Effect of Polymerization Reactivity, Interfacial Strength, and Gravity on Polymerization-Induced Phase Separation

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ABSTRACT: The effect of polymerization reactivity, interfacial strength, and gravity on the size and distribution of the liquid crystal droplets in polymer-dispersed liquid crystal (PDLC) films obtained by a polymerization-induced phase separation (PIPS) process is studied by a newly developed reversible cluster−cluster aggregation model. These parameters directly influence the formation of polymer networks and, therefore, can modify the final state of PDLC films. Our simulation shows that the droplet distribution function P of the liquid crystal assumes a narrower spectrum when the polymerization reactivity and the interfacial strength between the liquid crystal and the polymer increases, while its main peak position remains virtually unchanged (at around $N = 1$). At weak interfacial strength the gravity is found to play a minor role in the controlling of the size of the liquid crystal droplets. However, the gravity effect on the size of the liquid crystal droplets becomes a dominant factor when interfacial strength increases.

I. Introduction

Polymer dispersed liquid crystal (PDLC) materials have recently been extensively studied because of their wide range of potential industrial applications, such as switchable windows, optical shutters, and information displays.[1,2] A PDLC film is composed of microdroplets of liquid crystal finely dispersed in a polymer matrix. The size and distribution of these droplets have a significant impact on the film's electro-optical property.[3,4] Therefore, a key step in the control of the quality of PDLC films is to adjust the size and distribution of the liquid crystal droplets according to specific needs. Polymerization-induced phase separation (PIPS) and thermally induced phase separation (TIPS) are two of the commonly used phase separation techniques in the preparation of PDLC thin films. In order to control and optimize the electro-optical properties of PDLC films, it is imperative to identify and to understand the importance of the parameters involved in the phase separation process. There is a fundamental difference between the TIPS and PIPS processes. In the former case the thermodynamic instability in either the metastable (nucleation and growth) or the unstable (spinodal decomposition) zone is responsible for the phase separation. The growth of the new phases in this case can be described by aggregation. In the PIPS case, the phase separation is a kinetic process and both the separation and growth may be described by cluster aggregation. Having discussed the TIPS process in our early work,[5,6] we consider, in this study, only the PIPS process where the phase separation and coarsening are described by cluster aggregation. The PIPS process may be described by a sol−gel type of transformation. In the sol phase the mobilities of the prepolymers and the liquid crystal molecules in their mixture are large so that there is *a priori* an equal probability of finding these particles at all the points in space, leading to what we call a homogeneous solution. As the polymerization reaction starts, a randomly distributed network begins to form by the prepolymers. The network is rather loosely bonded up to the equilibrium gel phase. Due to the formation of the polymer network, the liquid crystal molecules first nucleate to form small-size droplets, and then these droplets aggregate and coalesce at a later stage of phase separation. This process is within the framework of phase separation and coarsening.[7,8] Apart from some obvious factors that affect the polymer network (e.g., nucleation/growth or spinodal decomposition), the evolution of the polymer network may also be influenced by several other parameters, such as concentration, temperature, polymerization reactivity, and gravity,[9−16] and possibly the interfacial strength between liquid crystal and polymer. The final state of the PDLC film is very sensitive to these parameters. In this investigation we consider only three parameters, i.e., the polymerization reactivity, the interfacial strength between liquid crystal and polymer, and the gravity. We examine the way liquid crystal droplets aggregate, collide, and eventually coalesce in the PDLC mixture, and how the polymerization reactivity, interfacial strength, and gravity influence the size and distribution of the liquid crystal droplets.

The Monte Carlo (MC) simulation technique has been widely applied and proven useful in the studies of the phase separation process for binary alloy[17] and binary polymer,[18,19] although relatively little work has been done with the liquid crystal−polymer system.[5,6] In this work we employ the MC method to study the PIPS process in a PDLC mixture, in particular, we adopt a new reversible cluster−cluster aggregation model[6] to take into account the effect of interfacial strength between liquid crystal and polymer in an explicit way.

II. Model

The mixture of liquid crystal and prepolymer is simulated on a 100 × 100 square lattice with periodic boundary conditions. Each liquid crystal molecule occupies a single lattice site; therefore, for a given liquid crystal concentration c, a total of cn sites (where n [$= 10^4$] is the total number of lattice sites) are occupied by the liquid crystal, while the other sites by the prepolymer. Here, as a first degree of approximation, the liquid crystal molecules are considered to possess orientational symmetry; i.e., no orientational order parameter is involved in our simulation. The steric restrictions are applied as usual to exclude double

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occupancy of any lattice sites. Only the nearest-neighbor interaction energy (ϵ) between the molecules of liquid crystal and prepolymer is considered and assumed to be positive to favor the separation between the liquid crystal and polymer, while the other interactions are zero. While the prepolymer acts as a uniform medium, the liquid crystal molecules or droplets are free to move and stick together on nearest-neighbor contacts with probability p. Our model differs from both the irreversible cluster aggregation model[20] and the reversible growth model[21] in that the probability p itself is not simply set to unity but determined instead by the energy barrier between the droplets; i.e., p is proportional to $\exp[-E_I/kT]$, where E_I is the energy barrier for the sticking process. We would like to point out that since the above models[20,21] simply assume the sticking probability p to be equal to 1, no energy barrier exists for the sticking process. However, this is not true for the phase separation process in the PDLC system, as seen later. Therefore, these models are not suitable for the purpose of our study. As shown in ref 6, the energy barrier E_I in a liquid crystal–polymer system can be understood from a simple thermodynamic argument.[22] Considering the case of two liquid crystal droplets in a prepolymer medium, the Gibbs free energy of the system is written as $U = H - TS$, with H being the enthalpy and S the entropy of the system. When the two droplets move toward each other, the space between them narrows, decreasing the possible configurations which the prepolymer molecules (in that region) might assume; therefore, the entropy of the prepolymer molecules in that region decreases concurrently. As a result, the Gibbs free energy of the system increases, provided that the enthalpy and the temperature of the system are not changed. Once the two droplets overcome the energy barrier to merge as one single droplet, the Gibbs free energy of the system decreases due to an overall reduction in interfacial energy. Moreover, we assume that E_I is proportional to the interfacial strength ϵ_i (which characterizes the specific liquid crystal–polymer system) and the size of the droplets involved in the collision, since the space confined between the droplets in the collision (therefore the entropy S of the system) is proportional to the size of the droplets. Similar to the reversible-growth model,[21] a single liquid crystal molecule is allowed to make local adjustment within the same droplet or break away from that droplet with a probability which is proportional to $\exp[-\Delta E/kT]$, where ΔE is the change in energy due to such a move. As the polymerization reaction starts, small-size liquid crystal droplets first form and aggregate; then the polymerization reaction manifests itself in the decrease of the mobility of these liquid crystal droplets. The dependence of the mobility coefficient μ on the polymerization reactivity parameter α_p might take some complicated forms for a real system, but we, without loss of generality, simply assume that the mobility coefficient μ in our model system has a linear relationship with simulation time t. Specifically, we assume $\mu = 1 - \alpha_p t$ for $t \leq \alpha_p^{-1}$ and $\mu = 0$ for $t > \alpha_p^{-1}$, where α_p is the degree of the polymerization reaction. This linear relationship of mobility coefficient with respect to time is chosen purely for convenience. Nevertheless, it describes the main feature of the polymerization reaction in the PDLC system; i.e., upon polymerization, the mobility coefficient μ of the liquid crystal decreases as the simulation time t proceeds and finally reaches zero when a completely rigid polymer network is formed. The gravity field is introduced in the form of the gravitational potential energy $E_g = mgh$, where m is the mass of the liquid crystal cluster (m is proportional to the size of the cluster), g is the gravitational acceleration, and h is the vertical position of the center of mass of the cluster relative to the reference level (the middle row of the square lattice in the model). The standard Metropolis algorithm[23] is employed to sample the states with the correct thermodynamic distribution proportional to $\exp[-E/kT]$, where E is the total energy of each configuration. An attempted move is accepted if both the steric restrictions and the following condition are satisfied:

$$\min [\exp(-\Delta E/kT),1] \geq \zeta \qquad (1)$$

where min stands for taking the minimum of the two quantities. $\Delta E = E_f - E_i$ is the change in energy between two configurations after and before the attempted move, and ζ is a random number which is distributed uniformly in the interval between 0 and 1. These random numbers are generated by a standard subroutine available in most computer libraries. Starting from some initial configurations, the system is first homogenized at a constant temperature and then allowed to evolve according to the condition in eq 1 until a thermodynamic equilibrium state is reached. The intermediate configurations, as well as other quantities, are monitored and recorded at a certain interval of Monte Carlo steps (MCS). One MCS is one attempted move for the liquid crystal molecules, and the number of MCS measures the evolution time of the system.

III. Results and Discussion

We investigate the effect of the polymerization reactivity and the interfacial strength between liquid crystal and polymer in the PIPS process as well as the influence of the gravity field. The temperature of the system is kept constant and above the critical value since our intention here is to study the PIPS process; more precisely, we choose $\gamma = \epsilon/kT = 1.0$ (the critical value of our model[6] $\gamma_c = \epsilon/kT_c = 1.5$). The concentration of the liquid crystal in the model is also fixed, i.e., $c = 0.20$ throughout this work, but other values have the same importance. Since the aim of this work is to examine the size and distribution of liquid crystal droplets at various conditions, we first define a droplet distribution function P which is the probability of finding a liquid crystal droplet containing N molecules in a given configuration. P is obtained by counting the number of liquid crystal droplets at different sizes (N) in a given configuration and averaging for a certain time duration at the final stage of a simulation. Moreover, in order to reduce the computational error, an additional average is made over 10 different computer runs which are carried out with the same parameters but different sets of random numbers. Therefore, P directly measures the size and distribution of the liquid crystal droplets in the system.

The first simulation is carried out for a system at a fixed value of interfacial strength, i.e., $\gamma_i = \epsilon_i/kT = 0.005$, with the polymerization reactivity α_p acting as an adjustable parameter. As mentioned before, the system is first homogenized at a constant temperature, i.e., $\gamma = \epsilon/kT = 1.0$, and then allowed to develop into its equilibrium state. Figure 1 shows the variation of P (in arbitrary units) with N for polymerization reactivity $\alpha_p = 0.5$ (curve A), 2.5 (curve B), and 5.0 (curve C) (α_p is in units of 10^{-7} MCS^{-1}). The three curves have their

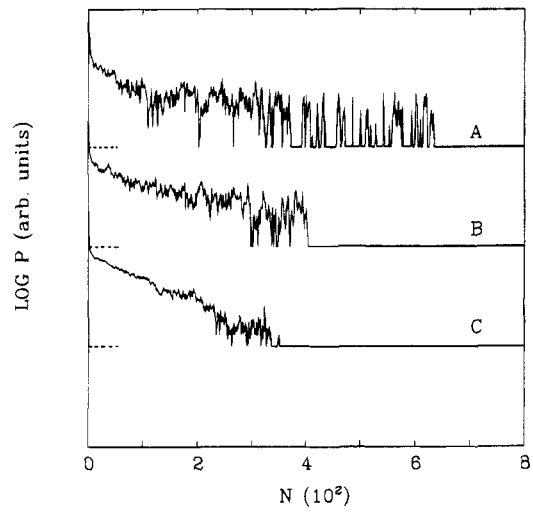

Figure 1. log P vs N showing the dependence of the droplet distribution function P (in arbitrary units) on the number of liquid crystal molecules in a droplet, N, for polymerization reactivity $\alpha_p = 0.5$ (A), 2.5 (B), and 5.0 (C) (in units of 10^{-7} MCS^{-1}). The concentration of the liquid crystal $c = 0.20$, the temperature of the system $\gamma = \epsilon/kT = 1.0$, and the interfacial strength $\gamma_i = \epsilon_i/kT = 0.005$. The short dashed line indicates the zero point for each curve.

main peak near $N = 1$, implying that the system abounds with single liquid crystal molecules or small-size droplets. Another common behavior for these curves is that there exists a maximum value for the size of the liquid crystal droplet, N_{max}, above which the droplet distribution function P drops to zero. The main difference in these curves lies in their broadness. As the polymerization reactivity increases from (A) to (C), the broadness of the curve decreases consequently with the largest size $N_{max} = 620$ in curve A and $N_{max} = 350$ in curve C. It is known that the liquid crystal droplets grow either by diffusion of single molecules or by mutual collision among the droplets. When the polymerization reactivity is relatively low (curve A), the decrease in the mobility of the molecules (or droplets) is relatively slow. Consequently, the molecules and droplets have sufficient time to diffuse and collide to form big-size droplets. However when the polymerization reactivity increases (curves B and C), the decrease in the mobility is fast, resulting in reducing the chance of forming big-size droplets, which is in line with the experimental results.[15]

Next, we examine how the size and distribution of liquid crystal droplets are affected by the interfacial strength between liquid crystal and polymer. Figure 2 shows the dependence of the droplet distribution function P on the interfacial strength γ_i with a fixed polymerization reactivity $\alpha_p = 1.0$ (10^{-7} MCS^{-1}). Curves A, B, and C represent the cases for $\gamma_i = \epsilon_i/kT = 0.002$, 0.005, and 0.02, respectively. The general appearance of the graphs is similar to the ones shown in Figure 1. The curves position their main peak around $N = 1$ and differ in their broadness. As the interfacial strength $\gamma_i = \epsilon_i/kT$ increases from 0.002 to 0.02 (curve A to C), the broadness of the curve decreases from $N_{max} = 1000$ to 200. As pointed out earlier, the diffusion and collision of the molecules and droplets are the dominant factors determining the size distribution of the liquid crystal droplets. The increase in the interfacial strength leads to the increase of the energy barrier among the liquid crystal droplets, thereby decreasing the chance of their collisions. Hence, the size of liquid crystal droplets decreases with the increasing of the interfacial strength.

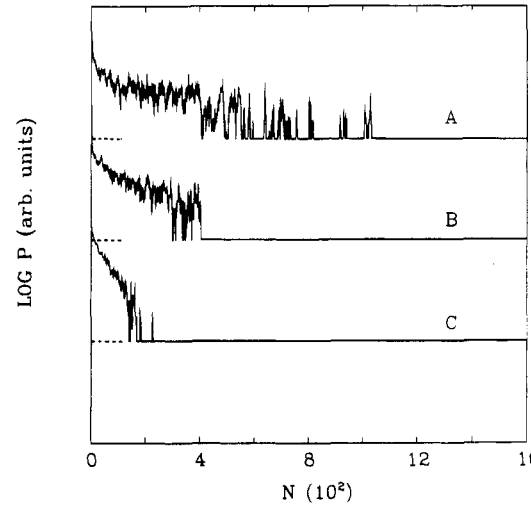

Figure 2. Variation of log P (in arbitrary units) with N for different values of the interfacial strength. Curves A, B, and C are respectively for $\gamma_i = \epsilon_i/kT = 0.002$, 0.005, and 0.02. The concentration of liquid crystal and the temperature of the system are the same as in Figure 1, but the polymerization reactivity is fixed at $\alpha_p = 1.0$ (10^{-7} MCS^{-1}). The zero point for each curve is indicated by a short dashed line.

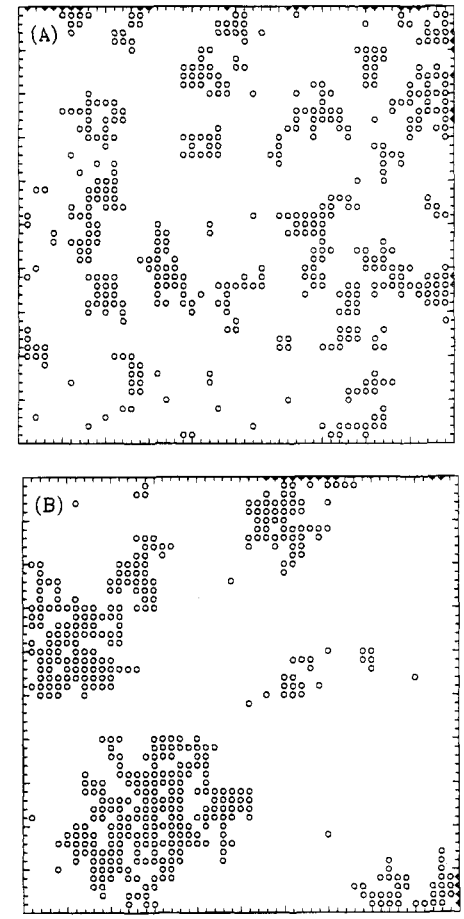

Figure 3. Comparison of two final configurations with different interfacial strengths. (A) and (B) are respectively for $\gamma_i = \epsilon_i/kT = 0.05$ and 0.005. The small open circles represent the single molecules of liquid crystal, and the white background the polymers. Other parameters are the same as in Figure 2.

In Figure 3, we present two final configurations obtained with the same polymerization reactivity $\alpha_p = 1.0$ (10^{-7} MCS^{-1}) at different interfacial strengths. Parts A and B of Figure 3 are respectively for $\gamma_i = \epsilon_i/kT$

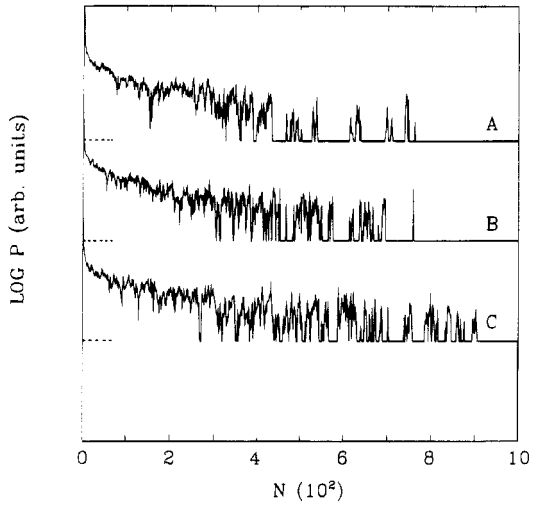

Figure 4. Dependence of log P (in arbitrary units) on N. Curves A, B, and C are respectively for $g = 0.001$, 0.002, and 0.005 (in units of kT/m_0a). The interfacial strength is chosen to be $\gamma_i = \epsilon_i/kT = 0.005$, while other parameters are the same as in Figure 2.

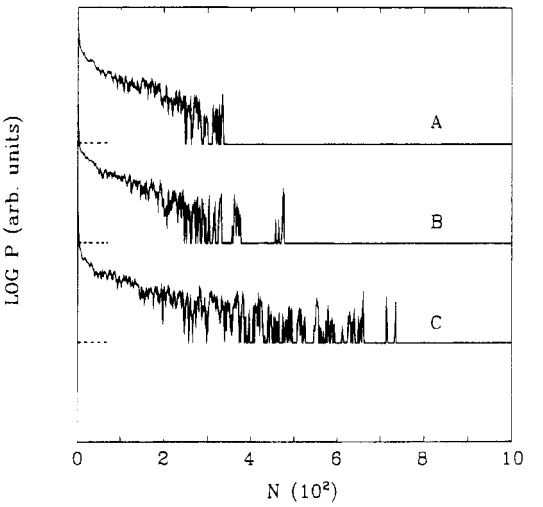

Figure 5. Relationship between log P (in arbitrary units) and N in the case of $\gamma_i = \epsilon_i/kT = 0.01$. Other conditions are the same as in Figure 4.

= 0.05 and 0.005. The difference in the size of the liquid crystal droplets is evident in these figures. This result indicates that the selection of liquid crystal and polymer in terms of their interfacial strength is crucial in the control of the quality of the PDLC films.

Finally, since most of the PDLC films are prepared under terrestrial conditions, it is interesting to see if the microgravity environment has an effect on the size and distribution of the liquid crystal droplets in PDLC films. For this purpose, we take the gravitational acceleration g as an adjustable parameter (drop tower facilities, space ships, rockets, and parabolic flights offer opportunities to carry the experiments under different gravitational environments[24]) but fix the values for both the polymerization reactivity $\alpha_p = 1.0\ (10^{-7}\ \mathrm{MCS}^{-1})$ and interfacial strength $\gamma_i = \epsilon_i/kT = 0.005$. The simulation results are shown in Figure 4, which gives the droplet distribution function P for three different values of g, i.e., $g = 0.001$ (A), 0.002 (B), and 0.005 (C). Here g is in units of kT/m_0a, with m_0 being the mass of a single liquid crystal molecule and a the lattice constant of the square lattice. From Figure 4, the general shapes are apparently similar for these curves, while the major difference lies only in the curves' broadness. This difference is, however, small, with N_{max} ranging from 800 to 900 for all three curves, indicating that under these specific conditions the gravity plays a minor role in the control of the size of the liquid crystal droplets. The results are quite different when the interfacial strength is increased. Figure 5 shows the simulation results where the interfacial strength γ_i is increased to 0.01 from 0.005 (value used in Figure 4), with the remaining parameters unchanged. Now, the effect of gravity can be seen in the changes of the broadness of the curves. As g increases from 0.001 (curve A) to 0.005 (curve C), the largest size of the liquid crystal droplets, N_{max}, increases from 350 to 750. It is well-known that the gravity field forces the liquid crystal droplets to move in the direction opposite to the gravity force (provided that the liquid crystal is lighter than the polymer) and increases their chance of mutual collision, thereby broadening the spectrum of the size distribution. In the case where the interfacial strength is weak and the energy barrier between the droplets is small, the collision rate is already very high even under the low-gravity condition. Therefore, the interfacial strength is a major factor which controls the size distribution spectrum, while the gravity plays only a minor role. On the other hand, when the interfacial strength is strong, the mutual collision rate among droplets is relatively low due to the large energy barrier between droplets, the gravity then becomes a dominant factor in the size control.

IV. Conclusions

In summary, we have studied the way the size and distribution of the liquid crystal droplets are affected by the polymerization reactivity, the interfacial strength between liquid crystal and polymer, and the gravity in the PIPS process. We have found that the polymerization reactivity and the interfacial strength between liquid crystal and polymer plays an important role in reducing the size of the liquid crystal droplets by preventing them from colliding with each other. The gravity influences the droplet size when the interfacial strength between liquid crystal and polymer is strong.

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References and Notes

(1) Doane, J. W.; Vaz, N. A.; Wu, B. G.; Zumer, S. *Appl. Phys. Lett.* **1986**, *48*, 269.
(2) Doane, J. W. *MRS Bull.* **1991**, January, 22.
(3) Alt, P. M.; Pleshko, P. *IEEE Trans. Electron Devices* **1974**, *21*, 146.
(4) Montgomery, G. P., Jr.; West, J. L.; Tamura-Lis, W. *J. Appl. Phys.* **1991**, *69*, 1605.
(5) Jin, J.-M.; Parbhakar, K.; Dao, L. H. *Comput. Mater. Sci.* **1995**, *4*, 59.
(6) Jin, J.-M.; Parbhakar, K.; Dao, L. H. *Comput. Mater. Sci.*, in press.
(7) Smith, G. W. *Int. J. Mod. Phys. B* **1993**, *7*, 4187.
(8) Kim, J. Y.; Cho, C. H.; Palffy-Muhoray, P.; Mustafa, M.; Kyu, T. *Phys. Rev. Lett.* **1993**, *71*, 2232.
(9) Doane, J. W.; Golemme, A.; West, J. L.; Whitehead, J. B., Jr.; Wu, B. G. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 511.
(10) Jiang, P.; Asada, T. *Mol. Cryst. Liq. Cryst.* **1992**, *222A*, 87.
(11) West, J. L. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 427.

(12) Golemme, A.; Zumer, S.; Doane, J. W.; Neubert, M. E. *Phys. Rev. A* **1988**, *37*, 559.
(13) Tahata, S.; Masumi, T.; Kaho, S.; Mizunuma, M. *Mol. Cryst. Liq. Cryst. Lett.* **1992**, *8*, 99.
(14) Golemme, A.; Zumer, S.; Allender, D. W.; Doane, J. W. *Phys. Rev. Lett.* **1988**, *61*, 2937.
(15) Fuh, A. Y. G.; Caporaletti, O. *J. Appl. Phys.* **1989**, *66*, 5278.
(16) Parbhakar, K.; Dao, L. H.; Tabrizian, M.; Gingras, S.; Campbell, G. *Proceedings of Drop Tower Days 94*, Bremen, Germany, July 8, 1994; pp 18–25.
(17) Pan, M.-X.; Chen, X.-S.; Sun, J.-R.; Zhao, D.-Q. *Microgravity Q.* **1993**, *3*, 209.
(18) Cifra, P.; Karasz, F. E.; Macknight, W. J. *Macromolecules* **1989**, *22*, 3089.
(19) (a) Baumgartner, A. *J. Chem. Phys.* **1984**, *81*, 484. (b) Baumgartner, A.; Heermann, D. W. *Polymer* **1986**, *27*, 1777.
(20) Meakin, P. *Phys. Rev. Lett.* **1983**, *51*, 1119.
(21) Shih, W. Y.; Aksay, I. A.; Kikuchi, R. *Phys. Rev. A* **1987**, *36*, 5015.
(22) Hunter, R. J. *Foundations of Colloid Science*; Clarendon Press: Oxford: U.K., 1987; Vol. 1, Chapter 8.
(23) Metropolis, N.; Rosenbluth, A. N.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.
(24) Antar, B.; Nutio-Antar, V. S. *Fundamentals of Low Gravity Fluid Dynamics and Heat Transfer*; CRC Press: Boca Raton, FL, 1993.

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