Monte Carlo Simulations of an Oriented Semirigid Polymer Film−Formation of Band Textures

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Introduction

Liquid crystalline polymers (LCPs) exhibit distinct physical properties that cannot be expected in flexible polymers or in small-molecule liquid crystals. One of the most interesting and puzzling phenomena is the band texture, which is common to all main-chain lyotropic and thermotropic LCPs.[1−4] Band textures observed in the polarizing microscope are alternating dark and bright bands perpendicular to the preshearing direction. Usually, the band texture forms during shear relaxation,[1] although it can also be found during elongational relaxation.[5] It is also found experimentally that, after cessation of shear flow, there exists an induction period before the bands appear.[6] The scanning electron microscopy (SEM)[7] observation on a band-textured sample shows that the macromolecular chains are aggregated into zigzag bent fibrils perpendicular to the optical bands. It is known that the band texture can affect the mechanical properties of LCP materials. Therefore, there is a widespread interest in understanding the mechanism of band texture formation both for practical and theoretical purposes. Marrucci[8] suggested that the bands arise from the coherent tumbling of neighboring domains, i.e., the spatial inhomogeneity caused by shear flow. Fincher[9] proposed the idea that a large value of the splay elastic constant in LCPs favors a rapid lateral relaxation. Picken et al.[6] presented a model along similar lines.

Although many efforts have been made, the molecular mechanism of band formation is still an open question. In this note, we present a two-dimensional Monte Carlo (MC) simulation result, demonstrating the spontaneous formation of band textures during relaxation of an oriented semirigid polymer film. Many experimental observations have been performed on thin films although some experiments have studied quite thick samples.[10] We believe the two-dimensional model studied here may shed new light on the basic physics of the problem. Compared with one-dimensional simulations based on Frank's elastic energy expression,[6,9] our model is somewhat more realistic, and the results may therefore be more reliable.

Model and Simulation

The MC simulation is carried out on a $x \times y = 300 \times 60$ simple square lattice with periodic boundary conditions in both directions. The self-avoiding four-site lattice chain model introduced by Camesin and Kremer[11] was applied in this study, in which each segment occupies four lattice sites and the bond length l is larger than a lattice spacing and is allowed to fluctuate, e.g., $2 \le l \le 13^{1/2}$ (in units of the lattice spacing). With this choice, the number of bond orientation directions in the four-site two-dimensional lattice model is up to 36 and is rather close to the continuum orientation limit. In our simulations, the chain length is $n = 50$ (each chain has 50 segments and each segment occupies four sites).

A reasonable and simple model for a main-chain LCP is a lattice chain with an intrachain energy depending on the angle (between two successive bonds[12,13]

$$\epsilon(\phi) = \epsilon_0(1 + \cos\phi)^2 \tag{1}$$

Note that $\epsilon(\phi)$ is dimensionless and ϵ_0 is in units of kT.[13] It is clear that the energy of a bent configuration depends on the angle ϕ, with $\epsilon(\pi) = 0$ for a fully stretched configuration and $\epsilon(0) = 4\epsilon_0$ ($\epsilon_0 = 15$ for a typical example in this study) for the most bent configuration. No potential is introduced between nonbonded segments except the excluded volume interaction, which is intrinsically included in this model. A standard MC sampling procedure with the transition probability[12,13]

$$W = \exp\{-[\epsilon_a(\phi') - \epsilon_b(\phi)]\} \tag{2}$$

leads to the configurational evolution of the system. In eq 2, $\epsilon_b(\phi)$ and $\epsilon_a(\phi)$ are the energies before and after the trial monomer jumps, respectively.

Although lattice chains under simple shear flow can be simulated by a MC algorithm developed recently,[14] for simplicity, the following procedure has been used to mimic the state just after the cessation of shear flow: on the lattice, fully extended chains are perfectly aligned in the x-direction. Then, following the MC algorithm for the dynamics of polymers proposed by Camesin and Kremer,[11] the perfectly aligned state evolves under a strong external field along the x-direction

$$\epsilon_e(\theta) = \epsilon_{e0} \sin^2\theta \tag{3}$$

where θ is the angle between the bond vector and the external field direction and ϵ_{e0} is assigned the value 25. Note that one Monte Carlo step (MCS) equals to $n \times N$ trial jumps (N is the number of chains on the lattice). After evolving for 5000 MCS, the chains are almost fully aligned along the x-direction with some random fluctuations and with chain mass centers randomly distributed in the x- and y-directions (Figure 2a). We take the state of Figure 2a as the initial state. This initial state is then relaxed free of external field by using the standard MC sampling algorithm of a four-site lattice chain model.[11] The snapshot pictures shown in Figures 2 and 3 are taken at designated MCS.

Results and Discussions

To characterize the rigidity of the chain, we first examined the relation between the bending energy ϵ_0 and the persistence length L_p,[15] (Figure 1a). It is shown that the persistence length increases with an increase in ϵ_0. It is interesting to note that the four-site chain model fits the wormlike chain model very well. For the wormlike chain model, the relation between the persis-

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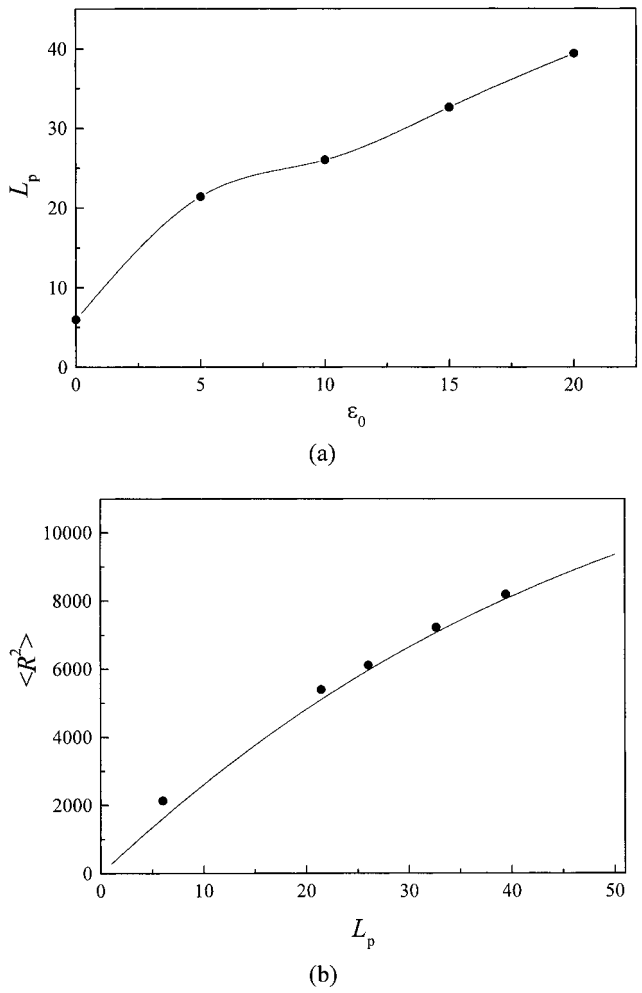

Figure 1. (a) Bending energy dependence of the persistence length for a self-avoiding four-site lattice chain model. (b) Relation between the mean-square end-to-end distance $\langle R^2 \rangle$ and the persistence length L_p, where the symbols are the simulated data and the line is calculated according to eq 4.

tence length L_p and the mean-square end-to-end distance $\langle R^2 \rangle$ is written as[15]

$$\langle R^2 \rangle = 2LL_p - 2L_p{}^2[1 - \exp(-L/L_p)] \qquad (4)$$

where L is the contour length of the chain. In Figure 1b, the simulated data agrees with eq 4 quite well. Following the theoretical prediction of Khokhlov,[16] for the wormlike chain, the critical concentration for the appearance of an LC phase φ_c is related to the persistence length L_p by $\varphi_c L_p/d = 5.695$ with d being the segment diameter (d is two lattice spacings for the four-site lattice chain model). With the choice of the volume fraction $\varphi = 0.44$ and the bending energy $\epsilon_0 = 15$ ($L_p =$ 32.64 lattice spacings), Khokhlov's relation results in ($\varphi L_p/d \sim 7.18$, which is much higher than the critical volume fraction. Therefore, this density guarantees that our system is in the lyotropic LC phase.

Starting from the prepared oriented state, we first freely relaxed the initial state (Figure 2a) with $\epsilon_0 = 0$, which corresponds to the flexible chain model. After evolving for 40 000 MCS, the system reasonably relaxes to the flexible polymer melt (Figure 2e) with the ratio $\langle R^2 \rangle / \langle S^2 \rangle = 6.02$, which agrees with the previous results very well.[11]

For a semirigid chain system, however, band textures can always be seen, provided that the system is in the

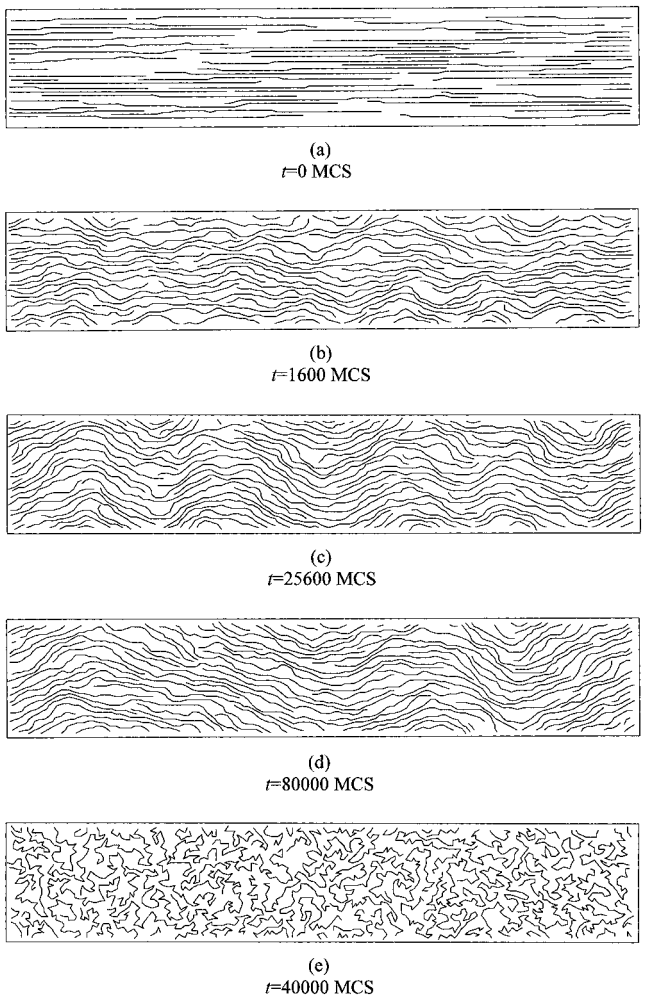

Figure 2. Snapshot pictures of Monte Carlo simulation on the band formation process. The lattice size is 300 × 60, the segment volume fraction is $\varphi = 0.44$ and the number of chains on the lattice is $N = 40$. (a) Initial state prepared by the procedure described in the main text. (b−d) Snapshot pictures during the free relaxation for the system with bending energy $\epsilon_0 = 15$. The numbers in the figure are the evolution time (in MCS). (e) Snapshot picture obtained after evolving for 40 000 MCS for the system with bending energy $\epsilon_0 = 0$. The ratio of $\langle R^2 \rangle / \langle S \rangle = 6.02$ is obtained for this system.

LC regime. A typical example given here is a system with $\epsilon_0 = 15$ and $\varphi = 0.44$ (Figure 2b−d). As observed experimently,[6] after turning off the external field, there is an induction period before the band clearly appears. After the induction period, the band texture forms spontaneously during the relaxation of the semirigid chain system. An important feature of the snapshot pictures is that the band spacing increases with time, which qualitatively agrees with experimental observations.[6] It should be noted that the above results are entirely reproducible in more than 30 independent runs.

To confirm that our simulation results are not affected by finite-size effects, we have also performed the simulation on an 800 × 125 square lattice with $\epsilon_0 = 15$ and $\varphi = 0.48$. A typical result is shown in Figure 3. It reproduces the results observed in the earlier simulation on a 300 × 60 lattice without exception.

Though we cannot yet properly characterize the simulated band texture and its evolution dynamics quantitatively, several conclusions may be drawn from the results presented above. The most important conclusion is that the band texture can spontaneously

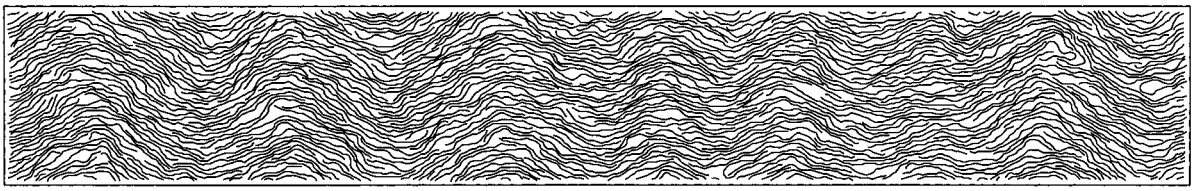

Figure 3. The snapshot picture obtained after evolving for 40 000 MCS for the system with bending energy $\epsilon_0 = 15$. The lattice size is 800 × 125, the segment volume fraction is $\varphi = 0.48$, and the number of chains on the lattice is $N = 240$. The initial state is prepared by the same procedure as that of Figure 2a.

form from an oriented semirigid chain film during free relaxation. Although we cannot completely disprove the tumbling mechanism suggested by Marrucci,[4] at least we have shown that band texture formation is not necessarily the result of coherent tumbling in main-chain LCPs during shear flow. We conjecture that the preshear flow only generates the oriented LC state. Therefore, it has also been observed that band textures can form during elongational relaxation.[5] It is well-known that no director tumbling mode exists in the elongational flow; thus, the idea of Marrucci is not relevant in this case it seems. Our results appear to support the mechanism proposed by Fincher.[9]

A molecular process leading to band formation is presented in this paper. The chain rigidity and the anisotropic excluded volume effect of the semirigid chain may be of central importance for the formation of band texture. At the present stage, we are not able to give a theoretical interpretation for the molecular mechanism of band formation. Nevertheless, our results can give some hints for developing a new theoretical model to quantitatively interpret the band formation in LCP systems. The most important conclusion is that additional experimental and theoretical studies are required for understanding the mechanism of band formation.

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