Macromolecules 2019, 52, 7762–7778

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Dynamics and Viscoelasticity of Disordered Melts of Symmetric **Diblock Copolymers**

Taher Ghasimakbari † and David C. Morse $^{*,\ddagger_{\square}}$

[†]Department of Physics and [‡]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, United States

ABSTRACT: Simulations of coarse-grained models are used to study relationships among chain motion, composition fluctuations, and stress relaxation in unentangled melts of symmetric diblock copolymers. Measurements of the dynamic structure factor S(q,t) are reported as a function of wavenumber q, time t, and χN , where χ is the Flory-Huggins interaction parameter and N is degree of polymerization. The function S(q,t) is found to be a nearly exponential function of time, $S(q,t) \propto e^{-t/\tau(q)}$, for wavenumbers similar to or less than the wavenumber q^* at which the static structure factor $S(q) \equiv S(q,t=0)$ is maximum. The relationship between the decay time $\tau(q)$ and S(q) is used



to define an effective wavenumber-dependent diffusivity D(q) for fluctuations of wavenumber q. The function D(q) is shown to change very little with changes in χN and to be a monotonically decreasing function of the nondimensional wavenumber qR_{er} where R_{o} is polymer radius of gyration. The linear shear stress relaxation modulus G(t) is inferred from measurements of the shear stress autocorrelation function. At low values of χN , far from the order-disorder transition (ODT), the modulus G(t)agrees with predictions of the Rouse model. Near the ODT, G(t) develops an additional slowly decaying feature arising from slow decay of composition fluctuations with $q \sim q^*$. The behavior of G(t) near the ODT is predicted nearly quantitatively by a modified version of the model of Fredrickson and Larson (FL), in which the prediction of the FL theory for the slowly decaying component is added to the prediction of the Rouse theory for contributions arising from single-chain relaxation, using the independently measured behavior of S(q,t) as an input to the theory.

1. INTRODUCTION

In a disordered diblock copolymer melt near its orderdisorder transition (ODT), results of rheological and dynamic scattering experiments reflect the presence of large, slowly evolving composition fluctuations.¹ This paper presents an analysis of dynamical properties and viscoelastic properties measured in molecular dynamics simulations of unentangled symmetric diblock copolymer melts. The degree of repulsion between the two blocks of the copolymer is controlled by the quantity χN , where χ is the Flory-Huggins interaction parameter and N is degree of polymerization. At sufficiently low values of χN , dynamical and rheological properties of such a melt are found to be adequately described by the Rouse model. As χN approaches the value $(\chi N)_{ODT}$ at the ODT, however, chain motion and stress relaxation are both affected by the appearance of long-lived composition fluctuations. The relaxation of composition fluctuations can be characterized most directly by measuring the dynamic structure factor S(q,t). This paper presents and analyzes simulation results for singlechain dynamical properties, the dynamic structure factor S(q,t), and the linear shear stress relaxation modulus G(t) in disordered diblock copolymer melts over a range of values of χN.

2. BACKGROUND

The dynamical behavior of block copolymer melts can be probed by measuring tracer diffusion, dynamics of composition fluctuations, and linear viscoelastic properties. All of these properties have measured extensively in experiments and somewhat less extensively in simulations.

Tracer Diffusion. Self-diffusion coefficients of polymers within diblock copolymer melts and solutions have been measured by several techniques, including forward recoil spectroscopy,² forced Rayleigh scattering³⁻⁷ and pulsed field gradient nuclear magnetic resonance spectrometry.⁸⁻¹²

Tracer diffusion experiments on unentangled diblock copolymers⁴ have shown that composition fluctuations do not drastically reduce the diffusivity in the disordered phase, even near the ODT. Experiments on highly entangled polymers^{4,5} showed a more significant decrease in diffusivity in the disordered phase near the ODT, as well as in the lamellar phase, where diffusion becomes anisotropic. Interestingly, experiments on both unentangled and entangled polymers have shown little or no change in tracer diffusivity

Received: June 21, 2019 Revised: September 13, 2019 Published: October 8, 2019

of symmetric diblock copolymers upon transformation from a disordered phase to a polycrystalline lamellar phase. $^{2-6}$

A theoretical model of chain diffusion in ordered and disordered block copolymers near the ODT was developed in several papers by Fredrickson and co-workers. Fredrickson and Milner¹³ developed a theory of chain diffusion in a weakly ordered lamellar phase. Barrat and Fredrickson¹⁴ used a combination of single-chain simulations and analytic methods to analyze the dependence of the diffusivity D_{\perp} along the direction perpendicular to the layers for unentangled polymers in more strongly segregated lamellar phases. These authors concluded that the decrease in D_{\perp} should remain modest (less than about a factor of 2) near the ODT and become more severe only deeper in the ordered phase. Leibig and Fredrickson developed a theory of chain diffusion in the disordered phase near the ODT¹⁵ that was shown to be in qualitative agreement with experiments.^{5,15}

Dynamics of Composition Fluctuations. The dynamic structure factor S(q,t) in diblock copolymer melts and solutions has been measured by photon correlation spectroscopy (PCS) using both optical dynamic light scattering (DLS)^{16–24} and, more recently, using small-angle X-ray PCS.²⁵

Most optical DLS experiments on diblock copolymer melts and solutions have measured S(q,t) only at low values of wavenumber q, less than inverse polymer coil size. DLS experiments by several groups^{16–23} showed evidence of both a nondiffusive mode, for which the decay rate $\Gamma(q)$ remains nonzero as wavenumber q approaches zero, and a diffusive mode, for which $\Gamma(q) \propto q^2$. The nondiffusive mode was well anticipated by theories of idealized monodisperse block copolymers. Because it arises from relative motion of A and B blocks, this mode is sometimes termed an "internal" or "breathing" mode. The diffusive mode was initially unexpected but was shown to arise from relative diffusion of fractions of different molecular weight in a slightly polydisperse melt.^{20,26} Simulations of strictly monodisperse polymers, such as those presented here, are expected to exhibit only the internal mode.

One set of DLS experiments on solutions containing an extremely high-molecular-weight, highly entangled copolymer²⁴ have managed to move the wavenumber q^* at which the static structure factor is maximum into the experimentally accessible range. These experiments were able to demonstrate that near the ODT, the decay rate $\Gamma(q)$ has a minimum at a wavenumber q very near q^* .

X-ray PCS experiments can measure S(q,t) at wavenumbers of order the inverse coil size in diblock copolymer melts involving chains of more modest length. Comparison of X-ray PCS and rheology measurements on a melt of highly asymmetric sphere-forming diblock copolymers²⁵ led to the somewhat surprising conclusion that the characteristic relaxation time for G(t) in this system is 1–2 orders of magnitude less than the longest relaxation time for S(q,t) in PCS experiments.

The dynamical random phase approximation (RPA) provides the best available theoretical framework for predicting the behavior of S(q,t) in either homopolymer solutions or diblock copolymer solutions and melts.^{27–29} The dynamic RPA formalism can be applied either to unentangled polymers, by using a Rouse model to describe the motion of individual chains, or for entangled polymers, by instead using a tube model. In either case, the dynamic RPA allows relatively straighforward derivation of predictions for the temporal Laplace transform of S(q,t). It also provides relatively simple

predictions for a few properties that can be easily evaluated in the Laplace domain, including the initial rate of decay of the ratio S(q,t)/S(q, 0) and the mean decay time. Evaluation of predictions for S(q,t) in the time domain is generally more complicated. Detailed predictions for S(q,t) in the time domain have nonetheless been worked out for homopolymer solutions using a Rouse–Zimm formalism. Predictions for S(q,t) have also been worked out for highly entangled solutions of diblock copolymers by Semenov to allow comparison of theory to the experiments reported in ref 24. We are not aware of any published computations of the full time dependence of S(q,t)for unentangled diblock copolymer melts, the case of immediate interest here.

Linear Viscoelasticity. Rheological measurements are the most common experimental probe of dynamical phenomena in block copolymer liquids. Measurements of linear viscoelasticity are useful, in part, as a way of identifying phase transitions. It was first demonstrated by Gouinlock and Porter and Chung^{30–32} that studies of the temperature dependence of the storage and loss moduli $G'(\omega)$ and $G''(\omega)$ can be used to identify order–disorder and order–order transitions in diblock copolymers.

Composition fluctuations in the disordered phase also generate a distinctive signature in the linear viscoelastic moduli near the ODT. The first experimental evidence of this rheological signature of fluctuations within the disordered phase was reported by Bates and co-workers,^{33–35} who observed the appearance of a low-frequency shoulder in the storage modulus of several well-entangled polymer melts. Neutron scattering experiments on the same set of sample confirmed the presence of strong composition fluctuations.^{33,36,37}

Fredrickson and Larson³⁸ formulated a theory to explain the relationship between the long-lived composition fluctuations in the melt near the ODT and the appearance of the secondary shoulder in the storage modulus. Their predictions for the stress relaxation function produces a low-frequency feature in the complex shear stress modulus, in qualitative agreement with observations. The work presented here provides a more quantitative test of the Fredrickson–Larson theory.

Simulation Studies. Relatively few computational studies of disordered diblock copolymers have focused on characterizing dynamical or rheological behavior. Of those that have reported dynamical measurements, most have focused on tracer diffusion, which is relatively easy to measure. Some of the earliest simulation studies of the dynamics of diblock copolymers were lattice Monte Carlo simulations by the Binder group, some of which characterized chain diffusion.³⁵ Fried and Binder also reported measurements of the dynamic structure factor S(q,t) and used the appearance of a dramatic slowdown of the relaxation time as a signature indicating near approach to the ODT.^{41,42} Pakula et al. used a cooperative motion algorithm in their Monte Carlo simulation to measure the center of mass diffusion, bond relaxation, and chain end-toend autocorrelation time.43 Murat et al. used molecular dynamics simulations to study chain diffusion in both the disordered and ordered phases of diblock copolymers.⁴⁴

3. SIMULATION METHODOLOGY

The simulations presented here are molecular dynamics simulations of a simple coarse-grained model of a melt of symmetric diblock copolymers. The model consider here is identical with one used in several previous studies of

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equilibrium properties, which is referred to in this earlier work as model S^{45,46} or model S1.^{47,48} The systems studied here are all melts of symmetric AB copolymers with either N = 16 or N = 32 beads per chain, with equal numbers of A and B beads. All pairs of beads with monomer types *i* and *j* (which can each denote A or B) interact via a nonbonded pair potential $V_{ij}(r)$ of the form originally introduced in dissipative particle dynamics simulations, for which

$$V_{ij}(r) = \frac{1}{2} \epsilon_{ij} \left(1 - \frac{r}{\sigma} \right)^2 \tag{1}$$

for $r < \sigma$ and $V_{ij}(r) = 0$ for $r > \sigma$, where r is inter-particle distance, σ is the range of interaction and ϵ_{ij} is a parameter with units of energy. All simulations use $\epsilon_{AA} = \epsilon_{BB} = 25k_BT$ and variable values of a parameter $\alpha = (\epsilon_{AB} - \epsilon_{AA})/k_BT$. Here and hereafter, k_B is Boltzmann's constant and T is absolute temperature. Consecutive beads in the same chain also interact via a harmonic bond potential

$$V_{\text{bond}}(r) = \frac{1}{2}\kappa r^2 \tag{2}$$

with $\kappa = 3.406 k_{\rm B} T / \sigma^2$.

The simulations presented here are all NVT molecular dynamics (MD) simulations in a cubic unit cell with periodic boundary conditions. Results of NVT simulations for the static structure factor S(q) have been reported previously for this model in refs 45 and 46, whereas subsequent work that focused on order-disorder transitions^{47,48} used constant pressure (NPT) simulations. All simulations reported here were performed using a Nosé-Hoover thermostat and a time step of $\Delta t = 0.005$ in natural simulation units in which bead mass, thermal energy $k_{\rm B}T$, and σ are all set to 1.

The size of the simulation unit cell and the number of chains in the system were chosen so as give a concentration of $c = 3\sigma^{-3}$ beads per unit volume in all simulations. The length *L* of each edge of the cubic unit cell was selected such that $L \approx 10R_{\rm g0}$, where $R_{\rm g0} = \sqrt{Nb/6}$ is the random-walk radius of gyration of homopolymer chains, with $\alpha = 0.0$. Simulations of chains with 16 beads contained 2007 chains in a box of length $L = 22.04\sigma$, while simulations of chains with 32 beads contained 2839 chains in a box of length $L = 31.17\sigma$. Values of $\overline{N} = N(cb^3)^2$ are $\overline{N} = 239$ for N = 16 and $\overline{N} = 478$ for N = 32.

Simulations for each system are performed over a range of values of α ranging from $\alpha = 0$ up to the value at the orderdisorder transition (ODT). Values of an effective Flory-Huggins parameter are calculated for each value of α using the calibration that was developed for NVT simulations of model S1 in ref 46. Hereafter, we use the symbol χ_e to denote estimates of the interaction parameter for our simulation model that have been computed by this method. The value of α at the ODT was accurately identified for each chain length by applying the well-tempered metadynamics algorithm described in previous work by our group,^{47,48} which is applied here to NVT simulations rather than the NPT simulations used in our previous study of phase transitions. SCFT predicts that symmetric diblock copolymers should undergo a secondorder phase transition at a critical value of $\chi N = 10.495$. For the two systems studied here, we find that the ODT occurs at α = 4.69 or $\chi_e N$ = 21.72 for chains of N = 16 beads and at α = 2.11 or $\chi_e N = 18.45$ for N = 32.

4. SINGLE-CHAIN DYNAMICS

We characterize the dynamics of individual polymers within a disordered melt by measuring the mean-squared displacement of a bead near the middle of the chain and the autocorrelation function of the vector that connects the first and last bead in the chain.

Mean-Squared Displacement and Diffusivity. We measure the mean-squared displacement g(t) of one of two beads that are nearest the center of a symmetric diblock copolymer, i.e., the first bead of the *B* block, which is bonded to the last bead of the *A* block. Let g(t) denote the function

$$g(t) = \langle |\mathbf{R}(t) - \mathbf{R}(0)|^2 \rangle$$
(3)

in which $\mathbf{R}(t)$ denotes the position of this center bead. For large values of t, much greater than the longest internal relaxation time, the motion becomes diffusive and is given by a linear function

$$g(t) = 6Dt \tag{4}$$

in which *D* is the tracer diffusion coefficient of the molecule. Figure 1 shows the mean-square displacement g(t) for chains of length N = 16 over a range of values of α or $\chi_e N$. Both axes



Figure 1. Mean-squared displacement g(t) of a middle bead plotted versus time for chains of N = 16 beads, for several values of α or $\chi_e N$. Both time and mean-squared displacement are measured in reduced units in which σ , $k_B T$, and bead mass *m* are equal to unity. The ODT for this system occurs at $(\chi_e N)_{ODT} = 21.72$.

are plotted by using reduced units in which σ , $k_{\rm B}T$, and bead mass *m* are set to unity, giving a time unit $\tau_0 = \sigma/\sqrt{k_{\rm B}T/m} = 1$. Values of $\chi_{\rm e}N$ range from $\chi_{\rm e}N = 0$ up values very close to the ODT. The long time behavior of g(t) becomes linear at sufficiently long times even near the ODT. The diffusion coefficient *D* each system of interest has been extracted by fitting the late time behavior to a linear function of time.

The Rouse model predicts that the chain diffusion coefficient in a homopolymer melt should vary with degree of polymerization N as

$$D = \frac{k_{\rm B}T}{N\zeta} \tag{5}$$

where ζ is a bead friction coefficient. This prediction is consistent with our results for the homopolymer state obtained by setting $\alpha = \chi_e N = 0$. Analysis of the long time behavior of g(t) at $\alpha = 0$ yields diffusion coefficients of D = 0.0248 for N =16 and D = 0.0125 for N = 32 in Lennard-Jones units, corresponding to nearly equal values $\zeta = 2.52$ for N = 16 and ζ = 2.50 for N = 32 for the bead friction coefficient. Figure 2 shows how D varies with $\chi_e N$ for both chain lengths. In this plot, we show the ratio D/D_0 of D to its value



Figure 2. Tracer diffusivity *D* normalized by the value D_0 in a homopolymer melt plotted versus $\chi_e N$ for disordered melts of symmetric diblock copolymers of lengths N = 16 (circles) and N = 32 (squares).

in a homopolymer melt. We denote the homopolymer value by $D_0 = D(\chi_e N = 0)$. The dependence of the ratio D/D_0 on $\chi_e N$ is very similar for both chain lengths, but D/D_0 reaches a lower value at the ODT for the model with shorter chains (N = 16), for which $\chi_e N$ reaches a larger value at the ODT. In both cases D/D_0 decreases to a value of $D/D_0 \sim 0.6$ near the ODT.

Figure 2 shows that D/D_0 remains near unity while $\chi_e N$ remains less than the critical value of $\chi_e N = 10.5$ predicted by SCFT and that most of the decrease occurs at greater values of $\chi_e N$. It is known that the disordered phase develops increasing strongly segregated but disordered A and B domains over the range of values of $\chi_e N$ between the SCFT prediction and the true ODT. The observation that only a modest decrease in D $(\sim 40\%)$ occurs over this range does not necessarily imply that the chains can diffuse freely even near the ODT. In a state with sufficiently strongly segregated A and B domains, we expect the junction between A and B blocks in each block copolymer to become constrained to remain near interfaces between A and B domains. In the absence of entanglements, which do not occur in the soft-sphere model simulated here, we expect such chains to be able to move rather freely along these interfaces but only infrequently hop between neighboring interfaces. Free motion along AB interfaces is enough to give diffusivity that is a large fraction of that obtained in the homopolymer state. In the simple case of polycrystalline lamellar phase with a diffusivity D_{\parallel} for motion parallel to a layer and much lower diffusivity D_{\perp} for diffusivity along the direction normal to the layers, with D_{\perp} $\ll D_{\parallel}$, we would expect an orientationally averaged diffusivity $D \simeq 2D_{\parallel}/3$. The value of the ratio $D/D_0 \sim 0.6$ that we obtain near the ODT is thus comparable to the value of $D/D_0 \simeq 0.67$ what we would expect in a polycrystalline lamellar phase with $D_{\parallel} \simeq D_0$. This is also similar to what we would expect for diffusion along the nearly minimal surface of a bicontinuous morphology. The roughly 40% drop in the value of D is thus consistent with the result one would expect from a crossover from fully three-dimensional diffusion to two-dimensional diffusion along interfaces between A- and B-rich domains in a cocontinuous morphology.

End-to-End Relaxation. We monitor the relaxation of chain conformations and chain orientation by measuring the end-to-end vector autocorrelation

$$E(t) = \langle \mathbf{R}_{e}(t) \cdot \mathbf{R}_{e}(0) \rangle \tag{6}$$

in which $\mathbf{R}_{e}(t)$ is the vector separation of the first and last bead of a randomly selected chain at time *t*.

The Rouse model for a continuous Gaussian chain in a homopolymer melt predicts



Figure 3. Normalized end-to-end autocorrelation function E(t)/E(t = 0) vs normalized time t/τ_{e0} for chains of length N = 16, for varying values of $\chi_e N$. Here τ_{e0} denotes the autocorrelation time for a chain of the same length in a homopolymer melt ($\chi_e N = 0$). Values of $\chi_e N$ shown here range from $\chi_e N = 0$ to very close to the ODT value, ($\chi_e N$)_{ODT} = 21.72.



Figure 4. Normalized end-to-end autocorrelation function E(t)/E(t=0) vs normalized time t/τ_{e0} for chains of length N = 32, for varying values of $\chi_e N$. For N = 32, $(\chi_e N)_{ODT} = 18.53$.

$$E(t) = \frac{8b^2N}{\pi^2} \sum_{p=1,3,\dots}^{\infty} \frac{1}{p^2} \exp\left(-\frac{t}{\tau_p}\right)$$
(7)

where $\tau_p = \tau_1/p^2$ and $\tau_1 = \zeta N^2 b^2/3\pi^2 k_B T$. Here, the sum is taken only odd values of $p = 1, 3, 5, ..., \infty$. Note that the existence of a prefactor of $1/p^2$ in this sum yields an expression for E(t) that is dominated by the contribution of the terminal p= 1 mode, since the prefactor for the p = 3 mode that is already 9 times smaller than that of the p = 1 mode. As a result, we expect E(t) in a homopolymer melt to exhibit a nearly singleexponential decay with a decay time τ_1 .

We first consider the behavior of E(t) in the homopolymer limit, where $\alpha = \chi_e = 0$. This limiting behavior is shown for chains of length N = 16 and N = 32 as the leftmost curve in Figures 3 and 4, respectively. As expected, in unentangled homopolymer melts, E(t) exhibits a nearly exponential decay after a small nonexponential transient, yielding a nearly straight line in this semilogarithmic plot. By fitting the late time behavior of E(t) in a homopolymer melt to an exponential E(t) $\propto e^{-t/\tau_{e0}}$, we have extracted values of the terminal homopolymer end-to-end relaxation time for each chain length, denoted here by τ_{e0} . The measured value τ_{e0} corresponds to the terminal time τ_1 in the Rouse model. This analysis yields $\tau_{e0} = 29.64$ in LJ time units for N = 16, with values for the two values of N = 16 and 32 that satisfy the Rouse scaling $\tau_{e0} \propto N^2$.

Figures 3 and 4 display the dependence of E(t)/E(0) as a function of the normalized time t/τ_{e0} for each chain length over a range of values of $\chi_e N$. Consider the evolution of this behavior with increasing $\chi_e N$. Upon increasing $\chi_e N$ from zero, the decay of E(t)/E(0) is found to change very little until $\chi_e N$ exceeds approximately the SCFT critical point value of $\chi_e N = 10.5$. At higher values of $\chi_e N$, in the range $10.5 < \chi_e N < (\chi_e N)_{\text{ODT}}$, E(t)/E(0) relaxes in two stages, with a fast initial decay at a rate similar to that obtained in the homopolymer and slower final exponential decay with a relaxation time that increases with increasing $\chi_e N$. We define a terminal end-to-end relaxation time τ_e at each value of α or $\chi_e N$ by fitting the long-time behavior of E(t) to an exponential decay, $E(t) \propto e^{-t/\tau_e}$.

To examine the relationship between measured values of τ_e and diffusivity D, we use the diffusivity D to define an effective friction coefficient ζ at each value of $\chi_e N$ by setting $D = k_B T / N\zeta$ and then define the "diffusion time" τ_d to be the value of τ_e predicted by the Rouse model with this friction coefficient (i.e., the predicted value of the longest Rouse relaxation time, τ_1). Values of τ_e and τ_d agree very well in the homopolymer state $\chi_e N = 0$, confirming the accuracy of the Rouse model in this limit. Figure 5 shows a comparison of τ_e and τ_d as functions of



Figure 5. Evolution of the end-to-end autocorrelation terminal relaxation time τ_e and the diffusion time τ_d with $\chi_e N$. Both relaxation times are normalized by the value of τ_e in a homopolymer melt, denoted by τ_{e0} . The diffusion time τ_d is defined to be the terminal internal relaxation time τ_1 predicted by the Rouse model by using a friction coefficient ζ obtained from the tracer diffusivity, by setting $D = k_{\rm B}T/N\zeta$.

 $\chi_e N$ for both chain lengths, N = 16 and N = 32. The ratio τ_d / τ_{e0} is very nearly equal to the inverse of the ratio D/D_0 . Both τ_e / τ_{e0} and τ_d / τ_{e0} remain very close to unity in the weakly correlated regime $\chi_e N < 10.5$, and both increase at higher values of $\chi_e N$. The increase in τ_e / τ_{e0} is, however, much greater than the increases in τ_d / τ_{e0} or (equivalently) much greater than the decrease in diffusivity.

Figure 6 shows the same results for normalized values of τ_d and τ_e plotted vs χ_a^*N , rather than vs $\chi_e N$. We define the "apparent" interaction parameter χ_a^* to be the value of χ that



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Figure 6. Normalized diffusion time τ_d/τ_{e0} and end-to-end autocorrelation time τ_e/τ_{e0} plotted versus the "apparent" segregation parameter $\chi_a^*N \equiv 10.495 - cNS^{-1}(q^*)/2$.

we would infer by fitting the measured peak scattering intensity $S(q^*)$ to the RPA prediction, which gives the definition

$$cNS^{-1}(q^*) = 2[10.495 - \chi_a^*N]$$
 (8)

The quantity $\chi_a^* N$ is a dimensionless measure of the strength of composition fluctuations. When plotted as functions of $\chi_a^* N$, values of τ_d/τ_{e0} and τ_e/τ_{e0} for two different chain lengths nearly collapse. The success of this collapse suggests that the dependence of dynamical properties on $\chi_e N$ in the disordered phase is controlled primarily by the magnitude of composition fluctuations.

5. DYNAMICAL STRUCTURE FACTOR

The dynamics of the relaxation of composition fluctuations in block copolymer melt can be quantified by studying the dynamic structure factor $S(\mathbf{q},t)$. The function $S(\mathbf{q},t)$ is an autocorrelation function for Fourier modes of the composition field. In a symmetric AB block copolymer melt, we define an instantaneous composition field

$$\psi(\mathbf{r}, t) = [c_{\mathrm{A}}(\mathbf{r}, t) - c_{\mathrm{B}}(\mathbf{r}, t)]/2$$
(9)

at position **r** and time *t*, where $c_A(\mathbf{r},t)$ and $c_B(\mathbf{r},t)$ are the instantaneous concentrations of particles of types A or B, respectively, at position **r** and time *t*. The Fourier transform of this field, denoted here by

$$\hat{\psi}(\mathbf{q},t) = \int d^3 r \, \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{r}} \psi(\mathbf{r},t) \tag{10}$$

can also be expressed as a sum over monomer positions

$$\hat{\psi}(\mathbf{q}, t) = \frac{1}{2} \sum_{i} e^{-i\mathbf{q}\cdot\mathbf{r}_{i}} \epsilon_{i}$$
(11)

in which *i* is a monomer particle index, \mathbf{r}_i is the position of monomer *i*, the sum is taken over all monomers of both types (A and B) in a system containing many chains, and ϵ_i is a factor that is equal to +1 if particle *i* is of type A and -1 if particle *i* is of type B.

The dynamic structure factor $S(\mathbf{q},t)$ for wavevector \mathbf{q} and time separation t is given by the correlation function

$$S(\mathbf{q}, t) = \frac{1}{V} \langle \hat{\psi}^*(\mathbf{q}, t) \hat{\psi}(\mathbf{q}, 0) \rangle$$
(12)

in which V is the total system volume. In a homogeneous, isotropic liquid, $S(\mathbf{q},t)$ depends only on the wavenumber



Figure 7. Normalized dynamic structure factor S(q,t)/S(q,0) vs normalized time t/τ_{e0} for chains of length N = 16 at several values of $\chi_e N$. In each plot, the time dependence is shown for several values of the normalized wavenumber qR_{g0} , as indicated by the numbers below each curve. Solid lines show simulation results, and dashed lines show results of a fit to an exponential time dependence $S(q,t) \propto e^{-t/\tau(q)}$.

 $q \equiv |\mathbf{q}|$ and time *t* and so can be expressed as a function S(q,t). The static structure factor S(q) that is commonly measured by quasi-elastic small-angle X-ray and neutron scattering is given by the t = 0 value of the dynamic structure factor:

$$S(q) = S(q, t = 0)$$
 (13)

The static structure factor in a diblock copolymer melt has a maximum at a value q^* of order the inverse radius of gyration. The random phase approximation (RPA) for symmetric diblock copolymers predicts a value $q^*R_{\rm g0} = 1.95$, independent of $\chi_{\rm e}N$, where $R_{\rm g0} \equiv \sqrt{Nb^2/6}$. The peak wavenumber q^* measured in simulations and experiments instead generally decreases slightly with increasing $\chi_{\rm e}N$ and is typically 10–25% less than the RPA prediction near the ODT.

Results for S(q,t)**.** Figure 7 shows the decay of the normalized structure factor S(q,t)/S(q,0) vs normalized time t/τ_{e0} for chains of length N = 16 at several different values of $\chi_e N$, corresponding to different values of the simulation parameter α . Different lines in each plot show the time dependence of S(q,t) at several different values of q. The range of values of q shown in each plot includes the wavenumber q^* at which S(q) is maximum. In this and all subsequent plots that show a function of time, we normalize time by the value τ_{e0} of the end-to-end autocorrelation time at $\chi_e N = 0$.

The four panels of Figure 7 show the evolution of S(q,t) with increasing $\chi_e N$. The upper left panel shows results for $\chi_e N$ = 0, corresponding to a measurement in a homopolymer melt in which the two halves of each polymer have been artificially labeled A and B, analogous to a neutron scattering experiment in which half of each copolymer is deuterated to provide scattering contrast. The lower right panel shows results for a value of $\chi_e N = 20.79$ close to the value at the ODT. The fact that the results for each value of q are nearly straight lines in this semilogarithmic plot indicates that the dependence on

time is nearly exponential over the range of values shown here. Dashed lines show fits to a simple exponential decay

$$S(q, t) \propto e^{-t/\tau(q)} \tag{14}$$

with a wavenumber-dependent relaxation time $\tau(q)$ that is determined independently for each value of q. The nature of the dependence of $\tau(q)$ on q changes qualitatively as $\chi_e N$ is increased. At $\chi_e N = 0$, the slowest decay occurs at the smallest wavenumber shown, $qR_{g0} = 0.51$, and $\tau(q)$ appears to decrease monotonically with increasing q. In the other three plots, the slowest decay shown occurs at values of $qR_{g0} = 1.52$ for which q is relatively close to q^* . Near the ODT, the most slowly evolving Fourier modes are thus those with wavenumber near q^* , for which we obtain values of $\tau(q)$ much greater than any obtained at $\chi_e N = 0$.

Figure 7 show results for values of q that extend only to values slightly greater than q^* . The range of values for S(q,t)/S(q,0) in each of these plots was chosen to include the range over which adequate statistics were obtained for the most slowly decaying modes, for which statistical accuracy is worst. Within the range of q and t shown in these figures, the time dependence of S(q,t) is nearly single-exponential.

Measurements of S(q,t) at higher values of q over a wider range of values of t show a more complicated time dependence. Figure 8 shows results for S(q,t)/S(q,0) for N = 16 at a fixed, relatively large value of $qR_{g0} = 3.28$ at several values of $\chi_e N$. The comparatively fast decay of correlations at this value of qallowed us to obtain accurate measurements over a wider range of values of S(q,t)/S(q,0) than that shown in Figure 7. The results show that the time dependence is not singleexponential, particularly near the ODT. At $\chi_e N = 0$, S(q,t)shows a modest but clearly measurable deviation from singleexponential decay at this value of q. Results obtained near the ODT instead show a rapid, nearly exponential decay of S(q,t)by ~1 decade followed by a more slowly decaying tail. Notably,



Figure 8. Dynamic structure factor S(q,t) vs time t plotted at a fixed relatively high wavenumber $qR_g = 3.28$ over a range of values of $\chi_e N$. A single-exponential fit to the early time behavior is shown as a dashed line.

the rate of the initial decay at this relatively high value of q is approximately independent of $\chi_e N$, as shown by the dashed line in the figure, while the rate of decay at longer times depends very strongly on $\chi_e N$ and is slowest near the ODT. The decay time associated with this slowly decaying tail of S(q,t) at $q > q^*$ always remains less than the primary decay time of modes with $q \simeq q^*$. We assume that the fast initial decay of S(q,t) at high q is the result of an initial relaxation of composition fluctuations by relaxation of relatively high index Rouse modes of individual chains in an essentially static environment of disordered microdomains and that the slowly relaxing tail is a result of coupling of high wavenumber modes to the slower relaxation of this microdomain structure.

Our results for S(q,t) for q similar to and less than q^* show almost single-exponential behavior. For the most slowly decaying modes, with $q \sim q^*$, our results are limited to values of S(q,t) for which $S(q,t)/S(q,0) \geq 10^{-1}$ by the limited statistical accuracy of measurements for very slowly evolving modes. Deviations from single-exponential behavior as large as those found near the ODT for $qR_g = 3.28$ would, however, have been easily detectable even this range, and are not seen for $q \le q^*$. Measurements of S(q,t) at $q < q^*$ also show much smaller deviations than those found at $qR_{g0} > 3$. Even for the data shown for higher q near the ODT in Figure 8, the initial decay of S(q,t) is reasonably well described as a single exponential for S(q,t)/S(q,0) > 0.1.

Our data thus suggest that S(q,t) is reasonably well described by a single-exponential decay for $q \leq q^*$, while the behavior at higher q is characterized by an exponential initial decay followed by a small, more slowly decaying tail. We have thus chosen to define a characteristic relaxation time $\tau(q)$ at all q by fitting the first decade of decrease of S(q,t) at each q to an exponential, $S(q,t) \propto e^{-t/\tau(q)}$. For data taken at high q near the ODT, $\tau(q)$ should be understood to be the time associated with the large initial decay, rather than the smaller, more slowly decaying tail.

Figure 9 displays the dependence of the relaxation time $\tau(q)$ on wavenumber q at four different values of $\chi_e N_i$, for chains of N = 16. To illustrate the relationship between the relaxation time and static structure, each of these plots also includes simulation results for the static structure factor S(q), for which the axis is shown on the right of each plot. Figure 10 show analogous data for N = 32. At $\chi_e N = 0.0$, shown in the upper left plot of Figure 9, the maximum of $\tau(q)$ appears to occur at q = 0. At higher values of $\chi_e N_r$, however, $\tau(q)$ exhibits a maximum at a value very close to the position q^* of the peak in S(q) as $\chi_e N$. At the highest two values of $\chi_e N$ shown here, both $\tau(q)$ and S(q) exhibit a sharp peak, and the peaks in both curves seem to have the same position and shape. Note that the maximum value of $\tau(q)$ increases dramatically as $\chi_e N$ increases, increasing by approximately a factor 25 over the range shown here. Also note, however, that $\tau(q)$ and S(q)exhibit qualitatively different behavior near q = 0 because S(q)



Figure 9. Wavenumber dependence of the structural relaxation time $\tau(q)$ (circles, left axis) and the static structure factor S(q) (squares, right axis) plotted vs qR_{e0} for chains of length N = 16 at several values of $\chi_e N$.



Figure 10. Structural relaxation time $\tau(q)$ (circles, left axis) and the static structure factor S(q) (squares, right axis) plotted vs qR_{g0} for chains of length N = 32 at several values of $\chi_e N$.

→ 0 as $q \rightarrow 0$, but $\tau(q)$ appears to approach a nonzero limit as $q \rightarrow 0$. The limiting value of $\tau(q)/\tau_{e0}$ as $q \rightarrow 0$ changes very little with changes in $\chi_e N$ and remains close to $\tau(q=0)/\tau_{e0} \simeq 0.9-1.0$ almost independent of $\chi_e N$. This limiting value corresponds to the relaxation time of the internal "breathing" mode seen optical DLS experiments performed with $qR_g \ll 1$.

Wavenumber-Dependent Effective Diffusivity. We now consider a simple phenomenological model of the relationship between S(q,t) and S(q), which we use to define an effective wavenumber dependent diffusivity.

The field $\psi(\mathbf{r},t)$ is a conserved order parameter and so satisfies a conservation equation

$$\frac{\partial \psi}{\partial t} = -\nabla \cdot \mathbf{J} \tag{15}$$

in which $J(\mathbf{r},t)$ is a relative monomer flux. Because $\psi(\mathbf{r}) = [c_A(\mathbf{r}) - c_B(\mathbf{r})]/2$ is a field with units of monomer concentration, the flux is naturally written as a product

$$\mathbf{J} = c\mathbf{v} \tag{16}$$

in which *c* is the total monomer concentration and **v** is a relative velocity of A and B monomers. To construct a minimal model, let us assume for the moment that the velocity **v** is related to an exchange chemical potential $\mu(\mathbf{r}) = \delta F[\psi]/\delta\psi(\mathbf{r})$ by a gradient

$$\mathbf{v} = -\frac{1}{\zeta} \nabla \mu \tag{17}$$

in which ζ is an effective bead friction coefficient. We know from equilibrium linear response theory that Fourier amplitudes of fluctuations in μ and ψ are related to linear order in ψ by the relation

$$\hat{\mu}(\mathbf{q}) = k_{\rm B} T S^{-1}(q) \hat{\psi}(\mathbf{q}) \tag{18}$$

Here, $\hat{\mu}(\mathbf{q})$ and $\hat{\psi}(\mathbf{q})$ denote Fourier components of the deviations of $\mu(\mathbf{r})$ and $\psi(\mathbf{r})$ from their values in a homogeneous reference state, and S(q) is the static structure

factor, which controls the free energy cost of small composition fluctuations. By substituting eqs 18 and 17 into eq 15 and expressing the result in Fourier space (by replacing gradients by factors of iq), we obtain

$$\frac{\mathrm{d}\hat{\psi}(q,\,t)}{\mathrm{d}t} = -q^2 D c N S^{-1}(q) \hat{\psi}(q,\,t) \tag{19}$$

where $D \equiv k_{\rm B}T/\zeta N$ is the molecular diffusion constant. Using this as the deterministic part of the relaxation of $\psi(q,t)$ in a linear Langevin equation for $\psi(q,t)$ would give a correlation function S(q,t) with a decay rate $S(q,t) \propto e^{-t/\tau(q)}$, in which

$$\frac{1}{\tau(q)} = Dq^2 cNS^{-1}(q) \tag{20}$$

Because this highly simplified model predicts a decay rate $\tau^{-1}(q) \propto q^2/S(q)$, it naturally predicts the appearance of a maximum in the relaxation time $\tau(q)$ when there is a sufficiently sharp peak in S(q), as is true near the ODT.

We now generalize eq 20 so as to allow for the existence of a wavenumber dependent (i.e., nonlocal) effective friction, to account for the fact that polymers are extended objects. We do so by replacing D by an unknown wavenumber dependent function D(q), giving a relaxation rate

$$\frac{1}{\tau(q)} = D(q)q^2 c N S^{-1}(q)$$
(21)

In what follows, we analyze our data by treating eq 21 as a definition of D(q) and inferring a value for D(q) at each q from our measurements of $\tau(q)$ and S(q).

To put our expression for D(q) into an appropriate universal scaling form, we consider the ratio $D(q)/D_0$, in which D_0 is the chain diffusivity in the $\alpha = 0$ homopolymer state. We also normalize q by the length R_{g0} and normalize $\tau(q)$ by the a time scale $\tau_0 \equiv R_{g0}^2/D_0$. This yields an expression for the ratio $D(q)/D_0$ as

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$$\frac{D(q)}{D_0} = \frac{1}{q^2 R_{g0}^2} \frac{\tau_0}{\tau(q)} \frac{S(q)}{cN}$$
(22)

The ratio S(q)/cN is known to be a nondimensional function of $qR_{\rm g0}$ and the state parameters $\chi_{\rm e}N$ and \overline{N} . If we assume that $\tau(q)/\tau_0$ is also a universal function of these state parameters and $qR_{\rm g0}$, it follows that the ratio $D(q)/D_0$ should also be a universal function of $qR_{\rm gv}$, $\chi_{\rm e}N$, and \overline{N} .

Figures 11 and 12 show results for $D(q)/D_0$ vs qR_{g0} for chains of 16 and 32 beads, respectively. Values of D(q) were



Figure 11. Values of the normalized effective diffusivity $D(q)/D_0$ vs qR_{e0} for chains of N = 16 beads.



Figure 12. Values of the normalized effective diffusivity $D(q)/D_0$ vs qR_{g_0} for chains of N = 32 beads. Values of D(q) are computed from measurements of $\tau(q)$ and S(q), as described in the text.

computed by using measured values of $\tau(q)$ and S(q) for all q in the range shown. Different symbols represent results obtained at different values of α or $\chi_e N$.

The results for $D(q)/D_0$ shown in Figures 11 and 12 for chains of two different lengths are very similar. It is clear from this similarity that the ratio $D(q)/D_0$ depends very weakly on N or \overline{N} , when compared at equal values of qR_g and similar values of $\chi_e N$. The dependence on \overline{N} appears to be particularly weak at low values of $\chi_e N$, as shown by Figure 13, which shows the almost perfect overlap of results for $D(q)/D_0$ vs qR_g for systems with $\alpha = 0$ or (equivalently) $\chi_e N = 0$.

At fixed values $\chi_e N$ and \overline{N} , the ratio $D(q)/D_0$ is a smooth, monotonically decreasing function of q. This ratio appears to always approach a nonzero value of $D(q)/D_0 \simeq 0.18-0.28$ as $qR_{g0} \rightarrow 0$ and also appears to approach a a nonzero limit at high wavenumbers. A comparison of results for different values of $\chi_e N$ shows that the function $D(q)/D_0$ changes relatively little with changes in $\chi_e N$ compared to the much more dramatic changes seen in both S(q) and $\tau(q)$ near the ODT.



3

 qR_{g0}

4

Figure 13. Values of the normalized effective diffusivity $D(q)/D_0$ vs qR_{g0} for homopolymers of N = 16 and N = 32 beads ($\alpha = 0.00$).

2

1

 D/D_0

0

0

Values of $D(q)/D_0$ in the range $qR_{g0} \simeq 1.5-1.8$ in which the peak in S(q) appears to change particularly little with changes in $\chi_e N$ and have values in the range

$$D(q^*)/D_0 \simeq 0.16 \pm 0.03$$
 (23)

for $\chi_e N$ ranging from 0 up to to $(\chi_e N)_{ODT}$ for both chain lengths. Knowledge of this nearly universal value of $D(q^*)/D_0$ is sufficient to allow prediction of the longest structural relaxation time for an unentangled melt from a measurement or prediction of the absolute magnitude of the peak in S(q)and knowledge of an estimate of the intrinsic bead friction coefficient. Notably, the effective diffusivity $D(qR_{g}\chi_e N,\overline{N})$ is a much smoother, simpler function of both qR_g and $\chi_e N$ than either the relaxation time $\tau(q)$ or the static structure factor S(q). The appearance of a sharp peak in $\tau(q)$ near the ODT is thus a very direct result of the appearance of a corresponding peak S(q).

Our simulation results show that the relaxation time $\tau(q)$ for a monodisperse diblock copolymer melt approaches a finite value in the limit $q \rightarrow 0$. This behavior is peculiar to singlecomponent block copolyer melts and is qualitatively different from that obtained in a polymer mixture, for which $\tau(q) \rightarrow \infty$ as $q \rightarrow 0$. The difference can be explained within the context of the phenomenological model discussed above. In a thermodynamically stable polymer mixture, both the structure factor S(q) and the effective diffusivity D(q) remain finite as $q \rightarrow 0$. As a result, the explicit factor q^2 in eq 21, which is characteristic of diffusive dynamics, yields a relaxation rate $1/\tau(q)$ that vanishes $1/\tau(q) \propto q^2$ as $q \to 0$. The fact that the τ (*q*=0) remains finite here can be understood as a result of the fact that the diffusivity approaches a nonzero limit, but the structure factor S(q) of a diblock copolymer melt approaches zero as $S(q) \propto q^2$ as $q \rightarrow 0$, thus canceling this factor of q^2 .

Terminal Structure Relaxation Time. The time constant $\tau(q)$ measures the time required for the value of a Fourier amplitude $\psi(\mathbf{q},t)$ to become decorrelated with its value at an earlier time. Near the ODT, the modes of largest mean-squared amplitude and longest relaxation time are those with $q \sim q^*$. The value of $\tau(q)$ for the most slowly decaying modes is thus a measure of how long it takes for a transient spatial arrangement of A- and B-rich regions to become re-randomized. We thus consider the behavior of the quantity

$$\tau_{\rm S} = \max_{q} \tau(q) \tag{24}$$

5

which we refer to as the terminal structure relaxation time. This quantity is a function of $\chi_e N$ that increases rapidly with increasing $\chi_e N$ near the ODT.

Figure 14 shows simulation results for τ_s normalized by τ_{e0} as a function of $\chi_e N$ for chains of both 16 and 32 beads. At low



Figure 14. Terminal structure relaxation time, τ_{s} , normalized by the homopolymer end-to-end relaxation time, plotted versus $\chi_e N$ over a wide ranged of $\chi_e N$ values, for chains of both 16 and 32 beads.

values of $\chi_e N$, well below the SCFT critical value of 10.5, τ_s is nearly equal to the single-chain end-to-end relaxation time τ_{e0} and changes rather little with changes in $\chi_e N$. For $\chi_e N$ between 10.5 and $(\chi_e N)_{ODT}$, τ_s increases increasing rapidly with increasing $\chi_e N$, reaching a value of 25–30 times greater than τ_{e0} at the ODT. The simulation results for these two systems indicate that the ratio of the value τ_s at the ODT to its value at $\chi_e N = 0$ is larger for shorter chains. More generally, this ratio is presumably larger for smaller values of \overline{N} , for which the degree of local segregation is larger at the ODT. Figure 15 shows the



Figure 15. Normalized terminal structure relaxation time τ_S/τ_{e0} plotted versus χ_a^*N for chains of both 16 and 32 beads.

same comparison plotted vs the "apparent" interaction χ_a^*N . The near collapse of results with different chain lengths shows that the ratio τ_S/τ_{e0} is a nearly universal function of χ_a^*N .

Figures 16 and 17 compare the behavior of the terminal structure relaxation time τ_{s} , the end-to-end time τ_{e} , and the diffusion time τ_{d} , plotted as functions of $\chi_e N$ for chains of length N = 16 and N = 32, respectively. All three times are very similar to each other, at low values of $\chi_e N$. Near the ODT, however, τ_s becomes much larger than τ_e and increases more rapidly than τ_e with increasing $\chi_e N$.



Figure 16. Comparison of different relaxation times τ_{S} , τ_{er} and τ_{d} plotted versus $\chi_e N$ for systems with N = 16. All times are normalized by the homopolymer end-to-end relaxation time τ_{e0} .



Figure 17. Comparison of different relaxation times τ_S , $\tau_{e'}$ and τ_d plotted versus $\chi_e N$ for systems with N = 32. All times are normalized by the homopolymer end-to-end relaxation time τ_{e0} .

6. LINEAR VISCOELASTICITY

The most common experimental methods for characterizing dynamical properties of a polymer liquid are measurements of linear viscoelastic behavior. Measurements of linear viscoelastic properties also provide an excellent method of identifying order—disorder transitions in block copolymer melts. Here, we present measurements of the shear relaxation modulus G(t) of our simulation model in the disordered phase. The modulus G(t) characterizes the decay of the macroscopic shear stress $\sigma(t)$ after step shear strain of magnitude γ and is given by the limiting value of the ratio $G(t) = \sigma(t)/\gamma$ in the limit of small strain γ .

Green–Kubo Relation. The results for G(t) presented here were measured using the fluctuation–dissipation or Green–Kubo relationship that relates G(t) to fluctuations in shear stress. In its simplest form, this relationship states that G(t) for an isotropic liquid is given by the autocorrelation function

$$G(t) = \frac{V}{k_{\rm B}T} \langle \sigma_{ij}(t) \sigma_{ij}(0) \rangle$$
(25)

where $\sigma_{ij}(t)$ is the instantaneous value at time t of any offdiagonal component of the stress tensor, with $i \neq j$, of a system of total volume V in thermal equilibrium at time t. To improve statistics of such a measurement, we use the equivalent relationship Macromolecules

$$G(t) = \frac{V}{10k_{\rm B}T} \sum_{i,j=1}^{3} \langle \tilde{\sigma}_{ij}(t) \tilde{\sigma}_{ij}(0) \rangle$$
(26)

in which $\tilde{\sigma}$ denotes the deviatoric (i.e., traceless) part of the symmetric stress tensor, with elements given by

$$\tilde{\sigma}_{ij}(t) = \sigma_{ij}(t) - \frac{1}{3}\delta_{ij}\sum_{i=1}^{3}\sigma_{ii}(t)$$
(27)

where $\sigma_{ij}(t)$ is an element of the full stress tensor. Equation 26 can be obtained by noting that the requirements imposed by isotropy, the traceless symmetric nature of $\tilde{\sigma}$, and eq 25 together require that $\langle \tilde{\sigma}_{ij}(t)\tilde{\sigma}_{kl}(0)\rangle V/k_{\rm B}T = G(t)[\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - (2/3)\delta_{ij}\delta_{kl}].$

The instantaneous stress tensor $\sigma(t)$ is given by a sum

$$\sigma_{ij} = \sigma_{ij}^{(kin)} + \sigma_{ij}^{(vir)}$$
(28)

of a kinetic component and virial component. The kinetic stress is given by a sum

$$\sigma_{ij}^{(\text{kin})} = \frac{1}{V} \sum_{\alpha} m_{\alpha} v_{\alpha,i} v_{\alpha,j}$$
(29)

over all particles in the system, in which α is a particle index, m_{α} is the mass of particle α , and $v_{\alpha,i}$ is the *i*th component of that particle's velocity. The virial component for a model with purely pairwise forces, such as the model used here, is given by a sum over particle pairs

$$\sigma_{ij}^{(\text{vir})} = \frac{1}{V} \sum_{\alpha > \beta} r_{\alpha\beta,j} f_{\alpha\beta,j}$$
(30)

in which $r_{\alpha\beta,i}$ is a component of the separation of particles α and β and $f_{\alpha\beta,j}$ is a component of the force between these two particles.

The autocorrelation function for the traceless symmetric stress defined in eq 26 has been computed by measuring the stress every 10 molecular dynamics steps and averaging using the hierarchical averaging scheme introduced for this purpose by Likhtmann and Ramirez.⁴⁹ Our analysis of G(t) does not explicitly take into account any contributions arising from the thermostat, which would in any case be of no physical interest. We have instead attempted to choose a thermostat coupling constant small enough to have no measurable effect on G(t) and other correlation functions.

Because the model simulated here relies on a soft pair potential that allows chains to cut through one another, these simulations do not exhibit entanglement. The starting point for our analysis of results for G(t) is thus a Rouse model of unentangled polymer melts. The Rouse model for a continuous Gaussian chain in a homopolymer melt predicts

$$G(t) = \frac{ck_{\rm B}T}{N} \sum_{p=1}^{\infty} \exp\left(-\frac{p^2 t}{\tau_{\rm R}}\right)$$
(31)

in which *c* is the number concentration of monomers and *N* is the number of monomers in a chain, so that c/N is the number concentration of molecules, and τ_R is the terminal relaxation time for stress. The terminal stress relaxation time τ_R predicted by the Rouse model is half the relaxation time τ_1 for the mode amplitude of the most slowly decaying Rouse mode, $\tau_R = \tau_1/2$. The terminal relaxation time τ_e for the end-to-end autocorrelation function E(t) introduced previously in eq 7 is instead equal to τ_1 , $\tau_e = \tau_1$. The Rouse model predicts a power law decay $G(t) \propto t^{-1/2}$ at times $t \ll \tau_R$ followed by exponential decay at times $t > \tau_R$.

Overview of Results. Figure 18 shows the evolution of the behavior of G(t) with increasing degree of segregation within



Figure 18. Normalized stress relaxation modulus, $NG(t)/ck_BT$ for disordered melts of chains of length N = 16 over a wide range of values of $\chi_e N$. The value at the ODT is $(\chi_e N)_{ODT} = 21.72$.

the ordered phase. In this and subsequent plots of G(t) vs time, time *t* is normalized by the terminal time $\tau_{e0}/2$ predicted by the Rouse model for a homopolymer, while the modulus G(t) is normalized by the prefactor $ck_{\rm B}T/N$ that appears in the Rouse model prediction of eq 31.

At $\chi_e N = 0$, the simulation model considered here reduces to a model of a homopolymer melt. We show in what follows that in this limit the behavior of G(t) is predicted nearly perfectly by the Rouse model. At relatively low but nonzero values of $\chi_e N$, up to $\chi_e N \simeq 10$, the behavior remains similar to that found for a hompolymer. Throughout this regime of weak composition fluctuations, G(t) is characterized by a single crossover from a power law decay at early times to exponential decay after a terminal relaxation time, with a crossover time that increases slightly with increasing $\chi_e N$.

At higher values of $\chi_e N$, closer to the ODT, the function G(t) develops a second feature that is a result of strong composition fluctuations. At the two highest values of $\chi_e N$ shown in Figure 18, a second shoulder develops at long times, which becomes more prominent as $\chi_e N$ increases. We show in what follows that the decay time associated with this new feature is approximately the same as the terminal relaxation time τ_s for the relaxation of the composition fluctuations.

Figure 19 shows the rheological signature of the spontaneous formation of lamellar order. The highest two values of $\chi_e N$ shown in this plot ($\chi_e N = 22.02$ and $\chi_e = 22.26$) are slightly above the value $\chi_e N = 21.72$ at the equilibrium ODT. Both of these samples spontaneously crystallized into lamellar structures. The formation of lamellar order is visible in our measurement of G(t) by the appearance of a plateau in G(t) at long times. To explain why a plateau forms in the lamellar phase, recall that G(t) is measured by measuring an autocorrelation of the deviatoric (i.e., traceless) part of the stress tensor, denoted by $\tilde{\sigma}$. In a lamellar phase with layers oriented perpendicular to a normal vector **n**, the system stress can have a nonzero average uniaxial stress of the form $\tilde{\sigma}$ = $\sigma_0(n_i n_i - \delta_{ii}/3)$, in which σ_0 is a slight tensile or compressive stress arising from any mismatch between the actual layer spacing and the preferred layer spacing at which the tensile



Figure 19. Normalized stress relaxation response, $NG(t)/ck_{\rm B}T$, for chains of length N = 16 over a range of values of $\chi_e N$ that spans the order-disorder transition at $(\chi_e N)_{\rm ODT} = 21.72$. Measurements of G(t) in samples that have spontaneously ordered show an elastic plateau at long times.

stress vanishes. Such a mismatch will generally arise because the periodic boundary conditions only allow lamellar alignment along specific directions, none of which may allow the formation of a structure with a spacing exactly equal to the preferred spacing. Formation of a persistent stress of this form yields a plateau of magnitude $G(t) = V\sigma_0^2/15k_BT$ as $t \to \infty$ in the stress inferred from ref 26. The existence of such a plateau is a finite-size effect, insofar as the stress σ_0 would vanish in the limit $L \to \infty$ of an infinite unit cell, but has a significant effect on the results reported here.

Weak Correlation Regime: Rouse Model. Figure 20 shows a comparison of Rouse model predictions to results for



Figure 20. Normalized relaxation modulus $NG(t)/ck_{\rm B}T$ vs normalized time for chains of N = 16 beads at $\chi_e N = 0.00$, corresponding to homopolymers. Simulation results are shown by the red dotted line. Rouse model predictions computed using $\tau_1 = \tau_{e0}$ are shown by the solid blue line.

G(t) in the limit $\chi_e N = 0.0$, corresponding to a homopolymer melt. In this comparison, the time constant τ_1 used in the Rouse prediction was taken to be equal to the terminal relaxation time τ_{e0} obtained from an independent measurement of the end-to-end autocorrelation function E(t). For a homopolymer, excellent agreement with the Rouse model is thus obtained with no adjustable parameters.

Figures 21 and 22 show fits of the Rouse model to results obtained at relatively low values of $\chi_e N = 8.94$ and $13.97(\alpha = 2.00$ and 3.00), in which the stress relaxation time $\tau_R = \tau_1/2$ has been adjusted to fit these data. A similar fit was performed



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Figure 21. Normalized relaxation modulus $NG(t)/ck_{\rm B}T$ vs normalized time for symmetric diblock copolymers chains of N = 16 beads at $\chi_e N = 8.75$ ($\alpha = 2.0$). Simulation results are shown by the red dotted line. A fit to the Rouse model computed using $\tau_{\rm R}$ as the only fitting parameter is shown by the solid blue line.



Figure 22. Normalized relaxation modulus $NG(t)/ck_{\rm B}T$ vs normalized time for symmetric diblock copolymers chains of N = 16 beads at $\chi_e N = 13.50$ ($\alpha = 3.0$). Simulation results are shown by the red dotted line. A fit to the Rouse model computed using $\tau_{\rm R}$ as the only fitting parameter is shown by the solid blue line.

at $\chi_e N = 4.21$ ($\alpha = 1.0$) but is not shown here. These fits yield values of τ_1 that increase slightly with increasing $\chi_e N$, giving $\tau_1/\tau_{e0} = 1.051$, 1.259, and 2.123 at $\chi_e N = 4.21$, 8.95, and 13.97, respectively. Allowing adjustment of τ_R is found to be sufficient to fit this data for the first three values of $\chi_e N = 0.0$, 4.21 and 8.94, for which $\chi_e N < 10$. For $\chi_e N = 13.97$, however, we can see an additional shoulder in G(t) beginning to appear at long times, near the end of the range of times shown here.

The shoulder in G(t) at long times becomes more pronounced as $\chi_e N$ increases, causing the attempt to fit the data with a Rouse model to fail closer to the ODT. This can be seen in Figure 23, where we show a failed attempt to fit results for G(t) at $\chi_e N = 18.35$ by the Rouse model.

The time constants associated with the two shoulders in G(t) differ by an order of magnitude at $\chi N = 18.35$ ($\alpha = 4.0$) and seem to grow further apart as we increase χN . The presence of the second shoulder can be understood as a result of the appearance of transient well-segregated domains in the disordered melt. Upon exerting an external strain, a diblock copolymer melt with strong composition fluctuations reacts in two stages. First, individual molecule relax relative to an essentially fixed composition profile, which provides the chemical potential landscape for individual chains. Over a somewhat longer period of time, collective motion of many



Figure 23. Normalized relaxation modulus $NG(t)/ck_{\rm B}T$ vs normalized time for symmetric diblock copolymers chains of N = 16 beads at $\chi_e N = 18.35$ ($\alpha = 4.0$). Simulation results are shown by the red dotted line. The blue line shows an unsuccessful attempt to fit this data to the Rouse model using $\tau_{\rm R}$ as an adjustable parameter and attempting by eye to fit the region near the feature indicated by the arrow at $\tau_{\rm R}$.

chains leads to relaxation of the composition profile. This relaxation of composition fluctuations is directly measured by S(q,t) and is complete only at times longer that the longest structural relaxation time τ_S obtained in measurements of S(q,t). This picture suggests that the terminal viscoelastic relaxation time should be given by τ_S , in agreement with our results. Therefore, we assume that the initial decay and the first shoulder in G(t) is related to molecular relaxations in a system of nearly constant composition field, and the second shoulder is caused by relaxation of residual stress associated with the slower relaxation of composition fluctuations.

Strong Correlation Regime: Theory. Upon increasing $\chi_e N_i$, the main new feature of viscoelastic behavior near the ODT is the appearance of a slowly decaying shoulder in G(t), in addition to the more rapidly decaying shoulder observed at lower values of χN . The appearance of this feature in G(t) is consistent with the appearance of a corresponding lowfrequency shoulder in the frequency-dependent storage modulus $G'(\omega)$ in experiments on disorder diblock copolymers near the ODT. Near the ODT, the disordered phase is characterized by long-lived composition fluctuations. Relaxation of these composition fluctuations is characterized most directly by S(q,t), which yields a terminal structural relaxation time $\tau_{\rm S}$ much longer than the time required for relaxation of individual chains in a fixed environment. When a strongly correlated diblock copolymer melt is subjected a macroscopic strain, relaxation of stress and G(t) thus proceeds in two stages: First, over a time comparable to τ_{e0} , the distribution of conformations of individual chains relaxes to a state of local equilibrium in a nearly constant composition landscape. Over somewhat longer times, the composition field itself reequilbrates, with a terminal time similar τ_s . The component of the stress that persists to long times is the stress of a system in which chains are in local equilibrium in an environment defined by a more slowly evolving composition field.

In an attempt to model this slowly decaying component of the stress, we have compared our simulation results to a variant of the Fredrickson–Larson model (FL) of low-frequency stress relaxation.³⁸ The original derivation of this model was presented in the frequency domain by considering an oscillatory strain and using the response to compute $G'(\omega)$ and $G''(\omega)$. Because we use the model here in the time domain, to predict G(t), we begin by outlining a derivation of the FL theory in the time domain.

Fredrickson–Larson Theory in the Time Domain. The Fredrickson–Larson theory attempts to describe linear viscoelastic behavior at long times or low frequencies in a melt of very long diblock copolymer near the ODT. It assumes that the instantaneous stress in this regime can be approximated by the stress generated from a quasi-equilibrium free energy $F[\hat{\psi}]$ that is a functional of the slowly relaxing composition field. The functional $F[\hat{\psi}]$ is further approximated by a harmonic approximation

$$\frac{F[\hat{\psi}]}{Vk_{\rm B}T} \simeq \frac{1}{2} \int \frac{{\rm d}^3 q}{(2\pi)^3} S_{\rm eq}^{-1}(q) |\hat{\psi}(q)|^2$$
(32)

where $S_{eq}(q)$ is the equilibrium static structure factor. The quasi-equilibrium stress arising from this free energy can be computed using the principle of virtual work by computing the change in free energy induced by an affine deformation of the composition field. This yields a stress given to within an isotropic component by

$$\sigma_{ij}(t) = -k_{\rm B}T \int \frac{{\rm d}^3 q}{(2\pi)^3} q_i q_j \frac{{\rm d}S_{\rm eq}^{-1}(q)}{{\rm d}(q^2)} \delta S_{\rm ne}(q, t)$$
(33)

as given in eq 2.12 of ref 38, in which we use $S_{eq}(\mathbf{q})$ to denote the equilibrium value of the static structure factor and

$$\delta S_{\rm ne}(\mathbf{q}, t) = S_{\rm ne}(\mathbf{q}, t) - S_{\rm eq}(\mathbf{q})$$
(34)

to denote the deviation of the instantaneous static structure factor $S_{\rm ne}(\mathbf{q},t)$ from the equilibrium value. The subscript "ne" on the symbols $S_{\rm ne}(\mathbf{q},t)$ and $\delta S_{\rm ne}(\mathbf{q},t)$ denotes "nonequilibrium", which is used to indicate that $S_{\rm ne}(\mathbf{q},t)$ is the instantaneous nonequilibrium value of the static structure factor

$$S_{\rm ne}(\mathbf{q}, t) = \langle |\hat{\psi}(\mathbf{q}, t)|^2 \rangle / V \tag{35}$$

evaluated at time *t* after a step strain. The subscript is needed to distinguish this quantity from the equilibrium dynamic structure factor S(q,t) measured in section 5, which is instead given by the equilibrium autocorrelation function $S(q,t) = \langle \hat{\psi}^*(\mathbf{q},t) \hat{\psi}(\mathbf{q},0) \rangle / V$.

To describe relaxation after a step strain, the function $\delta S_{ne}(\mathbf{q},t)$ is assumed to decay exponentially with time *t* after a step strain, giving

$$\delta S_{\rm ne}(\mathbf{q}, t) = \delta S_{\rm ne}(\mathbf{q}, 0^+) e^{-2t/\tau(q)}$$
(36)

Here, $\delta S_{ne}(\mathbf{q},0^+)$ is the deviation immediately after a step deformation, and $\tau(q)/2$ is a wavenumber-dependent decay time. The time scale $\tau(q)$ that appears in eq 36 is taken to be equal to the relaxation time of the equilibrium dynamic structure factor S(q,t) measured in section 5. The prediction that the relaxation time $\tau(q)/2$ for the relaxation of the nonequilibrium structure factor is half the relaxation time $\tau(q)$ of the correlation function S(q,t) follows from a linear stochastic model in which each Fourier amplitude $\hat{\psi}(\mathbf{q})$ behaves like an overdamped Brownian harmonic oscillator with a decay rate $1/\tau(q)$. Such a model generically gives a decay rate for quantities such as $S_{ne}(\mathbf{q},t)$ that are quadratic in the oscillator amplitude that is twice the decay time of the oscillator amplitude or of the associated equilibrium autocorrelation function. This is also the reason that in the Rouse model the stress component associated with each Rouse mode decays with a decay time half of that seen in the corresponding contribution to the end-to-end autocorrelation time.

The initial deviation $\delta S_{ne}(\mathbf{q},t=0)$ caused by a small amplitude step deformation is computed by assuming an affine deformation of the equilibrium distribution. We consider a deformation characterized by a strain tensor γ , in which a material element at \mathbf{r} is displaced to $\mathbf{r} + \gamma \mathbf{r}$. Assuming that $S_{ne}(\mathbf{q}) = S_{eq}(\mathbf{q})$ prior to the deformation yields

$$\delta S_{\rm ne}(\mathbf{q}, 0^+) = 2 \frac{\mathrm{d}S_{\rm eq}(q)}{\mathrm{d}(q^2)} \sum_{ij} q_j q_i \gamma_{ij}$$
(37)

To compute the resulting stress σ_{ij} , we must combining eqs 33, 36, and 37. After defining a unit vector $\hat{\mathbf{q}} = \mathbf{q}/q$, where $q = |\mathbf{q}|$, and explicitly carrying out averages over orientation of the unit vector $\hat{\mathbf{q}}$, we obtain a stress $\sigma(t) = G(t)[\gamma + \gamma^{\mathrm{T}}]$ characterized by a modulus

$$G(t) = \frac{2k_{\rm B}T}{15} \int \frac{{\rm d}^3 q}{(2\pi)^3} \left[q^2 \frac{{\rm d} \ln S_{\rm eq}(q)}{{\rm d}q^2} \right]^2 {\rm e}^{-2t/\tau(q)}$$
(38)

or, equivalently,

$$G(t) = \frac{k_{\rm B}T}{15\pi^2} \int_0^\infty {\rm d}q \ q^2 \left[q^2 \frac{{\rm d} \ln S_{\rm eq}(q)}{{\rm d}q^2} \right]^2 {\rm e}^{-2t/\tau(q)}$$
(39)

By taking the Fourier transform of this result, by setting $G^*(\omega) = i\omega \int_0^\infty dt \ G(t)e^{-i\omega t}$, we obtain a corresponding complex frequency-dependent modulus

$$G^{*}(\omega) = \frac{k_{\rm B}T}{15\pi^{2}} \int_{0}^{\infty} \mathrm{d}q \; q^{2} \left[q^{2} \frac{\mathrm{d}\ln S_{\rm eq}(q)}{\mathrm{d}q^{2}} \right]^{2} \frac{i\omega\tau(q)/2}{1 + i\omega\tau(q)/2}$$
(40)

in agreement with the result obtained by Fredrickson and Larson by considering a small amplitude oscillatory flow.

Rouse/Fredrickson–Larson (R/FL) Theory. The Fredrickson–Larson theory was intended to describe the behavior of G(t) or $G^*(\omega)$ at very long times, or low frequencies, in diblock copolymer melts with $N \gg 10^4$ very close to the ODT. The theory assumes the existence of a large separation between the terminal relaxation time τ_s and the time required for local chain equilibration and was designed to describe only the most slowly decaying contributions to the stress. The resulting theory was never intended to be used to describe the behavior of G(t) at early times or low or intermediate values of $\chi_e N$.

The simulation data shown here include data over a wide range of values of time and $\chi_e N_i$ in which the separation between the terminal structural relaxation time and the shorter time for chain equilibration never exceeds about 1 order of magnitude. We know that the behavior observed at low and intermediate values of $\chi_e N$ is well described by a Rouse model in which we treat the terminal Rouse time as an adjustable parameter. It appears likely that the first feature in the behavior observed near the ODT might also be reasonably well described by a Rouse-like contribution. Because the original Fredrickson-Larson model assumes local equilibration of the distribution of chain conformations in a slowly evolving composition landscape, it cannot describe the Rouse-like relaxation of G(t) at early times that occurs even in systems near the ODT and would yield qualitatively incorrect behavior at all times if applied to systems with lower values of $\chi_e N$.

To combine the realistic aspects of the Rouse and Fredrickson–Larson models, we propose an approximation for G(t) as a sum

$$G(t) = G_{\rm R}(t) + \delta G_{\rm FL}(t) \tag{41}$$

Here, $G_{\rm R}(t)$ is a contribution that is computed using the Rouse model with an adjustable terminal time scale, while $\delta G_{\rm FL}(t)$ is the difference between the prediction of the FH model at the value of $\chi_e N$ of interest and that at $\chi_e N = 0$. More explicitly

$$\delta G_{\rm FL}(t) = G_{\rm FH}(t, \chi_{\rm e}N) - G_{\rm FH}(t, \chi_{\rm e}N = 0) \tag{42}$$

where $G_{\rm FH}(t,\chi_e N)$ denotes the FL prediction for G(t) at a specified value of $\chi_e N$ and $G_{\rm FH}(t,\chi_e N=0)$ represents the corresponding prediction for a homopolymer, with $\chi_e N = 0$. By construction, this model reduces to a Rouse model in the homopolymer limit $\chi_e N = 0$ and always contains a Rouse-like feature at early times. In addition, the model contains a contribution $\delta G_{\rm FL}(t)$ for which both the magnitude and long decay time increase gradually with increasing $\chi_e N$.

Strong Correlation Regime: Analysis of Simulations. Figure 24 shows a comparison of simulations results at $\chi_e N =$



Figure 24. Comparison of the normalized stress relaxation modulus $NG(t)/ck_{\rm B}T$ to predictions of the Rouse/Fredrickson–Larson model, for chains of N = 16 beads at $\chi_e N = 18.35$ ($\alpha = 4.00$). The indicated value of $\tau_{\rm S}$ was obtained from independent measurements of S(q,t). The terminal Rouse stress relaxation time $\tau_{\rm R}$ in the Rouse contribution $G_{\rm R}(t)$ has been treated as an adjustable parameter, for which we used $\tau_{\rm R} = \tau_1/2$ and $\tau_1/\tau_{\rm e0} = 1.34$.

19.17 to predictions of the Rouse/Fredrickson-Larson model for chains of N = 16 beads. The only adjustable parameter in this comparison is the terminal Rouse relaxation time $\tau_{\rm R} = \tau_1/2$ used in the Rouse contribution to the model, for which we used τ_1/τ_{e0} = 1.34. Both the magnitude and time dependences of the contribution $\delta \delta G_{FL}(t)$ that produces the second shoulder have been predicted by using information obtained from measurements of the intermediate structure factor S(q,t). Note that the predicted behavior of G(t) at times $t > \tau_{R}$ appears to be displaced from the measured behavior by a nearly constant distance on this log-log plot. This theory thus yields a prediction for the behavior of G(t) near the second shoulder in which the both terminal time and functional form of the time dependence are predicted correctly, but in which the magnitude of G(t) is slightly larger, by a nearly constant multiplicative factor.

Figure 25 shows a similar comparison of results for G(t) at $\chi_e N = 20.79$ to predictions of the Rouse/Fredrickson–Larson



Figure 25. Comparison of the normalized stress relaxation modulus $NG(t)/ck_{\rm B}T$ to predictions of the Rouse/Fredrickson–Larson model for chains of N = 16 beads at $\chi_e N = 20.79$ ($\alpha = 4.5$). The terminal Rouse relaxation time in the Rouse contribution $G_{\rm R}(t)$ has been treated as an adjustable parameter, for which we have used $\tau_{\rm R} = \tau_1/2$ and $\tau_1/\tau_{\rm e0} = 1.47$.

model described above. The model again predicts somewhat too large a value for G(t) in the vicinity of the second shoulder. Figure 26 and 27 show the results of a somewhat *ad hoc*

modification of the Rouse/Fredrickson-Larson model in



Figure 26. Comparison of the normalized stress relaxation modulus $NG(t)/ck_{\rm B}T$ for a melt with N = 16 and $\chi_{\rm e}N = 18.35(\alpha = 4.00)$ to predictions of the modified Rouse/Fredrickson–Larson model of eq 43, using a prefactor $\lambda = 2/3$.



Figure 27. Comparison of the normalized stress relaxation modulus $NG(t)/ck_{\rm B}T$ for a melt with N = 16 and $\chi_{\rm e}N = 20.79$ to predictions of the modified Rouse/Fredrickson–Larson model of eq 43, using $\lambda = 2/3$.

which we have simply replaced the original theory by a sum of the form

$$G(t) = G_{\rm R}(t) + \lambda \delta G_{\rm FL}(t) \tag{43}$$

in which the contribution $\delta G_{\rm FL}(t)$ arising from composition fluctuations is simply multiplied by an arbitrary factor λ whose value is chosen to fit the data. A value of $\lambda = 2/3$ was used to generate both Figure 26 and Figure 27, using the same value of λ for both values of $\chi_e N$. The fact that this modified theory fits the data reasonably well shows that the prediction of the time dependence of the fluctuation contribution is consistent with our simulation results for G(t), but that the unmodified theory predicts slightly too large a magnitude for the slowly decaying shoulder. More specifically, the comparison shows that the simulation data is consistent with the existence of a terminal rheological time equal to $\tau_S/2$, where τ_S is the terminal relaxation time obtained from independent measurements of S(q,t).

Our results show that the Rouse/Fredrickson-Larson model slightly overpredicts the magnitude of G(t) in the long time regime in which stress is controlled by relaxation of composition fluctuations. Because the theory is based on several approximations, it is not entirely clear which approximation is the main source of this discrepancy. One possibility is that the error may be primarily a consequence of the limitations of the harmonic approximation for the free energy functional that is used here to compute stress. This expression for the stress is being applied here to states near the ODT in which composition fluctuations are known to be quite strong, and in which anharmonic contributions to the free energy are thus potentially important. The fact that the model is based on measured values of the relaxation times $\tau(q)$ inferred from the relaxation of S(q,t) appears, however, to allow it make meaningful predictions about the spectrum of relaxation times in G(t).

7. CONCLUSIONS

Simulations of simple bead-spring models have been used to measure single-chain properties (tracer diffusion, end-to-end autocorrelation), the dynamic structure factor S(q,t), and the linear viscoelastic stress relaxation modulus G(t) in the disordered phase of a symmetric diblock copolymer and to characterize how these dynamical properties change with changes in the segregation parameter χN .

These dynamical properties (like equilibrium properties) behave somewhat differently in a regime in a weakly correlated parameter regime in which $\chi N < (\chi N)_{ODT}^{SCFT}$ and in strongly correlated regime in which $(\chi N)_{ODT}^{SCFT} < \chi N < (\chi N)_{ODT}$. Here, $(\chi N)_{ODT}^{SCFT} = 10.5$ denotes the value at which SCFT predicts an ODT, and $(\chi N)_{ODT}$ denotes the actual value at the ODT for a system of finite \overline{N} . In the weakly correlated regime $(\chi N) < (\chi N)_{ODT}^{SCFT}$, effects of composition fluctuations are small, and all of the measured dynamical properties are reasonably well described by a Rouse model with an effective friction coefficient that is almost independent of χN . In the strongly correlated regime closer to the ODT, all dynamical properties show evidence of the formation of increasingly strongly segregated transient microdomains. The effects of composition fluctuations show up much more strongly in some measured quantities than in others.

The effect of composition fluctuations upon tracer diffusivity is relatively weak. In the two systems studied here, the value of the diffusion coefficient at the ODT was 0.55–0.65 of its value in the homopolymer state, at $\chi N = 0$. A reduction of approximately this magnitude would be expected in a system of unentangled chains, even if chains were forced to follow interfaces between slowly evolving bicontinuous A and B domains, as the result of relatively free diffusion of unentangled chains along AB interfaces.

Composition fluctuations have a somewhat larger effect on the relaxation of the end-to-end vector. In the strongly correlated regime, the end-to-end autocorrelation function E(t) shows evidence of a two-stage relaxation. The rate of initial relaxation is similar to that seen in the homopolymer and is assumed to represent the relaxation of chains to a state of local equilibrium in a nearly fixed composition landscape. The relaxation time $\tau_{\rm e}$ associated with the final relaxation reaches a value at the ODT that is 6-7 times the value obtained in the homopolymer for the two systems studied here. A somewhat larger fractional increase is observed for shorter chains, which reach a somewhat higher level of local segregation before crystallizing into a lamellar phase. Near the ODT, τ_e remains significantly less than the terminal time for the relaxation of composition fluctuations at the ODT (discussed below). This implies that the end-to-end vector can relax before the microdomains have fully randomized. We speculate that final relaxation of E(t) in an unentangled melt may thus occur in part via diffusion of chains along tortuous interfaces between domains in a more slowly evolving composition landscape.

The time dependence of the dynamic structure factor S(q,t)can be described reasonably well as a single-exponential decay at wavenumbers similar to or less than the peak wavenumber q^* . Near the ODT, the wavenumber-dependent relaxation time $\tau(q)$ exhibits a peak at q^* . We have analyzed the relationship between $\tau(q)$ and the static structure factor S(q) using a simple phenomenological model in which the relationship between the relaxation rate $\tau(q)^{-1}$ and the free energy gradient driving that relaxation is controlled by a wavenumber-dependent diffusivity D(q). The effective diffusivity D(q) (or inverse mobility) for composition modes of wavenumber q is a smooth, monotonically decreasing function of qR_{σ} that depends only modestly on $\chi_e N$ and very weakly on \tilde{N} . The simplicity of the behavior of D(q) suggests that an empirical correlation for D(q) might be useful as the basis of a simple method of estimating $\tau(q)$ from knowledge of the static structure factor.

The stress relaxation modulus G(t) was inferred from measurements of spontaneous stress fluctuations via the appropriate Green-Kubo relation. The behavior of G(t) in the weakly correlated parameter regime $\chi_e N < 10$ is very well described by the Rouse model of stress relaxation. Near the ODT, G(t) exhibits a more slowly decaying shoulder due to stress that arises from the effect of strain upon slowly decaying composition fluctuations. The connection between this slowly decaying contribution to the stress and composition fluctuations is demonstrated more directly here than in experiments or previous simulations by showing that the terminal rheological relaxation time is indeed the same as the longest relaxation time τ_S obtained from independent measurements of S(q,t).

Simulation results for G(t) near the ODT are rather well described by a slightly modified variant of the Fredrickson– Larson theory of stress relaxation. The Rouse/Fredrickson– Larson model to which we compare is obtained by modifying the original Fredrickson–Larson model so as to guarantee that Rouse-like behavior is recovered at early times and low values of $\chi_e N$. This theory was then evaluated using independently measured values of the static structure factor S(q) and relaxation time $\tau(q)$ as inputs. The main limitation of the resulting theory is that it predicts slightly too large a value for the magnitude of the slowly decaying shoulder in G(t).

The work presented here provides both a relatively simple description of the behavior of S(q,t) from knowledge S(q), in terms of an effective diffusivity D(q) that we have characterized empirically. We have not attempted here to predict D(q) from first principles. This work also provides partial validation of a theory that predicts G(t) from knowledge of S(q,t). Taken together, these results provide a method of estimating expected structural relaxation times and linear viscoelastic properties in unentangled symmetric diblock copolymers from knowledge of homopolymer viscosities or measurements of single-chain motion (to calibrate friction coefficients) and the static structure factor S(q).

AUTHOR INFORMATION

Corresponding Author

*E-mail: morse012@umn.edu.

ORCID 💿

David C. Morse: 0000-0002-1033-8641

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by NSF Grant DMR-1310436 using computational resources of the Minnesota Supercomputing Institute.

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