Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Polymerization induced phase separation (PIPS) in a polymer dispersed liquid crystal (PDLC) system: A Monte-Carlo simulation approach

Jian-Min Jin[a]; K. Parbhakar[a]; L. H. Dao[a]
[a] Laboratoire de recherche sur les matériaux avancés, Varennes, Canada

To cite this Article Jin, Jian-Min , Parbhakar, K. and Dao, L. H.(1995) 'Polymerization induced phase separation (PIPS) in a polymer dispersed liquid crystal (PDLC) system: A Monte-Carlo simulation approach', Liquid Crystals, 19: 6, 791 — 795
To link to this Article: DOI: 10.1080/02678299508031101
URL: http://dx.doi.org/10.1080/02678299508031101

LIQUID CRYSTALS, 1995, VOL. 19, NO. 6, 791–795

Polymerization induced phase separation (PIPS) in a polymer dispersed liquid crystal (PDLC) system: A Monte-Carlo simulation approach

by JIAN-MIN JIN, K. PARBHAKAR* and L. H. DAO*
Laboratoire de recherche sur les matériaux avancés, INRS-Energie et Matériaux,
1650 Montée Sainte-Julie, Varennes, Québec, Canada J3X 1S2

(*Received 30 December 1994; in final form 16 May 1995; accepted 20 May 1995*)

The polymerization induced phase separation (PIPS) process in a polymer dispersed liquid crystal (PDLC) system was studied by using Monte-Carlo (MC) simulation methods. In particular, the dependence of the phase separation between liquid crystal and polymer on the parameters, such as temperature $\gamma = \varepsilon/kT$, polymerization reactivity p and curing time t_c, was examined. It was found that the pair correlation function $G(a, t)$ decreases with the decrease of temperature when the polymerization reactivity p is fixed. Our results also revealed that at a constant temperature, the final value of $G(a)$ first increases with the increasing of p, and finally approaches a constant value. This observation provides us an effective way of controlling the size of liquid crystal droplets as well as their distributions. It was observed that the equilibrium value of $G(a)$ increases as the curing time increases when both temperature and p are kept constant. This is another way of controlling the size of liquid crystal droplets.

1. Introduction

Polymer dispersed liquid crystal (PDLC) materials have potential for a wide range of applications, such as, information displays, switchable windows, optical shutters, etc. [1, 2]. PDLC devices usually consist of a thin film of polymer binder in which microdroplets of liquid crystal are dispersed, sandwiched between two glass slides containing a transparent conductive substrate such as indium–tin oxide (ITO) [1]. A common way of preparing PDLC films is to employ phase separation techniques. There are two basic approaches for phase separation: one is the thermally-induced phase separation (TIPS), another is polymerization induced phase separation (PIPS). Having studied the TIPS process before [3], we consider the PIPS process in this work. In the PIPS process, liquid crystal and polymer are first uniformly mixed, then a polymerization reaction is introduced and the system is allowed to evolve. The liquid crystal becomes immiscible upon polymerization and nucleates to form microdroplets. The qualities of the PDLC materials, for example, optical and mechanical properties, are strongly dependent on the liquid crystal droplet size, shape and distributions. It was reported that the steepness of the slope of a PDLC film's electro-optical response curve increases with the increasing of distribution uniformity [4] and the light scattering performance of a PDLC film can be optimized by controlling the size distribution of the liquid crystal in the film [5]. In practical applications, it is therefore desirable to obtain PDLC films with uniform size and uniform distribution of liquid crystal droplets in polymer binder.

To understand how the liquid crystal droplets are formed and separated from polymer matrix in the PIPS process and how the size and distribution of liquid crystal droplets are affected by various parameters, such as, viscosity, concentration, curing temperature, curing time, polymerization reactivity and film thickness, etc. [6–12], we employ the Monte-Carlo (MC) simulation technique which has proven to be a good substitute for, and in some cases, even superior to experimental and theoretical methods in the studies of phase separation processes. Moreover, the MC method is particularly useful when the nucleus size is very small or the system is at its initial stage of phase separation. Much computer simulation work has been reported on the phase separation of binary liquids [13] and binary polymers [14–17]. However, less attention has been paid to the phase separation between liquid crystal and polymer [3]. Our work is aimed at studying the basic mechanisms involved in the PIPS process and providing some guidance for the experiments.

This article is organized as follows: § 2 describes some details of the simulation model: the results and discussion are presented in § 3, and finally some concluding remarks are summarized in § 4.

---

* Authors for correspondence.

0267-8292/95 $10.00 © 1995 Taylor & Francis Ltd.

2. Simulation model

The mixture of liquid crystal and polymer is simulated on a 60×60 square lattice (a 100×100 square lattice produces only minor modifications) using periodic boundary conditions. The model is described in detail in [3], so we will simply give the essentials here. Each liquid crystal molecule occupies a single lattice site, where as each polymer molecule occupies $(m+1)$ lattice sites, with m being the number of segments (of the same length as the lattice constant). The polymer molecules are flexible and this is accomplished in our model by assuming that the interaction energy between the segment ends (each segment has two ends) of the same polymer molecule is zero. Because of this flexibility, the polymer molecules are free to assume any shape, from a straight line to a coil. Furthermore, the interaction energy (ε) between the liquid crystal molecules and the polymer segment ends is considered positive (this favours the separation between liquid crystal and polymer molecules), while all the other interactions are assumed zero. The steric interactions are taken into account as usual: double occupancy of any lattice sites is excluded. The reptation technique [15, 16, 18] is used to move the polymer molecules in simulation. The process of polymerization is simulated by polymerization reactivity parameter $p (0 < p < 1)$ which is assumed to be independent of temperature. At each MC step, the polymerization reaction occurs if two polymer molecules have at least one nearest neighbour and the following condition is satisfied:

$$p \geqslant \xi \tag{1}$$

where ξ is a uniformly distributed random number between zero and unity. If the polymerization reaction takes place the two polymer molecules involved in the reaction are linked together to form a polymer network. Since we are assuming that all the segment ends are active sites, the polymerization reaction can take place at any segment end of a polymer molecule producing polyfunctional polymerization. The standard Metropolis algorithm [19] 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, T the temperature of the system and k the Boltzmann constant. After an attempted move satisfies the steric restrictions, it is accepted if the following condition is satisfied:

$$\mathrm{MIN}\{\exp[-\Delta E/kT], 1\} \geqslant \zeta \tag{2}$$

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 between zero and unity. Starting from some initial configurations, the system is allowed to evolve according to the above probability until a thermodynamic equilibrium state is reached. The intermediate configurations, as well as other properties are monitored and recorded at certain intervals of Monte-Carlo steps (MCS). One MCS is defined as one attempted reptation move for the polymer molecules, and the number of MCS is a measure of the evolution time of the system. The system is first homogenized at a very high temperature, i.e. $T \to \infty$, which corresponds to $\gamma = \varepsilon/kT = 0$. Then it is cooled down to some lower temperatures (but still higher than the critical point) and allowed to evolve to equilibrium state.

3. Results and discussion

In this section, we present and discuss the simulation results for systems with different polymerization reactivity p, at different temperature T and with different curing time t_c. The concentration of liquid crystal is chosen to be $c = 0{\cdot}50$, close to the experimental value [2].

3.1. *Temperature dependence*

We first study the temperature dependence of phase separation between liquid crystal and polymer in PIPS process. The polymerization reactivity is chosen to be $p = 0{\cdot}002$, and the concentration of liquid crystal is fixed, i.e. $c = 0{\cdot}50$. Initially, there are totally 225 polymer molecules of chain length $m = 7$ which occupy $225 \times (7+1) = 1800$ sites on the 60×60 square lattice; while the liquid crystal occupies the rest sites of the lattice. Upon polymerization, the number of polymer molecules decreases and eventually a polymer network forms. To study the phase sparation process quantitatively, we introduce, as in our previous work [3], the pair correlation function $G(r,t)$ which measures the distribution of concentration fluctuations in the mixture, as suggested by Cifra *et al.* [14]:

$$G(r,t) = (1/n) \sum_i^n \eta(r_i,t)\eta(r_i + r, t), \tag{3}$$

where the summation is over all sites in the mixture. The occupation variable η for any site is not unique; and can have either of the two values, zero or unity. For the case where the two sites at r_i and $(r_i + r)$ are occupied by a heteropair, the product of the occupation variables is unity and zero otherwise. Here we choose $r = a$ (a is the lattice constant), i.e. we consider only the pair correlation function $G(a,t)$, since the small-scale fluctuations are dominant at the very early stage of phase separation process. Figure 1 shows the time dependence of $G(a,t)$ after the system is cooled to different low temperatures. We choose the temperatures to be higher than the critical value of our model [3], i.e. $\gamma_c = \varepsilon/kT_c = 1{\cdot}5$, in order to study the PIPS process. We point out that the critical value of our model is different from the value of $\gamma_c = 0{\cdot}441$ for the Ising Model in zero field [20], simply because of the difference in the model itself. In figure 1, curves A, B and

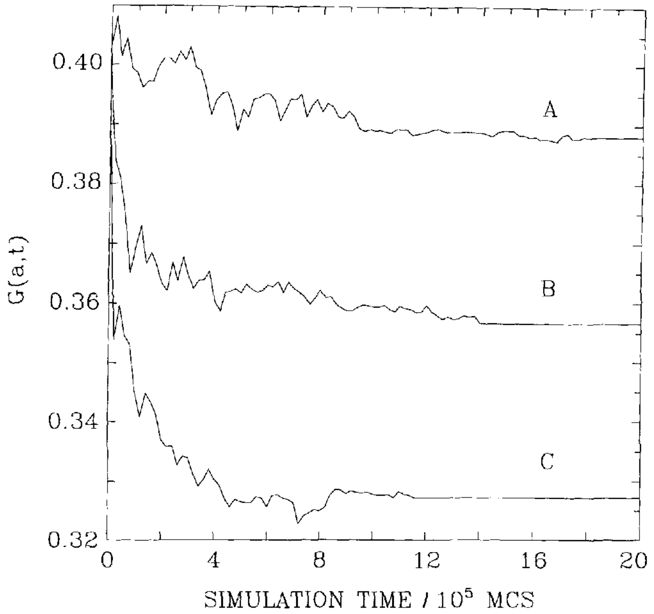


Figure 1. Time dependence of the pair correlation function $G(a,t)$ for $c = 0{\cdot}50$. The polymerization reactivity p is $0{\cdot}002$. Curves A, B and C are for the temperature $\gamma = \varepsilon/kT = 0{\cdot}1$, $0{\cdot}5$ and $1{\cdot}0$, respectively.

C are, respectively, for the system at temperatures $\gamma = \varepsilon/kT = 0{\cdot}1$, $0{\cdot}5$ and $1{\cdot}0$. It is observed that the pair correlation function $G(a,t)$ decreases with simulation time, and eventually approaches a constant. At the very beginning of time evolution, since the polymer network has not yet formed, the thermal effect plays a dominant role in the evolution of configuration. Because the thermal fluctuation decreases with the decreasing of temperature, the probability of forming clusters of liquid crystal (as well as clusters of polymer) is larger at low temperature than at high temperature. Therefore, the pair correlation function $G(a,t)$ is larger (i.e. the cluster size is smaller) at high temperature than that at low temperature, as expected. As the time goes on, the fluctuation in $G(a,t)$ diminishes and finally goes to zero ($G(a,t)$ becomes a constant). This indicates that the mobility of both polymer and liquid crystal molecules decreases due to the polymerization reaction, and finally approaches zero when a completely rigid polymer network is formed.

3.2. *Polymerization reaction effect*

We next consider the effect of polymerization reactivity p on phase separation in the PIPS process. For this purpose, the system is kept at a constant temperature $\gamma = \varepsilon/kT = 1{\cdot}0$ (below the critical value of $1{\cdot}5$ as said before), and allowed to evolve after the polymerization reaction is switched on at $t = 0$. The final value of the pair correlation function $G(a)$ is measured when a complete polymer network forms. Figure 2 shows the variation of the final value of the pair correlation function $G(a)$ with polymerization reactivity p. Each experimental point in figure 2 represents an average over 20 separate computer runs with the same value of p but different set of random numbers. The short vertical line at the experimental points sets the error bar for the calculations. From figure 2, it is observed that the final value of pair correlation function $G(a)$ first increases very rapidly with the increasing of the polymerization reactivity p, and finally reaches a constant. As p increases, the mobility of the molecules of both liquid crystal and polymer decreases due to the formation of polymer network, the average size of clusters decreases accordingly. Therefore, $G(a)$ increases with the increasing of p. However, as p increases much further, a complete polymer network forms within a short time (we will discuss this point later) that the molecules (and clusters of molecules) of liquid crystal are confined instantly by the polymer network. Since the mixture of liquid crystal and polymer is homogenized before the polymerization reaction is introduced, the droplet sizes of liquid crystal will take their initial values, i.e. the values before the polymerization reaction takes place. Hence, the value of $G(a)$ finally approaches a constant. This observation suggests that the increasing of polymerization reactivity p could decrease the size of liquid crystal droplets, and increase their dispersion in the polymer matrix. To see how the polymerization reaction affects the size of liquid crystal droplets, we show in figure 3 (*a*) and (*b*) respectively, the final configurations for $p = 0{\cdot}04$ and $0{\cdot}002$. It is evident that the average size of liquid crystal droplets is

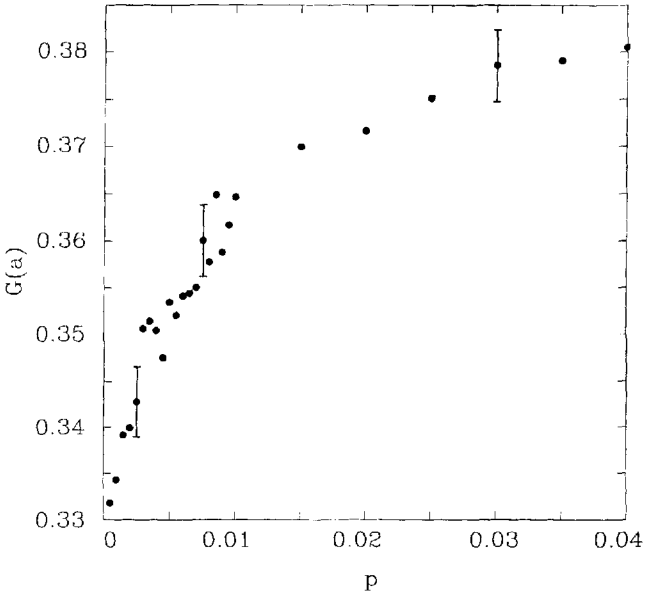
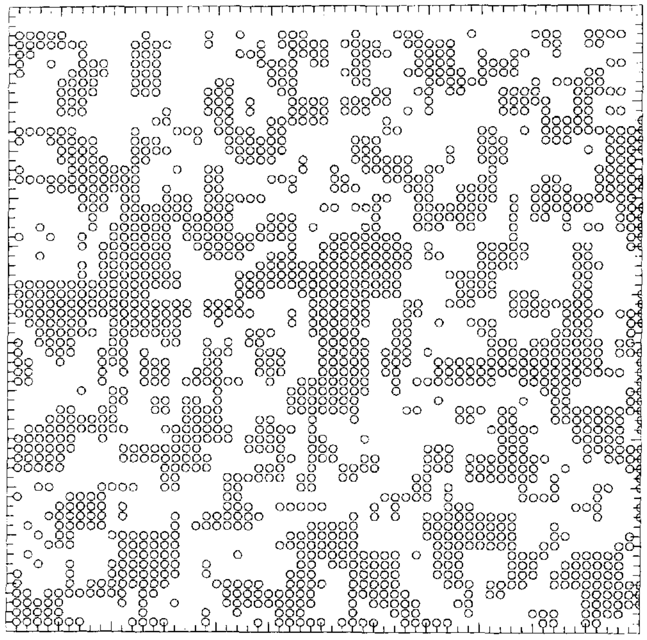
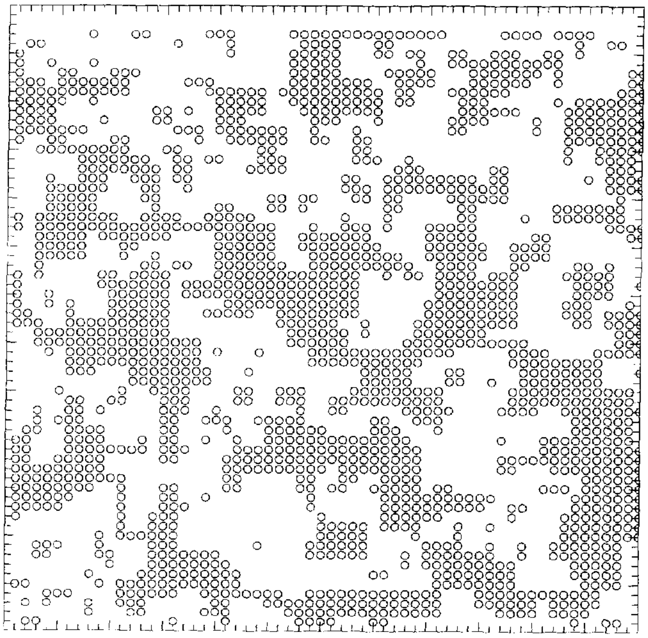


Figure 2. Variation of the final value of the pair correlation function $G(a)$ with polymerization reactivity p. The temperature of the system is $\gamma = \varepsilon/kT = 1{\cdot}0$.



(*a*)



(*b*)

Figure 3. The final configurations of the 60×60 liquid crystal–polymer system at the polymerization reactivity $p = 0{\cdot}04$ (*a*) and $0{\cdot}002$ (*b*), respectively. The temperature is $\gamma = \varepsilon/kT = 1{\cdot}0$. The molecules of liquid crystal are represented by small open circles, while those of polymer by white background.

smaller for $p = 0{\cdot}04$ than that for $p = 0{\cdot}002$, in line with the above observation. In order to examine how fast it is to form a complete polymer network at different values of p, we depict, in figure 4, the variation of the time t_p which

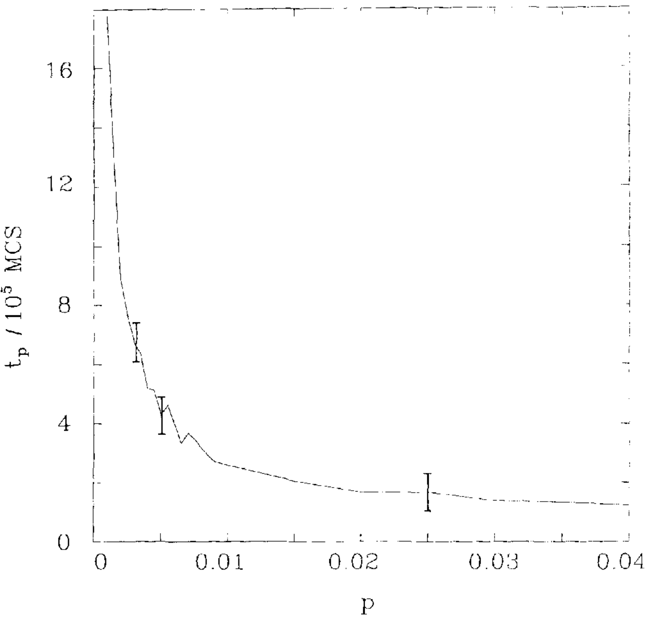


Figure 4. The dependence of t_p, the time needed to form a complete polymer network on the polymerization reactivity p. The temperature is chosen to be $\gamma = \varepsilon/kT = 1{\cdot}0$.

is needed to form a complete polymer network with the polymerization reactivity p. Here again, the curve is obtained by averaging over 20 separate runs with different set of random numbers. The short vertical line on the curve represents the accuracy of our calculations. It is seen that t_p first drops exponentially as p increases, then approaches a constant. This behaviour indicates that the polymerization effect is very strong. We note that as p increases, t_p approaches a non-zero constant which is found to be about $1{\cdot}2 \times 10^5$ MCS. This is the time needed for the polymers to diffuse and contact with each other in order to form a complete polymer network.

3.3. *Influence of curing time*

Finally, we study how the phase separation depends on the curing time t_c. In this case, the temperature is still kept at $\gamma = \varepsilon/kT = 1{\cdot}0$, and the polymerization reactivity fixed to be $p = 0{\cdot}04$. The polymerization reaction is switched on at $t = 0$, then switched off at $t = t_c$. And the system is allowed to evolve until it reaches the equilibrium state. Figure 5 shows the variation of the equilibrium value of pair correlation function $G(a)$ with curing time t_c. The experimental points are obtained in the same way as in figure 2. It is seen from figure 5 that $G(a)$ first increases very rapidly with the increasing of t_c and eventually reaches a constant. It can be understood that when the curing time t_c increases, the mobility of the polymer (as well as the liquid crystal) decreases, so that the chance of forming large clusters decreases. Therefore, adjusting of the curing time provides us another effective way to

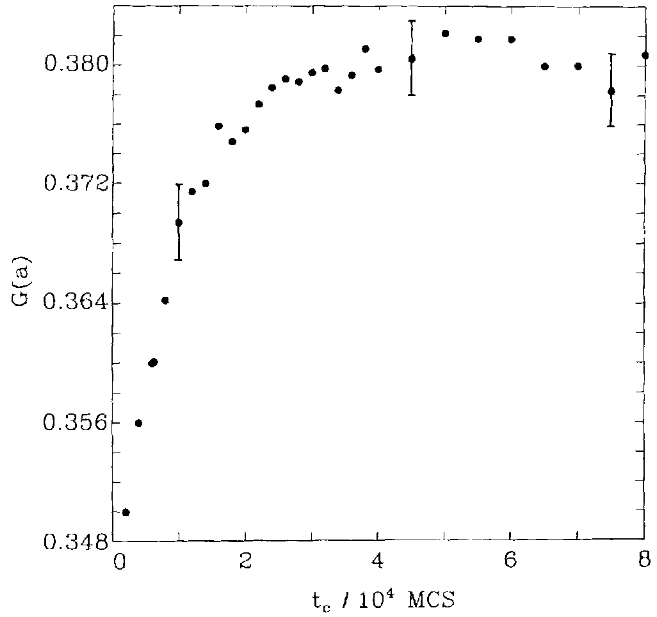


Figure 5. Variation of the equilibrium value of the pair correlation function $G(a)$ with curing time t_c. The temperature and polymerization reactivity are chosen to be $\gamma = \varepsilon/kT = 1{\cdot}0$ and $p = 0{\cdot}04$, respectively.

control the size and distribution of the liquid crystal droplets in polymer binder.

4. Conclusions

We have employed Monte-Carlo simulation techniques in the study of PIPS process in the PDLC system. We examine how the temperature of the system, the polymerization reactivity and curing time affect the phase separation between liquid crystal and polymer. We find that the size and distribution of the liquid crystal droplets can be affected either by the polymerization reactivity p or by the curing time t_c. This observation provides us two different ways in the quality control of the PDLC films.

This work was supported by the Natural Science and Engineering Research Council (NSERC) of Canada.

References

[1] Doane, J. W., Vaz, N. A., Wu, B. G., and Zumer, S., 1986, *Appl. Phys. Lett.*, **48**, 269.

[2] Parbhakar, K., Dao, L. H., Tabrizian, M., Gingras, S., and Campbell, G., 1994, *Proceedings of Drop Tower Days Bremen*, Germany, 18.

[3] Jin, J.-M., Parbhakar, K., and Dao, L. H., 1995, *Comput. Mater. Sci.*, **4**, 59.

[4] Alt, P. M., and Pleshko, P., 1974, *IEEE Trans. Electron Devices*, **21**, 146.

[5] Montgomery Jr., G. P., West, J. L., and Tamura-Lis, W., 1991, *J. appl. Phys.*, **69**, 1605.

[6] Doane, J. W., Golemme, A., West, J. L., Whitehead Jr., J. B., and Wu, B. G., 1988, *Molec. Crystals liq. Crystals*, **165**, 511.

[7] Jiang, P., and Asada, T., 1992, *Molec. Crystals liq. Crystals*, **222**, 87 A.

[8] West, J. L., 1988, *Molec. Crystals liq. Crystals*, **157**, 427.

[9] Golemme, A., Zumer, S., Doane, J. W., and Neubert, M. E., 1988, *Phys. Rev. A*, **37**, 559.

[10] Tahata, S., Masumi, T., Kaho, S., and Mizunuma, M., 1992, *Molec. Crystals. liq. Crystals Lett.*., **8**, 99.

[11] Golemme, A., Zumer, S., Allender, D. W., and Doane, J. W., 1988, *Phys. Rev. Lett.*, **61**, 2937.

[12] Fuh, A. Y. G., and Caporaletti, O., 1989, *J. appl. Phys.*, **66**, 5278.

[13] Pan, M.-X., Chen, X.-S., Sun, J. -R., and Zhao, D.-Q., 1993, *Microgravity Q.*, **3**, 209.

[14] Cifra, P., Karasz, F. E., and Macknight, W. J., 1989, *Macromolecules*, **22**, 3089.

[15] Baumgartner, A., 1984, *J. chem. Phys.*, **81**, 484.

[16] Baumgartner, A., and Heermann, D. W., 1986, *Polymer*, **27**, 1777.

[17] Jo, Won Ho, and Ko, Moon Bae, 1993, *Macromolecules*, **26**, 5473.

[18] Wall, F. T., and Mandel, F., 1975, *J. chem. Phys.*, **63**, 4592.

[19] Metropolis, N., Rosenbluth, A. N., Rosenbluth, M. N., Teller, A. H., and Teller, E., 1953, *J. chem. Phys.*, **21**, 1087.

[20] Onsager, L., 1944, *Phys. Rev.*, **65**, 117.