Networklike Pattern Formation in Phase Separating Polymer Solutions: A Molecular Dynamics Study

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(Received 11 August 1997)

The dynamics of phase separation of a quenched polymer solution is studied using a stochastic molecular dynamics simulation. At early times, the elastic nature of the polymer chains generates a networklike domain morphology for sufficiently dense polymer solutions. However, at late times, this network structure breaks up into disconnected polymer-rich domains to minimize the interfacial energy. Our simulations explain why different experiments carried out to different time regimes seem to produce contradictory results, and strongly indicate that the *true* late-time growth kinetics of quenched polymer solutions belong to the same universality class of small molecular mixtures. [S0031-9007(97)04972-7]

PACS numbers: 64.60.Cn, 61.41.+e, 64.60.My, 64.75.+g

The dynamics of phase separation in a quenched polymer solution [1–5] is a challenging subject to investigate due to the polymer-specific effects of chain conformation and entanglement on the dynamic process in addition to the usual nonlinearity present in the coarsening of quenched binary liquid mixtures. One of the most important problems is whether the large-scale, late-time characteristics of the phase separation process in polymer solutions belong to the *same* dynamical universality class [6] of small molecular liquid mixtures. Many experiments suggest this universality [1,2] and point out that phase separation in polymer mixtures can be understood in terms of a simple dynamical model [7] called *model H*. However, Tanaka [3] in his recent experiments has observed the formation of a spongelike network structure [4,5] during the evolution process of quenched polymer solutions and has identified this most unusual and polymer-specific pattern formation with viscoelastic effects [8]. Tanaka has also suggested that phase separation in polymer solutions may actually belong to a *different* dynamical universality class as the anomalously slow growth of the domains and the unusual morphology seen in his experiments cannot be reconciled with the late-time pattern formation in simple liquid mixtures. A detailed understanding of such a network pattern formation will be of utmost importance not just in phase separating polymer solutions, but also in other diverse complex fluid systems such as gels [9], an interpenetrating network of cross-linked polymers [10], telechelic polymers [11], and polymeric surfactants [12]. However, only limited theoretical effort [13,14] has been directed toward a thorough understanding of the network pattern formation and the associated viscoelastic effects [8]. Recently, Taniguchi and Onuki [14] have carried out a numerical simulation of a coarse-grained dynamical model in two dimensions, and found that the network domain structure is stabilized to a very late time. They found that in the absence of viscoelastic stress the growth law exponent is controlled by hydrodynamic interactions and the characteristic size of domains $[R(t)]$ grows with time as $R(t) \sim t^n$, with the growth exponent $n = \frac{2}{3}$. However, the model used by Taniguchi and Onuki neglects the inertial terms in the Navier-Stokes equation, and it is known that the growth exponent for such a viscosity-dominated model in two dimensions [15] is actually $\frac{1}{2}$ (and not $\frac{2}{3}$). Thus, the applicability of their model toward network pattern formation is not clear. Moreover, comprehensive experimental studies of Haas and Torkelson [2] strongly suggest that the growth law for quenched polymer solutions is identical to the small molecular systems at late times. This raises serious doubts about the importance of viscoelastic effects on the *late-time* dynamics of a phase separating polymer solution.

To understand the origin of the discrepancy between various experiments and to characterize the formation and subsequent relaxation of the network domain structure, we have carried out extensive molecular dynamics (MD) simulations in two dimensions in a model with explicit polymer chain conformations. Our main results are the following. During the early to intermediate stages of the coarsening process, a networklike structure is formed by the *minority* polymer-rich phase and solvent regions are encapsulated by the thin polymer-rich walls. This network pattern formation takes place for monomer concentrations larger than the overlap threshold [16] $c^*(N)$ for the polymer chain length N. At late times, however, the interfacial energy wins over the elastic stress and the network breaks into small, disconnected polymer-rich domains. We also find that the growth exponent characterizing the domain formation in this case is given by a purely diffusive value of $n \sim \frac{1}{3}$.

The molecular dynamics method that we have implemented here is similar to the one previously employed by Grest and co-workers [17]. To simulate a constant temperature ensemble, the monomers are coupled to a heat bath and the equations of motion read as

$$\ddot{\vec{r}}_i = -\vec{\nabla} U_i - \Gamma \dot{\vec{r}}_i + \vec{W}_i(t)\,, \qquad (1)$$

where Γ is the monomer friction coefficient and $\vec{W}_i(t)$, which describes the random force of the heat bath acting on each monomer, is a Gaussian white noise with zero mean and satisfies the fluctuation-dissipation relation: $\langle \vec{W}_i(t) \cdot \vec{W}_j(t') \rangle = 6k_B T \Gamma \delta_{ij} \delta(t - t')$. The potential U_i consists of two parts, $U_{\rm LJ}$ and $U_{\rm chain}$, where $U_{\rm LJ}$ is just a simple Lennard-Jones (LJ) potential acting between any two pair of monomers and $U_{\rm chain}$ is the anharmonic spring potential acting between pairs of successive monomers along a chain. We have integrated the equations of motion following an accurate scheme developed by van Gunsteren and Berendsen [18] which uses a bivariate distribution of Gaussian random numbers for the stochastic forces. A very fast Gaussian random number generator [19] and a link-cell list for calculating the forces [20] help to make the integration quite efficient. Time steps of 0.01–0.015 (in reduced units) produce stable integration at temperatures of interest.

Before performing the quench experiments, we have first estimated that the θ temperature for this model in two dimensions is $T_\theta(r_c = 2.5\sigma) \approx 0.9$ in reduced units, where σ is the standard LJ parameter and r_c is the cutoff distance. A quench of a polymer solution from a high temperature single phase to a temperature below T_θ should produce a phase separation of the polymer chains from the solution. Rather than carrying out such a temperature quench, we have prepared the solution as a good solvent for the polymer chains by using a cutoff distance $r_c = 2^{1/6}\sigma$. For this cutoff, the LJ interaction is purely repulsive, and this is an efficient way of producing an initial condition of a single, homogeneous state of the system at any temperature. We chose the initial temperature to be below $T_\theta(r_c = 2.5\sigma)$ but kept the cutoff at $r_c = 2^{1/6}\sigma$ and then abruptly increased the cutoff to $r_c = 2.5\sigma$ at time $t = 0$. The evolution of the system is then monitored at various times after such a quench and various quantities are measured to quantify the growth law of domains, and the dynamical scaling behavior of the scattering intensity. We have considered system sizes of 128^2 and 256^2 and considered chain lengths of $N = 100$ for monomer concentrations of about 20% and 30%. We have also carried out simulations for shorter chains of length $N = 10$.

In Figs. 1 and 2, we show two typical sets of evolutions for $N = 100$ and for polymer area fractions 30% and 20%, respectively. Note that, in all of these cases, the polymer-rich phase is a *minority* phase, and one expects nucleation and growth of *circular* droplets in a corresponding case of small molecular mixture. However, as one can see in Fig. 1, the polymer-rich phase at early times is made out of a percolating network structure while the solvent regions are enclosed by the network even though the solvent area fraction is much larger than the polymer area fraction. Another interesting observation is that the network is connected by thin polymer-rich regions. The morphology of this network domain structure closely resembles the experimental observation of Tanaka and the network

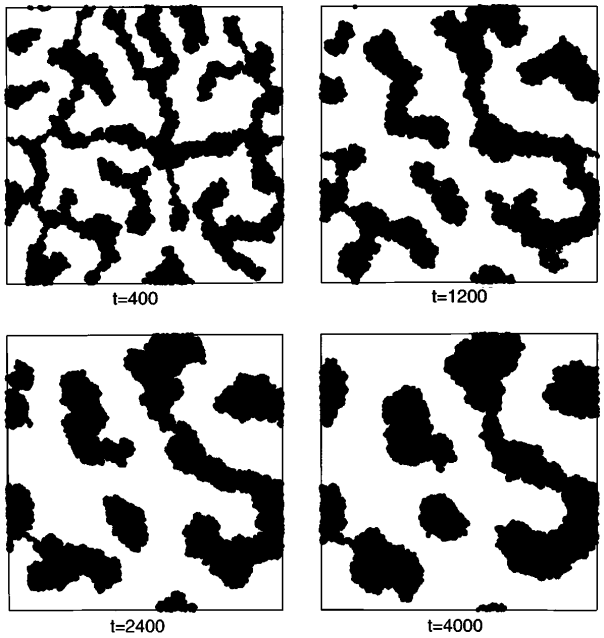

FIG. 1. Snapshots of evolutions for a 30% polymer solution with chain length $N = 100$ at a quench temperature 0.5 (in reduced unit) for times 400, 1200, 2400, and 4000, respectively. The MD simulations were done for 5000 monomers confined in a two-dimensional box of length 128 (in units of LJ parameter σ) with periodic boundary conditions along both x and y directions with $\Gamma = 1$, and MD time step 0.01.

[3] structure obtained in a simulation of a coarse-grained model [14]. This network, however, coarsens in time and at late times starts breaking into disconnected polymer-rich elongated domains. For a slightly lower area fraction with $N = 100$ (see Fig. 2), the network is present at very early times but it quickly breaks up into polymer-rich droplets, albeit noncircular ones. In contrast, a similar quench for $N = 10$ for both area fractions 30% and 20% produces droplets of the polymer-rich phase without forming any visible network structure.

The structure formation in the system during the phase separation process is analyzed in terms of the normalized time-dependent structure factor $S(\vec{k}, t)$ and the pair-correlation function $g(\vec{r}, t)$. As a measure of the domain size, we have used the location of the first zero of the correlation function which is denoted by $R_g(t)$. A log-log plot of $R_g(t)$ versus t for the area fraction 30% (corresponding to the case presented in Fig. 1) yields a straight line with a slope of about 0.28. This suggests that the growth-law exponent might actually be governed by an extended Lifshitz-Slyozov theory [21] of diffusive domain growth: $R_g(t) = a + bt^{1/3}$. This growth exponent is found in binary liquid mixtures at early to intermediate times before hydrodynamic effects become important [6]. We plot in Fig. 3 $R_g(t)$ versus $t^{1/3}$ and find that the straight-line fit works well for both quench temperatures $T = 0.5$ ($\equiv 0.55T_\theta$) and $T = 0.75$ ($\equiv 0.83T_\theta$), as well as for other area fractions and chain lengths.

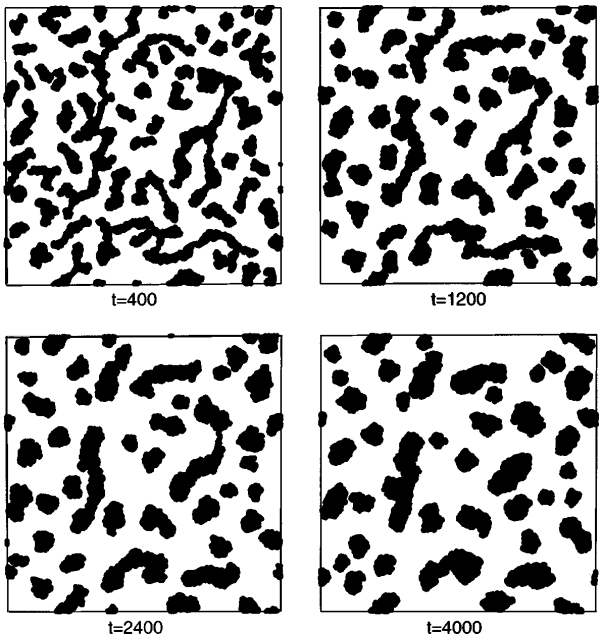

FIG. 2. Snapshots of evolutions for a 20% polymer solution with chain length $N = 100$ at a quench temperature 0.5 (in reduced unit) for times 400, 1200, 2400, and 4000, respectively. The MD simulations were done for 13 100 monomers confined in a two-dimensional box of length 256 (in units of LJ parameter σ) with periodic boundary conditions along both x and y directions with $\Gamma = 1$, and MD time step 0.01.

Next, we explore the possibility of a dynamical scaling behavior of the structure factor for a detailed comparison with small molecular mixtures. According to the dynamical scaling hypothesis [6], the structure factor behaves as $S(k,t) = R_g(t)^d \mathcal{F}[kR_g(t)]$, where d is the system dimensionality and $\mathcal{F}(x)$ is a time independent scaling function. A plot of $S(k,t)/R_g(t)^2$ versus $kR_g(t)$ in Fig. 4 shows that dynamical scaling holds reasonably well at late times. From a log-log plot of this scaling function, we find that, for large values of k, the structure factor satisfies the well-known Porod's law [6]: $S(k,t) \sim k^{-3}$ in two dimensions. Thus, even though the conformation of the phase-separated domains are quite different for the polymer case in comparison with a small molecular liquid mixture, the standard description of the phase separation kinetics in terms of a growth-law exponent and scaling behavior of the structure factor remain valid nevertheless.

In small molecular mixtures, surface tension is the main driving force behind the coarsening and growth of circular domains. In polymer solutions with the two components having widely different viscoelastic properties, it is possible that the viscoelastic stress would retard the formation of circular droplets and stabilize a network structure of elongated polymer-rich domains. From a numerical study of a coarse-grained model, Taniguchi and Onuki have suggested this mechanism to explain the network pattern formation seen in Tanaka's experiments. Although our MD simulations of a chain model seem to agree with this general view, some comments are in order. First, hydrodynamic interactions are screened [22] due to a violation of global momentum conservation in the constant-temperature stochastic MD simulation method that we have used. Even in the absence of hydrodynamics, the elastic nature of the polymer chains is a sufficient ingredient to produce a network pattern formation. For this reason, it is not surprising that the growth-law exponent found here is a purely diffusive one for all of the area fractions considered [6]. However, we have not observed any anomalously slow exponent as seen by Tanaka. We note here that the methodology used by Tanaka to extract the growth exponent has recently been criticized by Haas and Torkelson. Moreover, the chain lengths used in our MD

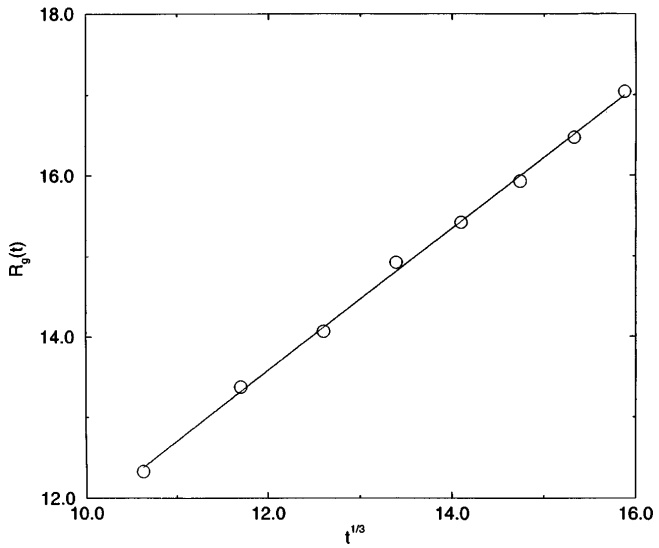

FIG. 3. Domain size $R_g(t)$ as a function of $t^{1/3}$ for a 30% polymer solution with chain length $N = 100$ at a quench temperature 0.5. The straight-line fit works quite well over the time span of the MD simulation. The fit also works for a quench temperature 0.75.

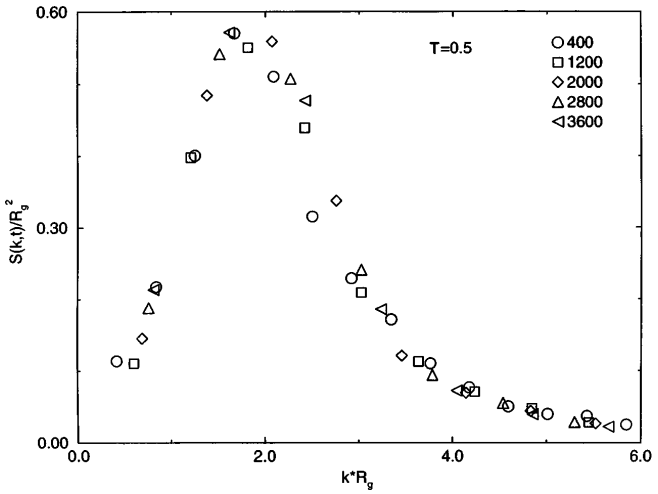

FIG. 4. Scaled structure factor $S(k,t)/R_g(t)^2$ versus $kR_g(t)$ for a 30% polymer solution with chain length $N = 100$ at a quench temperature 0.5. Scaling seems to hold reasonably well at late times.

study are quite smaller than those in a real, experimental study [23]. Thus, the time scales (and the solution concentration) over which the network forms and subsequently relaxes is expected to be quite different in experimental situations [24]. When one compares the time scales of MD with experimental time scales, it becomes immediately clear that the network structure can last only over an early to intermediate time regime of experimental time scales. In addition, our simulations also demonstrate that the network pattern formation can be seen at early stages only when the monomer concentration is larger than the overlap threshold c^*. Since the overlap threshold is a function of the molecular weight or chain length (in two dimensions $c^* \sim N^{-1/2}$), the network pattern formation at early stages can only be seen for those choices of N and monomer concentration c, such that $c > c^*(N)$. We note here that the overlap threshold concentration for $N = 100$ in two dimensions is about $c^* \approx 0.1$, while the network pattern formation for $N = 100$ is only seen for concentrations several times larger than this value. Thus, it is not surprising that in experiments with dilute or barely semidilute polymer solutions one would not observe this remarkable pattern formation at late times. This conclusion is supported by the experiments of Haas and Torkelson which have been carried out to a much later time than Tanaka. In contrast to Tanaka's observations, Haas and Torkelson do not find a network pattern formation for any value of the volume fraction of the polymer.

In summary, we have carried out molecular dynamics simulations of phase separation in a quenched polymer solution. Simulations clearly demonstrate the existence of a networklike pattern formation at an early to intermediate time regime for sufficiently dense polymer solutions. This network structure, however, relaxes at late times as the minimization of the interface energy wins over the elastic stress of the network. This explains why various experiments carried out to various time regimes claim contradictory results. Our results also strongly indicate that the *true* late-time growth kinetics of quenched polymer solutions belong to the same universality class of small molecular mixtures.

This work has been supported by National Science Foundation Grants No. CHE-9633798 (A. B. and S. D. M.) and No. DMR-9413513 (A. C.), and also by the Kansas Program for Complex Fluid Flows (NSF-EPSCoR). A. C. thanks Gary Grest for many useful discussions.

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