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SIMULATION ON THE KINETIC PROCESS IN POLYMER-DISPERSED LIQUID CRYSTALS: EFFECTS OF VARIOUS CONCENTRATION OF LIQUID CRYSTALS

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Abstract We developed a dynamical model for the formation in polymer-dispersed liquid crystals. The model has the key feature that the mechanism of polymerization obeys the radical addition polymerization and the movement of molecules is allowed by Kawasaki dynamics ¹. Monte Carlo computer simulations on this model show that the time evolutions of the structure factors exhibits dynamical self-similarity and the mean cluster size of liquid crystals has a peaking behavior until the phase separation is pinned ². In the study, the simulation was performed with various concentration of liquid crystals. The mean cluster size of liquid crystal increases as the concentration of liquid crystals increases. We found a relation between the mean cluster size and the concentration of liquid crystals. The simulation results are well consistent with recent experimental observations.

INTRODUCTION

Polymer-dispersed liquid crystals (PDLCs) derived from the polymerization in a solution of liquid crystals and monomers are a recently discovered new class of materials which have been used in many types of displays, switchable windows, and light shutters. It has been shown that the electro-optical properties of PDLC films depend strongly on the morphology of the materials ^{3, 4, 5}. The morphology of the resulting PDLC film can be controlled by the polymerization mechanism, the concentration ratios of monomer components, liquid crystal, and initiator. For example, the size of liquid crystal droplet formed by ultraviolet (uv) polymerization-induced phase separation is mainly controlled by the intensity of uv light, concentrations of liquid crystal, bifunctional monomer, tetrafunctional monomer, and polymerization photoinitiator.

For controlling the resulting morphology of PDLCs, many recent studies have focused on the materials formed by phase separation, especially, by polymerization-induced phase separation (PIPS) ^{6, 7}. Recently considerable progress has been made

in developing an understanding of polymerization and phase separation process which are of great importance in PDLC formation.

A qualitative model for description of PIPS has been developed ^{6, 8, 9}: An initially homogeneous solution of liquid crystal and multifunctional monomers is formed and thermal or radiation-induced cure reaction is initiated. During the course of curing process, the molecular weight of the polymer increases, leading to a decrease in the mutual solubility of the liquid crystal and polymer. As the solubility becomes low enough, the phase separation induced by polymerization commences. As phase separation continues, the liquid crystal droplets simultaneously grow by accretion of additional molecules as they come out of solution and diffusion and coalescence of the droplets themselves. The process continues until the polymer matrix gels and solidifies. The final resulting inhomogeneous composite materials of liquid crystals and polymers are formed.

Although a qualitative model for description of PIPS has been developed; however, the dynamical study of the system has not been well investigated in experiments and theoretical model. Recently we develop a dynamical model for PIPS. The model has key features including not only addition-polymerization between curing agent and monomer ^{10, 11, 12} but also the Kawasaki ¹³ exchange dynamics of nearest-neighbor monomer and liquid crystal molecule pair. In pervious studies, we showed that the time evolution of structure factors exhibits dynamical self-similarity and the mean cluster size of liquid crystals has an interesting peaking behavior ². Besides, we used a scaling concept to examine the final structure of the system and showed that the polymerization driven by the curing agent leads to revelation of new scaling relations and pinning exponents ¹. Here we represent our dynamical model for PIPS and study the behavior of cluster size of liquid crystals for various concentration of liquid crystals.

MODEL AND METHOD

The model consists of zero-functional liquid crystal molecules, bifunctional and tetrafunctional monomers and curing agents. In this model, the polymerization process is an addition-polymerization between curing agent and monomer, and the movement process is a Kawasaki exchange dynamics of nearest-neighbor monomer and liquid crystal. Initially, the bifunctional and tetrafunctional monomers and zero-functional liquid crystal molecules are randomly distributed on a lattice of size L , and a fraction C_i of curing agents are placed on randomly selected monomers. The concentration of bifunctional C_b and tetrafunctional C_t monomers and liquid crystal molecules C_{lc} are related with $C_b + C_t + C_{lc} = 1$. The functionality of

monomer gives the maximum number of bonds 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 a polymer. Active centers are annihilated when they both bond together. We assume that the interaction energies of nearest-neighbor pair are identical except that of chemical bond, and the interaction of chemical bond is much stronger. The assumption of the interaction energies can be represented as

$$|E_{i,j}| = |E_{k,l}| \ll |E_{p,p}|, \quad (1)$$

where the $E_{i,j}$ and $E_{k,l}$ are the van der Waals interaction energies between a nearest-neighbor pair of liquid crystal molecules, monomers, and active monomers. Each of the indices i, j, k and l can be one of the liquid crystal molecule, monomer and active monomer. $E_{p,p}$ is the interaction energy of chemical bond between polymers.

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. In addition, different polymerization and exchange rates are considered by introducing a time ratio θ which is defined as

$$\theta = \frac{t_p}{t_e}, \quad (2)$$

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. In most experimental conditions, the value of the time ratio is in the range $0 < \theta \leq 1$. Here the time ratios we studied are in the above range. During the course of the Monte Carlo simulation, a pair 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 none of these two sites belongs to a part of a polymer then the molecules on the two sites can exchange positions with a probability which equals to θ . Figure 1 shows a schematic view of the simulation process for three time steps.

To examine the size of liquid crystal droplet, we define the time evolution of the mean cluster size of liquid crystal molecules S_{lc} as

$$S_{lc}(t) = \frac{\sum_s s^2 N_s(t)}{\sum_s s N_s(t)}, \quad (3)$$

where $N_s(t)$ is the number of clusters of size s at time t divided by total number of sites, and a cluster is defined as a group of neighboring liquid crystal molecule sites.

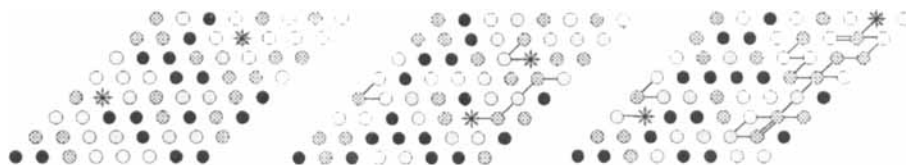


FIGURE 1 Schematic view of the simulation process for three time steps. Black circles represent liquid crystal molecules, white circles represent bifunctional monomers, grey circles represent tetrafunctional monomers, and starred circles indicate the position of active centers. Bonds are represented by lines between monomers.

In the study, the simulations are performed on a two-dimensional 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.

RESULTS AND DISCUSSION

In Fig. 2, Fig. 3 and Fig. 4, we show the time evolution of the mean cluster size of liquid crystal molecules $S_{lc}(t)$ for various concentrations of liquid crystal C_{lc} with three different sets of parameters.

In the figures, we can obviously observe the polymerization reaction forces the liquid crystal molecules into aggregation while it forms a solid connection between monomers. As seen from the figures, if C_{lc} is the value in a specific range, S_{lc} increases before reaching a maximum value and then decreases to a saturated value. The peaking phenomena are consistent with the simulations of our pervious work² and are found in experimental observation¹⁴. The peaking behavior can be explained by two competing mechanisms driven by polymerization. First, the polymerization reaction between monomers forces the liquid crystal molecules into aggregating. Second, the additional phase separation be confined in the mesh of formed polymers so that the cluster size of liquid crystal molecules decreases. It is apparent that the former and latter mechanisms dominate in the early and later stage, respectively; thus, these two mechanisms imply the liquid crystal molecules aggregate then separate during the course of the polymerization-induced phase separation.

Here we are interested in the resulting morphology of the simulations. In Fig. 5, we show the double logarithmic plot of the saturated values of the mean cluster size of liquid crystal molecules against the concentrations of liquid crystal molecules

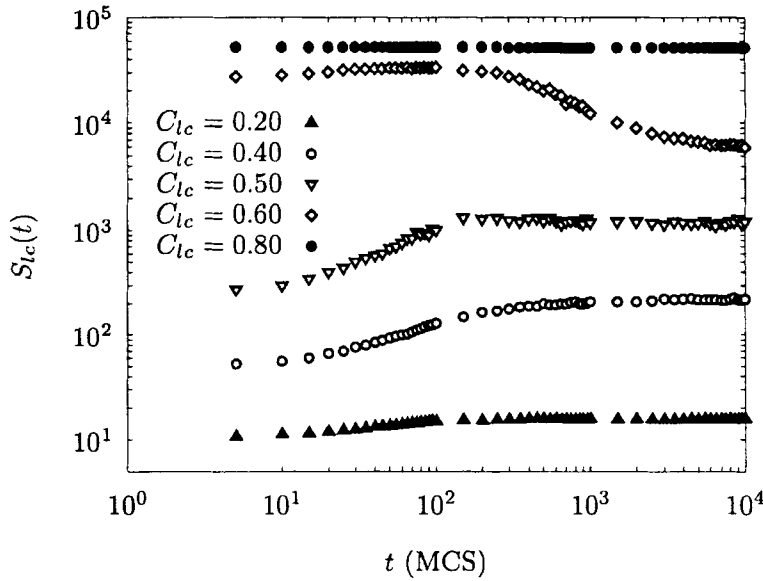


FIGURE 2 Double logarithmic plot of S_{lc} against time for various values of C_{lc} with $C_i = 0.015$, $C_b = 0.50$ and $\theta = 1.0$.

for the three different sets of parameters. As shown in this figure, we found that the three different sets of data fall in one curve and there is a region which the variation of resulting mean cluster size of liquid crystal is strongly dependent on the variation of concentration of liquid crystal molecules. The region is corresponding to the one which the peaking behavior obviously exists. We used a linear line to fit the data in the region and obtained a relation

$$S_{lc} \sim C_{lc}^{\alpha}, \quad (4)$$

where the exponent α is found to be 13.03 ± 0.41 .

Although the two-dimensional computer simulation of this model captures the essential physics that the polymerization forces the aggregation of liquid crystal molecules, the quantitative comparison between simulation and experiments is difficult because of the highly complicated phenomenon in the polymerization-induced phase separation. For a more realistic model, it is need to consider the mobility and flexibility of a polymer network, the elastic deformation of an anisotropic nematic solvent, the various initiation mechanism of initiator, the various interaction energies between a pair of monomer-monomer, monomer-liquid crystal, monomer-polymer, liquid crystal-liquid crystal, liquid crystal-polymer and polymer-polymer,

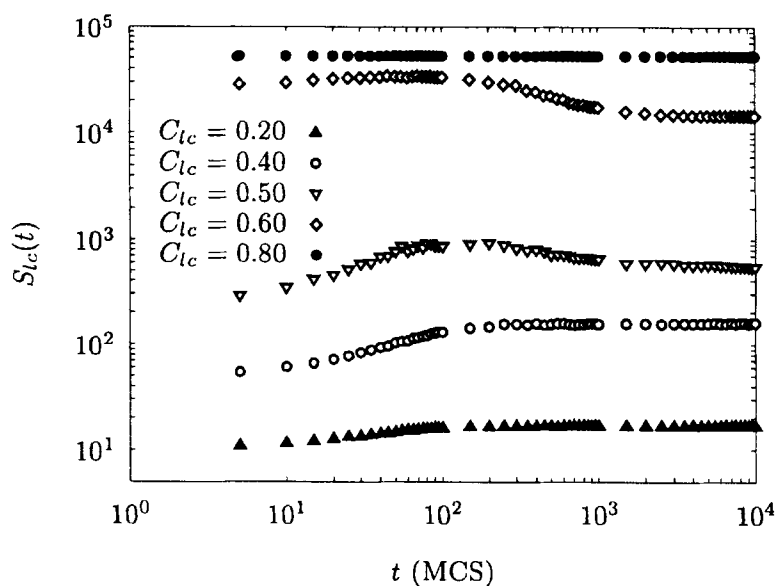


FIGURE 3 Double logarithmic plot of S_{lc} against time for various values of C_{lc} with $C_i = 0.030$, $C_b = 0.50$ and $\theta = 0.6$.

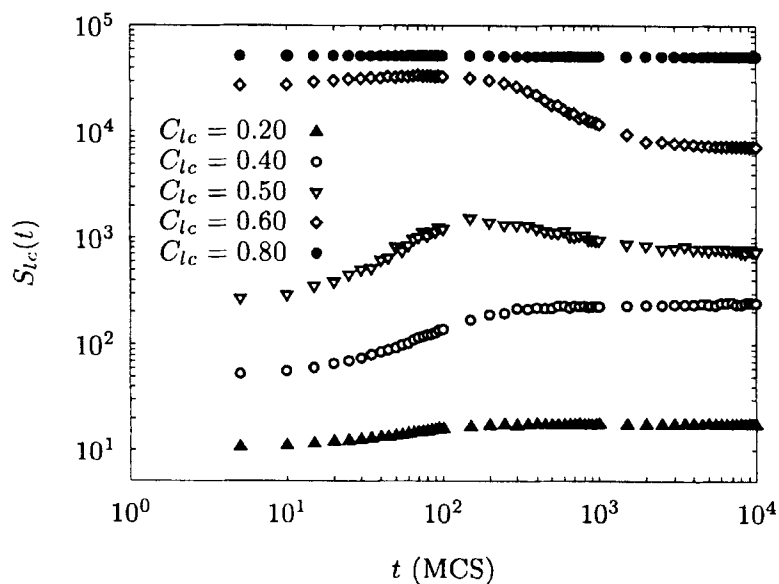


FIGURE 4 Double logarithmic plot of S_{lc} against time for various values of C_{lc} with $C_i = 0.015$, $C_b = 0.00$, and $\theta = 1.0$.

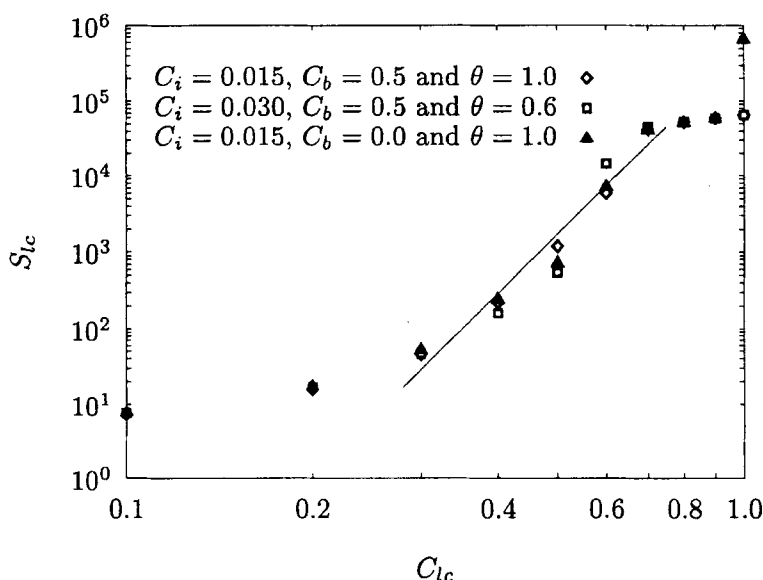


FIGURE 5 Double logarithmic plot of the saturated value of S_{lc} against various concentration of liquid crystal C_{lc} for three different sets of parameters used in Fig. 2, Fig. 3 and Fig. 4.

etc. For further understanding of polymerization-induced phase separation, more systematic experimental study is need and desirable to make experimental conditions as simple as possible to avoid unnecessary complications which prevent gaining useful information from experiments.

CONCLUSION

A model including addition-polymerization between curing agent and monomer, and the Kawasaki exchange dynamics of nearest-neighbor monomer and liquid crystal molecule pair has been used to study the phenomena of the polymerization-induced phase separation in the formation process of polymer-dispersed liquid crystals. In this study, the computer simulation of this model is preformed on a two-dimensional lattice with periodic boundary condition. We calculate the mean cluster size of liquid crystal molecules and focus on the saturated value of the mean cluster size of liquid crystal molecules for various concentrations of liquid crystal molecules. Polymerization reaction forces the aggregation of liquid crystal molecules can be obviously observed in the simulations. The mean cluster size of liquid crystal increases as the concentration of liquid crystals increases. We found a regin which

the variation of the saturated mean cluster size of liquid crystal is strongly dependent on the variation of concentration of liquid crystal molecules and the region is corresponding to the one which the peaking behavior obviously exists. We found a relation between the mean cluster size and the concentration of liquid crystals in the region. For further understanding of polymerization-induced phase separation, more realistic model is need, and systematic experimental study is need and desirable to make experimental conditions as simple as possible to avoid unnecessary complications.

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