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Kinetics of polymerization-induced phase separation

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Abstract

We have studied a Monte Carlo computer simulation on a model for polymerization-induced phase separation. The time evolution of the structure factor are found to preserve the scaling law obtained from the thermally quenched phase separation. A novel peaking behavior of the mean cluster size of solvent molecules has been found and can be explained by the irreversibility of polymerization. The simulation results are in agreement with experimental observations.

1. Introduction

Polymerization-induced phase separation (PIPS) can be demonstrated in a mixture of liquid crystal/epoxy [1,2] or liquid rubber/epoxy [3-5] with suitable amounts of curing agents. The mixture is initially homogeneous and remains miscible without polymerization. Upon polymerization, phase separation occurs causing the morphology of the mixture to separate into discrete domains. It has been shown that polymerization reaction drives the system unstable by increasing the average size of polymer molecules and phase separation takes place via spinodal decomposition [2,3]. Because of the presence of cross-linking polymers and the isothermal phase separation, the kinetics of the phase separation is different from the usual kinetics of spinodal decomposition.

Recently, a material consisting of liquid crystals and polymers formed by PIPS has received considerable attention in display applications and fundamental scientific interest [6]. For controlling the morphology and the properties of the material, it is important to study the formation process of PIPS. Here we use Monte Carlo computer simulations of PIPS to show that the time evolution of the structure factors exhibits dynamical self-similarity and that the mean cluster size of solvent molecules (liquid crystals or liquid rubbers) has an interesting peaking behavior.

2. Model

The model consists of zero-functional solvent molecules, bifunctional and tetra-functional monomers and curing agents. The key feature of this model includes not only addition-polymerization between curing agent and monomer [7–10], but also the Kawasaki exchange dynamics of nearest-neighbor monomer and solvent molecule pairs [11]. Initially, the bifunctional and tetrafunctional monomers and zero-functional solvent molecules are randomly distributed on a square lattice of size L , and a fraction C_i of curing agents is placed on randomly selected monomers. The concentration of bifunctional C_b and tetrafunctional C_t monomers and solvent molecules C_s are related by $C_b + C_t + C_s = 1$. The functionality of the monomer gives the maximum number of bonds that can be formed. The monomer connected to a curing agent reduces one bond and acts as the active center for polymerization. An active center and an available nearest neighbor, which is not fully bonded, can form a chemical bond and the active center is transferred to the nearest-neighbor site; then the pair of nearest neighbors become a part of the polymer. Active centers are annihilated when they both bond together. We assume that the interaction energies of nearest-neighbor pairs are identical except that of the chemical bond, and the interaction of the chemical bond 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. Besides, different polymerization and exchange rates are considered by introducing a time ratio θ which is defined as

$$\theta = \frac{t_p}{t_e}, \quad (1)$$

where t_p is the time to form a bond in polymerization and t_e is the time to exchange position between two nearest-neighbor molecules. The time ratio θ we studied is in the range $0 < \theta \leq 1$.

During the course of the Monte Carlo simulation, pairs of nearest-neighbor sites are 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 can exchange positions with a probability equal to θ .

In order to represent the spatial variation of the morphology, the spherically averaged structure factor $\bar{S}_f(k, t)$ is calculated. It is defined as the average of the structure factors over a spherical shell in wave vector \mathbf{k} space with $|\mathbf{k}| = k$. In an ordinary phase separation process, the characteristic wave vector k_m corresponding to the maximum of the structure factor $\bar{S}_f(k, t)$ decreases as the characteristic domain size increases. Experimentally a light-scattering profile is proportional to $\bar{S}_f(k, t)$ and k_m can be measured as a function of time by tracing the peak intensity of the scattered light. Another interesting quantity is the mean cluster size of solvent molecules $S_c(t)$ defined as

$$S_c(t) = \frac{\sum_s s^2 N_s(t)}{\sum_s s N_s(t)}, \quad (2)$$

where $N_s(t)$ is the number of clusters of size s at time t , and a cluster is defined as a group of neighboring solvent molecule sites. The quantity is important for the configuration of liquid crystals in the mesh of polymers in liquid-crystal-polymer mixtures. In this study, all of the calculations are performed on a lattice of $L = 256$ with periodic boundary conditions from 300 independent Monte Carlo simulations.

3. Results and discussion

Fig. 1a shows the time evolution of the structure factors $S_f(k, t)$ versus the wave vector k . As phase separation proceeds, the maximum of the structure factor moves to smaller wave vectors, while the maximum value of the structure factor increases with phase separation time. The result is similar to the behavior observed in the phase separation induced by the usual thermal quench. Another interesting result is that after a crossover time the structure factor ceases to evolve, *i.e.* the structure factor has become pinned, and this result is different from the usual kinetics of phase separation. As shown in Fig. 1b, the time dependence of k_m decreases with time until a pinning occurs. The power-law dependence of k_m on t before the pinning obeys

$$k_m \sim t^{-\alpha}, \quad (3)$$

and we find that $\alpha = 0.23 \pm 0.01$. Self-similarity in the late stages of phase separation demands a scaling law for the structure factor [12]

$$S_f(k, t) = k_m^{-d} F(k/k_m), \quad (4)$$

where k_m is the value of k corresponding to the maximum of S_f and d is the spatial dimension. If the simulation data are consistent with the scaling law, we should obtain the same scaling function by plotting the product $S_f(k, t)k_m^d$ as function of k/k_m where $d = 2$ for the two-dimensional simulation. As shown in Fig. 1c, reasonably superimposed master curves were obtained for different times in the late stages of phase separation.

Fig. 2 shows the time-dependent mean cluster size S_c of solvent molecules for different values of C_s . A peaking behavior of the mean cluster size is found: S_c increases before reaching a maximum value and then decreases to a saturated value, if C_s is larger than a specific value. In Fig. 3 we show the time dependence of S_c for different time ratios θ . As seen from the figure, the peak position of S_c is located at the later time for smaller time ratio θ , and the peak value of S_c increases with θ . Since smaller time ratio θ means slower mobile solvent molecules and monomers, it is reasonable that the aggregation rate of solvent molecules for smaller θ should be slower than the rate for larger θ . Besides, as the phase separation is derived from polymerization, the aggregation rate of solvent molecules should depend on the degree of polymerization. As shown in Fig. 3, the maxima of S_c occurs at almost the same degree of polymerization $p = p_m$ for different θ , where the degree of polymerization p is defined as the total number of bonds formed divided by maximum number of possible bonds $2L^2$.

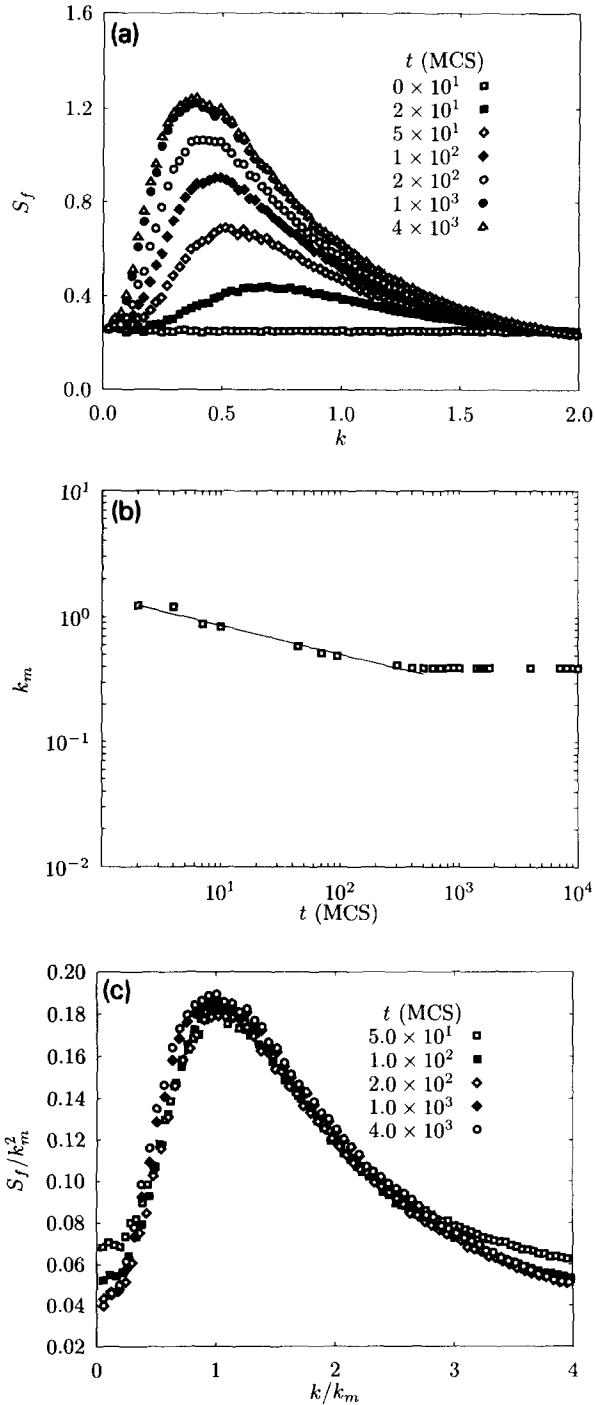


Fig. 1. (a) Time evolution of the structure factor $S_f(k, t)$ vs wave vector k for $C_i = 0.03$, $C_s = 0.50$, $C_b = 0.0$ and $\theta = 1.0$ (b) Double logarithmic plot of k_m against time with the same parameters given in (a). The line has slope 0.23. (c) The scaling function $F(k/k_m)$ vs the scaled wave vector k/k_m [obtained from (a)].

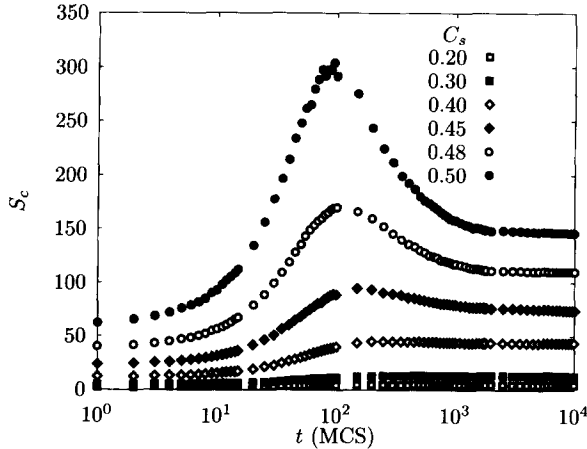


Fig. 2. Time dependence of S_c for various values of C_s , and $\theta = 1.0$, $C_i = 0.03$, $C_b = 0.0$.

To explain the peaking behavior of the mean cluster size S_c , we proposed two competing mechanisms driven by the polymerization. First, the polymerization reaction forces the solvent molecules into aggregation while it actively forms a solid connection between monomers. Second, beyond a specific degree of polymerization an additional phase separation is confined to the mesh of polymers so that the cluster size of the solvent molecules decreases. It is apparent that the former and latter mechanisms dominate in the early and later stages of polymerization, respectively. These two mechanisms imply that the solvent molecules first aggregate and then separate during the course of polymerization.

Recently, a light-scattering study on the kinetics of polymerization-induced phase separation in a liquid-crystal-polymer mixture found that the scaling law (4) exists in experiment [2]. These results show that dynamic self-similarity is preserved in the PIPS process and our simulation is consistent with the experimental observation. In the same experiment, a second phase separation process, where the spontaneous phase separation takes place for a second time in the already phase-separated domains, has been observed. In our study, the behavior of the mean cluster size of the solvent molecules, which initially increases and decreases at a later time, is in agreement with the experimental observations.

4. Conclusion

A model including addition-polymerization between curing agent and monomer, and the Kawasaki exchange dynamics of nearest-neighbor monomers and solvent molecule pairs has been used to study the phase separation induced by polymerization. The time-dependent structure factor exhibited a scaling behavior obtained from a thermally quenched binary mixture. This result is in agreement with experimental studies of

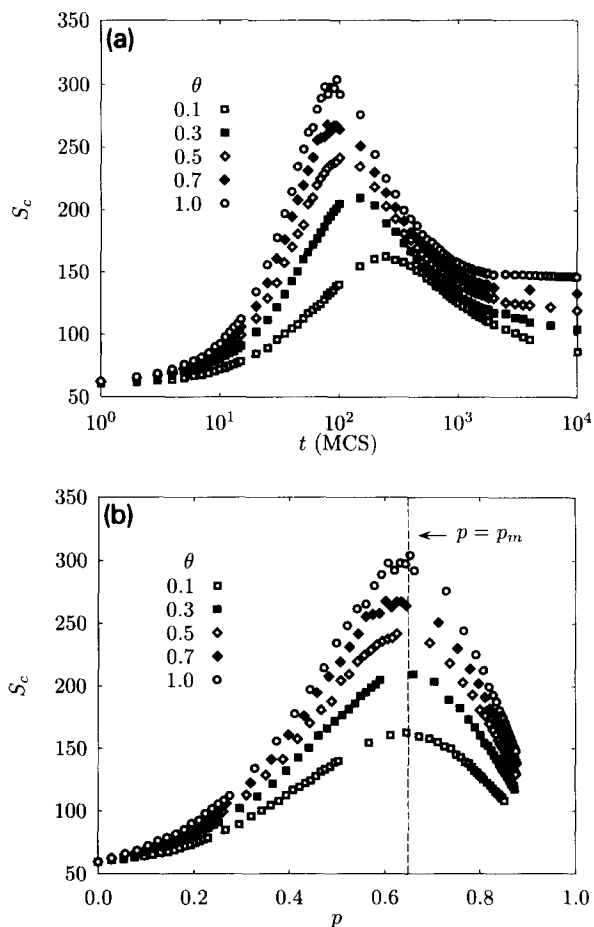


Fig. 3. (a) Time dependence of S_c for various values of θ , and $C_i = 0.03$, $C_x = 0.50$, $C_b = 0.0$ (b) Plot of S_c with degree of polymerization p [obtained from (a)].

a liquid-crystal-polymer mixture. A novel peaking behavior of the mean cluster size of the solvent molecules is found and can be explained by the irreversibility of the polymerization reaction. The simulation results are found to be consistent with the experimental observation. We suggest that this model can be used to study the formation process of polymerization-induced phase separation.

Acknowledgements

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