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Scaling behaviors of pinning in polymerization-induced phase separation

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A dynamical model for the phase separation induced by polymerization has been developed and studied by Monte Carlo simulations. The model shows a pinning of the structure factor and exhibits scaling relations and exponents. We propose a theoretical argument to predict the pinning exponents, which are in agreement with simulation values. For a different concentration ratio of bifunctional to tetrafunctional monomers, the simulation results are also found to be consistent with the theoretical predictions.

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Phase separation with simultaneous polymerization, which can be induced by thermal quench and/or polymerization, has received considerable attention. In the presence of simultaneous polymerization, the kinetics of phase separation is different from the usual kinetics of spinodal decomposition [1–7]. The branching and cross-linking polymers that influence the process of phase separation give rise to a pinning of the time-dependent structure factor, i.e., after a crossover time the morphology of a system has no further change. For controlling the morphology, many studies have focused on the system of polymerization-induced phase separation (PIPS) [4–8]. The phase separation induced by polymerization can be demonstrated in a mixture of monomers in a good solvent with a suitable amount of curing agent. For example, polymer-dispersed liquid crystal (PDLC) materials are derived from the polymerization of a solution of liquid crystal in monomers with a photoinitiator. The mixture is initially homogeneous. When the cure reaction proceeds, the system is thrust into a two-phase regime caused by a molecular weight increase and phase separation takes place via spinodal decomposition [5,8]. As the polymerization completes, the materials are in a solid inhomogeneous microphase, which exhibit a frozen spatial domain size of a polymer-rich or solvent-rich phase as a pinning of the structure factor.

The study of the isothermal spinodal decomposition in the physics of ordering [9] is an interesting subject. In addition, controlling the final structure of the materials is important to acquire expected properties, for example, the electro-optical properties of PDLC's [10] and polymer stabilized cholesteric liquid crystals [11]. Recently, a theoretical model was developed for phase separation in a system with two disparate energy scales to study a pinning of the structure factor in a thermally quenched phase separation with simultaneous polymerization and a scaling idea was proposed to describe the pinned domain size and crossover time [12,13]. However, for PIPS, using a scaling concept to realize the final structure of the system has not been addressed in either experimental and theoretical studies. Here we develop a model for the PIPS process and show that the polymerization driven by the curing agent leads to the revelation of scaling relations and pinning exponents.

The model for the PIPS system has the key feature that the mechanism of polymerization is driven by the curing agent and obeys the radical addition polymerization [14,15]. The bifunctional and tetrafunctional monomers and zero-functional solvent molecules are initially randomly distributed on a periodic square lattice of L^2 sites. The concentration of bifunctional C_b and tetrafunctional C_t monomers and solvent molecules C_s is related to $C_b + C_t + C_s = 1$. The functionality of each monomer gives the maximum number of its available bonds. A number of isolated radical molecules (curing agent) L^2C_i are randomly placed on monomers by reducing one available bond. A site with a radical is called an active center. An active center and an available nearest neighbor that is not fully bonded can form a chemical bond and the radical moves to the nearest-neighbor site and then the pair of nearest neighbors become part of a polymer. Active centers are annihilated when they bond together. We assume that the interaction energies of nearest-neighbor pairs are identical, except that of a chemical bond; the interaction of a chemical bond in a polymer is much stronger. According to the above assumption, a chemical bond forms when an active center meets an available nearest neighbor and is not allowed to break, and the molecules excluding polymers are allowed to randomly exchange positions.

During the course of the Monte Carlo simulation, a pair of nearest-neighbor sites is randomly selected. If one of the sites is an active center and the other site is an available neighbor, a chemical bond forms. Otherwise, if neither of these two sites belongs to a part of a polymer, then the molecules on the two sites exchange positions via Kawasaki dynamics [16]. Here we assume that the time constants associated with bond formation and position exchanging are equivalent. In real experiments, the time constants may depend on the concentration, temperature, and ultraviolet (uv) light intensity for uv photo-polymerized systems. The simulations are performed on a lattice of size $L = 256$ with periodic boundary conditions from 50 independent Monte Carlo simulations. The time unit is the Monte Carlo step (MCS) including a process of L^2 pairs.

The quantity to represent the spatial variation of the morphology is the spherically averaged structure factor

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$\bar{S}(k,t)$, which is the average of $S(\vec{k},t)$ over a spherical shell in wave vector $\vec{k}$ space with $|\vec{k}| = k$. The structure factor $S(\vec{k},t)$ is defined as the Fourier transform of the spatial correlation function of the dielectric constant at time t. Here we assume that monomers have the same dielectric constant as polymers but different from solvent molecules. In an ordinary phase separation process, the characteristic wave vector k_m corresponding to the maximum of the structure factor $\bar{S}(k,t)$ decreases as the characteristic domain size increases. Experiments k_m can be measured as a function of time by tracing peak intensity of scattered light.

Figure 1 (a) shows the time dependence of k_m for $C_s = 0.5$, $C_b = 0.0$, and different values of C_i. We find that k_m decreases with time until a pinning occurs at a crossover time. In the two distinct time regimes of the phase separation process, k_m behaves as

$$k_m \sim \begin{cases} t^{-\alpha}, & t \ll t_c \\ k_f = \text{const}, & t \gg t_c, \end{cases} \tag{1}$$

where k_f is the frozen wave vector and t_c is the crossover time that separates these two regimes. For $C_i = 3.0 \times 10^{-4}$, we obtain $\alpha = 0.33 \pm 0.01$. Note that as the value of $C_i = 0$, the polymerization does not take place and it is impossible to progress phase separation. Furthermore, as $C_i = 1 - C_s$, the polymerization proceeds rapidly, and phase separation is not obvious. For $t \gg t_c$, Fig. 1(b) shows that k_f increases with C_i according to a power law

$$k_f \sim C_i^{\phi}, \tag{2}$$

with $\phi = 0.53 \pm 0.05$. Figure 1(c) shows that the crossover time decreases with C_i with the relation

$$t_c \sim C_i^{-\psi}, \tag{3}$$

with $\psi = 1.48 \pm 0.03$. The behavior of the wave vector k_m found above is consistent with the scaling form

$$k_m \sim t^{-\alpha} f(t/C_i^{-\psi}), \tag{4}$$

where the scaling function $f(x) \sim$ const for $t \ll t_c$ and $f(x) \sim x^{\alpha}$ for $t \gg t_c$. The above scaling form implies

$$\phi = \psi\alpha. \tag{5}$$

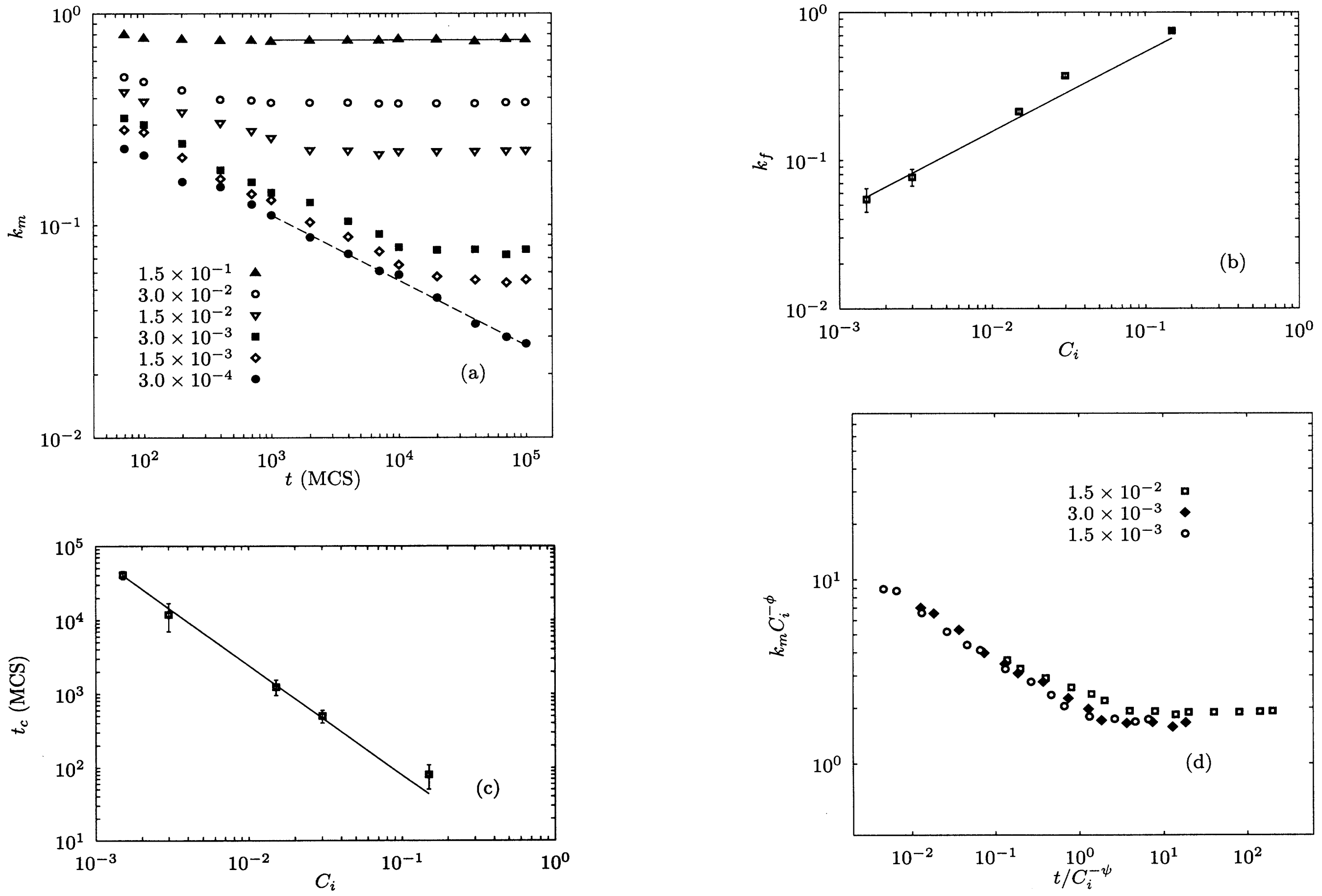

FIG. 1. (a) Double logarithmic plot of k_m against time for various values of C_i. The unit for k_m is inverse lattice spacing. The line through the $C_i = 3.0 \times 10^{-4}$ has slope 0.33. (b) Double logarithmic plot of k_f vs C_i [obtained from (a)]. The unit for k_f is inverse lattice spacing. The line has slope 0.52. (c) Double logarithmic plot of t_c vs C_i [obtained from (a)]. The line has slope 1.48. (d) The scaling function $g(t/C_i^{\psi}) = k_m C_i^{-\phi}$ vs the scaled time t/C_i^{ψ} [obtained from (a)].

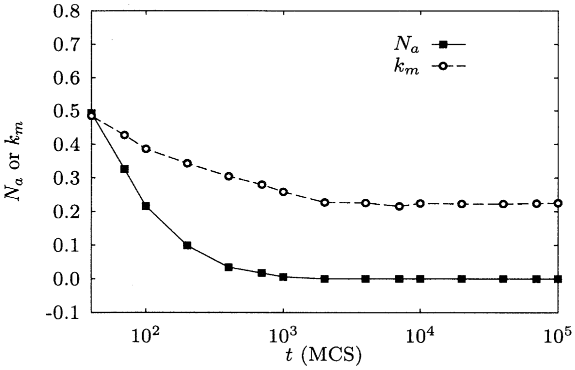

FIG. 2. Plot of N_a and k_m against time for $C_s = 0.5$, $C_i = 1.50 \times 10^{-2}$, and $C_b = 0.0$.

Equivalently, we can postulate that

$$k_m \sim C_i^{\phi} g(t/C_i^{-\psi}), \tag{6}$$

so that we should obtain the same scaling function if we plot the product $k_m C_i^{-\phi}$ as a function of $t/C_i^{-\psi}$. As shown in Fig. 1(d), a reasonably universal curve was obtained for small C_i.

To predict the pinning exponents ϕ and ψ, we should have another scaling relation. Since the phase separation is induced by polymerization, additional phase separation should not progress when polymerization is terminated. We propose that the mechanism for this pinning may be caused by the termination of polymerization. As the radius ξ of a polymer chain becomes of the order of the average distance l between the polymer chains, almost all of the useful active centers whose nearest neighbors are not fully bonded should annihilate, i.e., the number of the useful active centers decrease to a value of zero, and this leads to polymerization termination. To support our argument, Fig. 2 shows the time dependence of k_m and the normalized number N_a of useful active centers, which is defined as the number of useful active centers divided by the initial total number of active centers. Indeed, we can find that k_m has no obvious change after N_a reaches zero. Since the active centers are initially randomly distributed, the average distance between them is of order $C_i^{-1/d}$, i.e., $l \sim C_i^{-1/d}$. Consequently, at the crossover time t_c the characteristic polymer size $\xi(t_c)$ has

$$\xi(t_c) \sim l \sim C_i^{-1/d}, \tag{7}$$

where d is the spatial dimension. Since $\xi \sim k_m^{-1} \sim t^{\alpha}$, it implies $C_i \sim t_c^{-\alpha d}$. As $t_c \sim C_i^{-\psi}$, we hence obtain another scaling relation $\psi = 1/\alpha d$. Simply, the scaling relations for the pinning exponents can be written as

$$\phi = 1/d, \tag{8}$$

$$\psi = \frac{1}{\alpha d}, \tag{9}$$

where we can find that the exponent ϕ depends only on the spatial dimension d. For $\alpha = 1/3$ and $d = 2$, the above exponent relations Eqs. (8) and (9) predict $\phi = 1/2$ and $\psi = 3/2$, which agree with the values $\phi = 0.53 \pm 0.05$ and $\psi = 1.48 \pm 0.03$ found in our simulations. In addition, for a different concentration ratio $C_b/(C_t + C_b)$ of bifunctional to tetrafunctional monomers, the results of the simulation are compared with the exponents of theoretical predictions as shown in Fig. 3. Within the accuracy of the simulations, there is good agreement between theory and simulation.

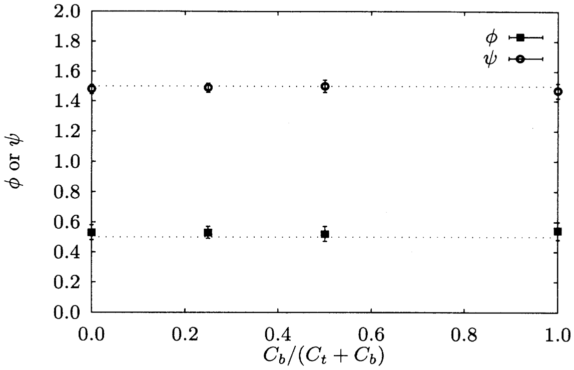

FIG. 3. Points for the pinning exponents ϕ and ψ are the simulation results obtained from fitting Eqs. (2) and (3). For each value of $C_b/(C_t + C_b)$, $C_s = 0.5$ and C_i is taken as 1.5×10^{-1}, 1.5×10^{-2}, and 1.5×10^{-3} individually.

The proposed model can be used to explain the phase separation phenomena derived from polymerization in mixtures such as liquid crystal–epoxy [4,5] and liquid rubber–epoxy [6,7] with initiators. The liquid crystals and liquid rubbers are regarded as the zero-functional solvent molecules. Without polymerization, the initially homogeneous mixture remains miscible. When the initiators are excited, the polymerization reaction begins and increases the average size of the polymer molecules; then the system becomes unstable and phase separation takes place. The phase separate proceeds until the polymerization reaction is completed. The concentration of initiator is critical in determining the morphology of the resulting materials. The larger concentration of initiator resulted in a smaller domain size and the shorter polymerization process are quantitatively in agreement with our study. However, more systematic experimental study is needed to examine the scaling ideas. The value α of the PIPS has been reported in recent experiments. In a mixture of liquid crystal and epoxy, α had two disparate values 1/3 and 1 in the early and late stages, respectively [5]. The values $\alpha = 0.83 - 1.07$ were obtained in a mixture of liquid rubber and epoxy [7]. In our study, we found that for small C_i, the value $\alpha \sim 1/3$. Since the movement and flexibility of polymers are neglected, coalescence due to surface tension is not included in our model. However, we propose a dynamical model that explains the nature of PIPS systems and the pinned structure and crossover time can be related to the concentration of the curing agent.

In conclusion, we have developed a dynamical model to study the phase separation induced by polymerization. The model takes into account the concentration of the curing agent and the functionality of the monomer in the radical addition polymerization. According to the assumption that interaction energies of nearest neighbors, except that of a chemical bond, are identical, we studied the phase separation induced by polymerization instead of the usual thermal quench. In the presence of strong chemical bonds, the phase separation leads to a pinning of the structure factor. Different scaling relations for the pinning in the phase separation were found. We proposed a mechanism to explain the nature of this pinning and predict the pinning exponents. The simulation data are also in agreement with the theoretical predictions for a different ratio of bifunctional to tetrafunctional monomers. We hope that our study will encourage more systematic experimental investigations to test these scaling ideas.

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