where $g_{xy}(r)$ is the *intermolecular* pair distribution function for monomers x and y. $\Delta g(r)$ would identically equal 0 for all r in systems where both components are randomly mixed, and hence any deviations from 0 are a measure of nonrandom packing (“concentration variations”). Figure 4 plots this quantity for both the $N=10$ and $N=2$ blends. It is immediately clear that the longer chain length blend has larger values of $\Delta g(r)$ suggesting that concentration variations are larger in this case. In addition to this intermolecular effect, past work has also suggested intrachain connectivity effects also become more important with increasing N. Thus, while we cannot resolve whether intermolecular or chain connectivity effects are more important in this context, the evidence here is conclusive that the blends with larger concentration variations show larger departure from thermorheologically simple behavior.

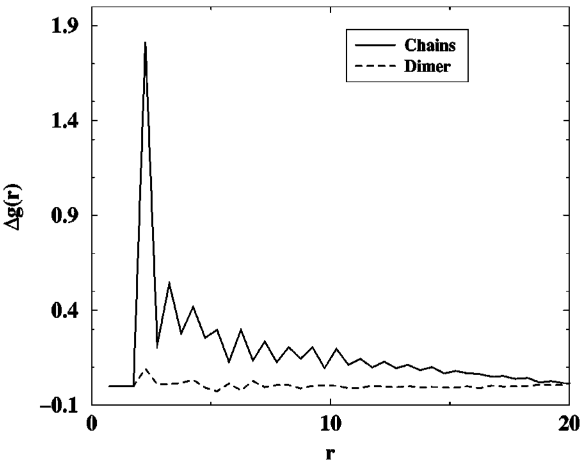

FIG. 4. Intermolecular $\Delta g(r)$ defined by the equation $2\Delta g(r)=g_{AA}(r)+g_{BB}(r)-2g_{AB}(r)$ for the $N=10$ blend system and the dimer system with 50/50 composition at $T^*=0.5$.

In summary, we have provided several lines of evidence which, in combination, unequivocally illustrate that local concentration variations are the source of thermorheological complexity in miscible polymer blends. Figure 1 shows that the $N=2$ and $N=10$ systems have similar inherent mobility differences between A and B, yet thermorheological complexity is only observed for the $N=10$ system. Thus, thermorheological complexity is not merely a reflection of the inherent differences in the local dynamics of the two components. We show that the measurement of probe diffusion provides complementary information to currently available diffusivity measurements on the two blend components. The temperature dependence of the D of small molecule probes should track that of the fast component in the blend, but its distribution of mobilities, if measurable, should provide a direct measure of the dynamical heterogeneities in the blend. Such data are currently unavailable, although we are aware of at least one group which is pursuing these measurements [17].

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[1] R.H. Colby, Polymer **30**, 1275 (1989).
[2] G.C. Chung, J.A. Kornfield, and S.D. Smith, Macromolecules **27**, 964 (1994); **27**, 5729 (1994).
[3] S. Saxena, D. Cizmeciyan, and J.A. Kornfield, Solid State Nucl. Magn. Reson. **12**, 165 (1998).
[4] A. Zetsche and E.W. Fischer, Acta Polym. **45**, 168 (1994).
[5] G. Katana, E.W. Fischer, T. Hack, V. Abetz, and F. Kremer, Macromolecules **28**, 2714 (1995).
[6] J.A. Zawada, *et al.*, Macromolecules **25**, 2896 (1992); **27**, 6851 (1994).
[7] J.A. Pathak, *et al.*, Macromolecules **31**, 8988 (1998); **32**, 2553 (1999).
[8] F. Alvarez, A. Alegria, and J. Colmenero, Macromolecules **30**, 597 (1997).
[9] T.P. Lodge and T.C.B. McLeish, Macromolecules **33**, 5278 (2000).
[10] S.K. Kumar, R.H. Colby, S.H. Anastasiadis, and G. Fytas, J. Chem. Phys. **105**, 3777 (1996).
[11] S. Kamath, R.H. Colby, S.K. Kumar, K. Karatasos, G. Floudas, G. Fytas, and J.E.L. Roovers, J. Chem. Phys. **111**, 6121 (1999).
[12] S. Hoffman, L. Willner, D. Richter, A. Arbe, J. Colmenero, and B. Farago, Phys. Rev. Lett. **85**, 772 (2000).
[13] M. Wolfgardt, J. Baschnagel, W. Paul, and K. Binder, Phys. Rev. E **54**, 1535 (1996).
[14] S. Kamath, R.H. Colby, S.K. Kumar, and J. Baschnagel, J. Chem. Phys. **116**, 865 (2002).
[15] S.K. Kumar, I. Szleifer, and A.Z. Panagiotopoulos, Phys. Rev. Lett. **66**, 2935 (1991).
[16] M. Muller, Macromolecules **28**, 6556 (1995).
[17] A. Jones (private communication).