Orientational Relaxation Together with Polydispersity Decides Precursor Formation in Polymer Melt Crystallization

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ABSTRACT: We studied the athermal relaxation of bulk extended chains and the isothermal crystallization in an intermediately relaxed melt by means of dynamic Monte Carlo simulations of lattice−polymer systems. The melt contained a memory of chain orientations but no more crystalline order. We found that the athermal relaxation is continuous and homogeneous among the bulk chains, and its rate depends on the chain length. The orientational memory in the melt significantly enhances the rate of crystallization. Nevertheless, no precursor of crystallization occurs in the melt of uniform chain lengths. But, in a binary blend of different chain lengths, the crystallization of oriented long chains acts as the precursor to induce epitaxial crystallization of the relaxed short chains. This mechanism explains the formation of shish-kebab crystals observed frequently in the processing of semicrystalline polymers. The results suggest that in flow-induced polymer crystallization the orientational relaxation of chains decides a selection of the long-chain component and then the precursor formation.

I. Introduction

Polymer melt crystallization is a typical first-order phase transition. The initiation of crystallization via crystal nucleation has a threshold of crystalline size, where for the formation of a crystal nucleus the body free energy gain should outgo the surface free energy penalty in their contributions to the rate of free energy changes.[1] Therefore, there are two natural ways to enhance the flux of crystal nucleation, namely decreasing the surface free energy penalty or increasing the body free energy gain. The first way is usually realized by introducing a foreign substrate of high affinity and switching the course to heterogeneous nucleation. A typical example in this way is the self-nucleation.[2] The second way commonly makes a mechanical manipulation to polymer chains and lets them extend so as to decrease the body entropy penalty of crystallization. A typical case in this way is the crystallization under a shear/elongation flow.[3]

The flow-induced crystallization is quite general in the processing of semicrystalline polymers.[4−7] It often produces a hierarchical crystal morphology, as like this, some stretched chains form the extended-chain crystals called shish and then the folded-chain crystals called kebabs grow on shish's lateral surfaces.[8] One may eventually find a stack of thin lamellae forming around a central fiber.[9] Sometimes, the central fiber is too thin to be visible, and one may only see a row structure in the melt under stress.[10] The shish-kebab crystallites have been found to be a general picture of structural development at the early stages of polymer melt spinning.[11] Even at the initial stage of spherulite growth from a quiescent liquid, lamella bundles like shish-kebabs have been observed.[12]

Recently, the precursor of polymer melt crystallization under shear field has become a hot topic in the research of X-ray scattering.[13] The precursor of primary crystal nuclei was suggested to be formed in a scaffold (network) of oriented structure[14] and to be a cooperative result of the long-chain component in a binary blend of isotactic polypropylene (iPP).[15] In another observation of iPP melt, the shear-induced precursor was suggested to be in a smectic mesophase.[16] Up to now, however, the details of precursor formation before any crystalline structure can be detected have not been well understood.

Both experiments and simulations have found that single macromolecules undergo end-over-end tumbling in the shear flow[17,18] or coil−stretch first-order-like transition in the elongation flow.[19,20] The results reveal a natural fact that under flow the stretching of chains is potentially followed with a reverse relaxation whenever the chain makes events of displacement. Hence, there comes the question: which process of polymer chains decides the precursor formation, the stretching or the relaxation? Experiments on binary iPP blend of different chain lengths reported that the life period of long-chain precursors decreases with increasing temperature.[21] Recently, experiments on binary polyethylene blends of different chain lengths also reported that the shear-induced structure formed by the long-chain component is related with the matrix viscosity and the length of shish decreases with time.[22] Furthermore, on commercial grade isotactic poly(1-butene)s, the lifetime of precursors in the period of thermal treatment after cessation of flow can be fitted by an Arrhenius-type equation.[23] On the other hand, when the stretching rate is higher than the chain retraction motion, no crystallization occurs during the drawing of poly(ethylene terephthalate).[24] These experimental results reflect the features of chain relaxation and, therefore, suggest the relaxation as a key process in the precursor formation for polymer melt crystallization.

Molecular simulations are useful tools to investigate the microscopic origin of precursors. Molecular dynamics simulations have demonstrated a fast crystallization induced by the uniaxial extension in the melt of

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polyethylene.[25] Further in this approach, a competition between the rate of nucleation, the rate of chain extension, and the rate of conformational relaxation has been observed.[26] Recently, the flow-induced shish formation and the subsequent kebab growth on the shish have been well reproduced in dilute solutions by Langevin dynamics simulations.[20] Dynamic Monte Carlo (MC) simulations even demonstrated that the shish could be so small as a single prealigned chain.[27] In this paper, by means of dynamic MC simulations, it will be shown that the coils, containing even no more crystalline order but only an orientational memory in their shapes, can act as the source of precursors (shish) in a binary blend of different chain lengths. Moreover, it will be demonstrated that the orientational relaxation selects the long-chain component to keep the orientational memory and by this way decides the precursor formation. These results, therefore, prove the essential importance of the relaxation process together with polydispersity in the texture formation of the flow-induced crystallization.

In this paper, after a simple introduction of simulation techniques, we first study the athermal relaxation of bulk extended chains. We prepare an intermediately relaxed melt in which all the local crystalline order have disappeared, but an orientational memory exists in the coil shapes. Then, we study the isothermal crystallization in the intermediately relaxed melt of both long-chain and short-chain cases. After that, we study the precursor formation in the intermediately relaxed binary blend of different chain lengths. Finally, we provide concluding remarks.

II. Simulation Techniques

Dynamic MC simulations of lattice polymer chains have been widely applied in the study of polymer freezing and melting.[28] In the lattice sites, a number of consecutive occupations represent a polymer chain, while the single voids can be regarded as solvent in a solution or as free volume in a bulk phase. Following the van der Waals approach, the interactions between local chain units can be simplified into a hard-core volume exclusion and various short-range attractions. The attractions include a potential energy E_c which favors the collinear connection of two bonds along the chain. Between the neighboring nonbonded sites, the attractions can be monomer−solvent mixing interaction B and the parallel interaction of two crystallizable bonds E_p. A microrelaxation model relaxed the chain conformation in a cubic lattice box with periodic boundary conditions. This model can be described as a step of monomer jumping from an occupied site to a void, with a slithering diffusion terminated by extending the nearest kink conformation along the chain if necessary.[29] The bonds are allowed to align either on the lattice axes or on the face and body diagonals, so the neighbors around each site can be as much as 26. In each step of microrelaxation, the well-known Metropolis sampling was employed with a potential energy penalty $cE_c + pE_p + bB = (c + pE_p/E_c + bB/E_c)E_c$, where c is the net number of noncollinear connections along the chain, p is the net number of nonparallel packing of two bonds, and b is the net number of chain−solvent contacts.[30] For the sake of simplicity, we fixed $E_p/E_c = 1$ and omitted B interactions in bulk polymer phases. We use only $E_c/(k_BT)$, where k_B is the Boltzmann constant and T the temperature, to adjust the system temperature.

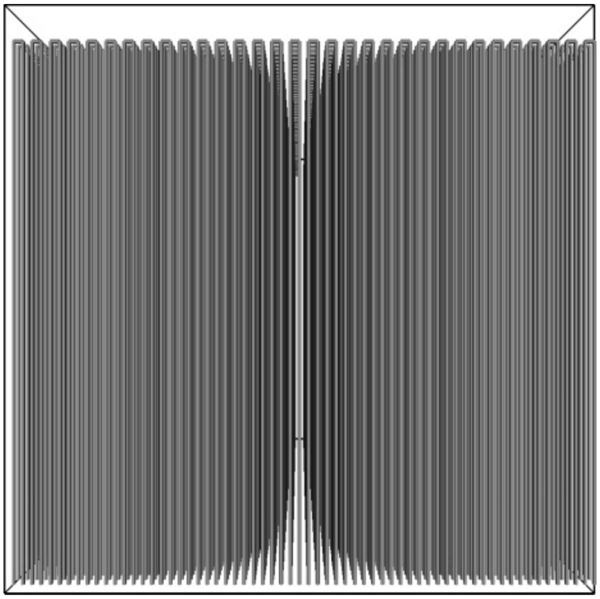

Figure 1. Snapshot of the initial relaxation state of bulk 120-mers in 64^3 cubic lattice with periodic boundary conditions. All the bonds are shown in cylinders.

In the following, we study the lattice−chain systems for different chain lengths, i.e., 120 units per chain and 30 units per chain. In both systems of uniform chain lengths, we first study the athermal relaxation of bulk extended chains, and then we compare the rates of isothermal crystallization in the melts produced from two different stages of relaxation. Further, we will study the isothermal crystallization of the intermediately relaxed melt in a binary blend of different chain lengths.

III. Results and Discussion

A. Athermal Relaxation of Bulk Extended Chains. In a cubic lattice box with the size of 64^3, we layer-by-layer regularly put 2048 chains, each containing 120 units with once-folded extended conformation, to construct the long-chain sample or, alternatively, put 8192 chains, each containing 30 units with fully extended conformation, to construct the short-chain sample. A snapshot of the long-chain sample is shown in Figure 1. The extended state of bulk chains can be regarded as a consequence of crystallization or impulse stretching under shear/elongation fluctuations. After that, without any potential energy (under an athermal condition), we let both samples relax and traced the time evolution of the mean-square radius of gyration as well as the time evolution of crystallinity. The crystallinity was defined as the fraction of bonds containing more than five parallel neighbors, in the total amount of bonds. The results are shown in Figure 2.

Figure 2a shows the relaxation process of the long-chain sample, while Figure 2b is for the case of the short-chain sample. In a parallel comparison of two cases, we found that the bulk long chains relax much slower than the bulk short chains. In each case, the coil size appears to relax much slower than the crystallinity. Therefore, during the athermal relaxation, there exist intermediately relaxed states, at which the elimination of the crystalline order has been saturated but the coil sizes are still large enough to maintain the orientational memory of the initial state. For the long-chain sample, we picked out the intermediately relaxed state at 250 MC cycles, where each MC cycle is defined as one trial

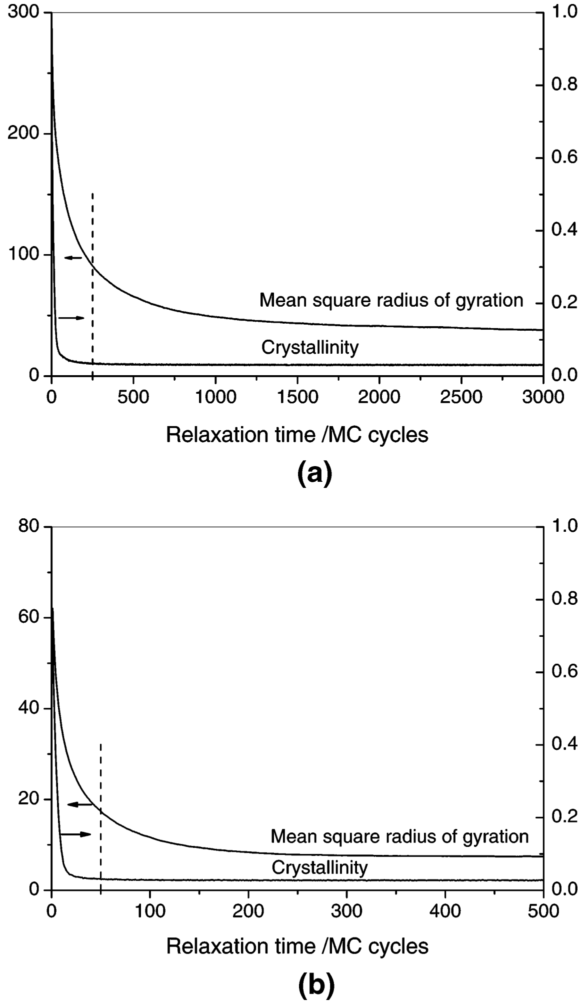

Figure 2. Athermal relaxation curves of mean-square radius of gyration (left axis) and crystallinity (right axis) for bulk extended chains of (a) 120-mers and (b) 30-mers. The vertical dashed lines indicate the instance where the intermediately relaxed melts were produced.

move per chain unit. For the short-chain sample, we chose the intermediately relaxed state at 50 MC cycles. In both cases, we also stored the comparable relaxed states at 3000 MC cycles. We will compare the crystallization behaviors of these melts in the next subsection.

The rates of athermal relaxations in our simulations have only qualitative meaning to the real polymer chains. This is not only because we use the lattice–chain model but also because Metropolis sampling assumes a constant prefactor to all the dynamical moves. In reality, it is well-known that the long-chain polymers are supposed to be speed up more by the reptation moves. Therefore, the relative magnitude of relaxation rate for long and short chains may not be accurate in reality.

We analyzed the size distribution of coils in the intermediately relaxed state of bulk long chains. In principle, the athermal relaxation can be regarded as crystal melting at the infinite temperature without the loss of molecular integrity. If this melting still keeps the kinetic feature of first-order phase transition, the size distribution of coils will show a double peak on the locations of the ordered and disordered phases. However, for the intermediately relaxed state, we see only a wide single peak located in the middle sizes, as shown in Figure 3. This indicates that with respect to a phase transition the relaxations of bulk chains are continuous and homogeneous, differing from the relaxation of single chains in dilute solutions under flow. This feature reveals the cooperative nature in the relaxation of bulk polymer chains, which coincides with the reported cooperativity in the long-chain component of blends for the precursor formation under shear field.[15] The spatial homogeneity of the relaxation can be demonstrated by the well distribution of those highly oriented coils shown in Figure 4. Figure 4 shares the same coordinate directions with Figure 1, so the uniform orientations of the coils demonstrate the orientational memory of the initial state. Upon further relaxation, the wide single peak in Figure 3 is expected to shift down to the sharp single peak of the relaxed state.

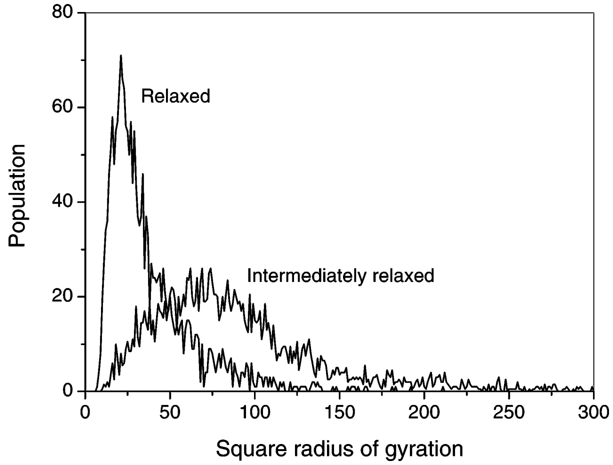

Figure 3. Distributions of the square radius of gyration in 120-mers at the intermediated relaxed state and the relaxed state as indicated in the figure.

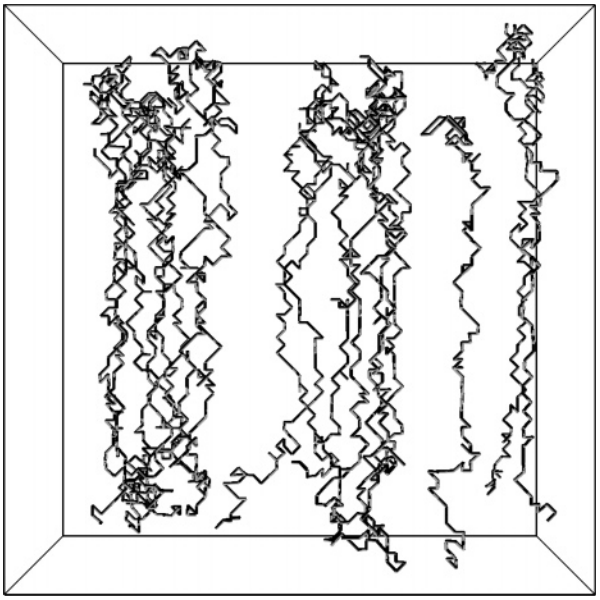

Figure 4. Snapshot of the melt at the intermediately relaxed instance of 250 MC cycles. Only are the chains having their square radius of gyration larger than 300 shown with the bonds in cylinders.

The intermediately relaxed state exists in real polymer systems. As a matter of fact, it has been reported that on the fast quenching of stretched poly(ethylene terephthalate) (PET), an amorphous state with a giving global chain orientation but nearly random bond orientations, can be frozen by the glass transition.[31] Molecular dynamics simulations even demonstrated the

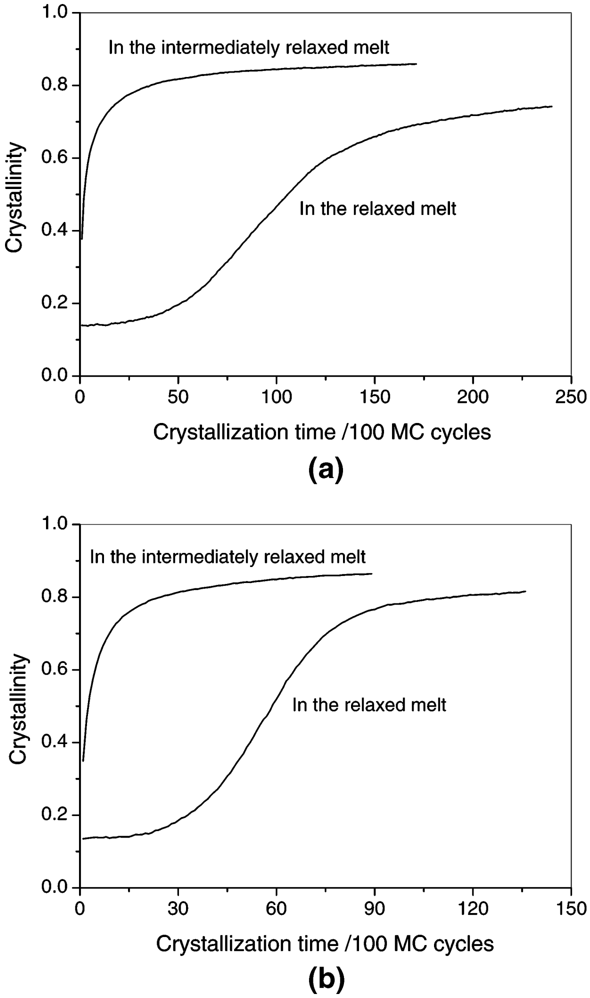

Figure 5. Time evolution curves of crystallinity in the intermediately relaxed melt and the relaxed melt for (a) 120-mers at the temperature of $E_c/(k_BT) = 0.25$ and (b) 30-mers at the temperature of $E_c/(k_BT) = 0.26$.

existence of such a kind of intermediate states during the orientational relaxation of a single extended polyethylene.[32]

B. Isothermal Crystallization. Since the relaxation rate depends on the chain length, the real long-chain macromolecules may keep the orientational memory in a macroscopic time scale. This memory is responsible for a fast crystallization rate at low temperatures. The orientational memory effect has a practical importance in polymer crystallization from a quiescent melt. For example, polyamides show a strong orientational memory in the melt even above their equilibrium melting temperatures,[33] provided that the thermal treatment is not long enough.[34] On the other hand, during annealing of the semicrystalline polymers, there exists a mechanism of melting−recrystallization.[35] Immediately after melting, polymer chains are expected to be disentangled, and the recrystallization from such a disentangled melt is much faster than the primary crystallization.[36,37]

To demonstrate this memory effect in polymer melt crystallization, we compared the rates of isothermal crystallization from the intermediately relaxed melt and from the relaxed melt. To enlarge their rate difference, we chose the temperature at which the crystallization from the relaxed melt has a significant incubation period for crystal nucleation. The results are shown in Figure 5. One can see that the intermediately relaxed melt exhibits a much faster crystallization than the relaxed melt in both long-chain and short-chain cases. This result verifies the fact that the orientational memory can significantly enhance the rate of crystallization in bulk polymer phases. This enhancement can be attributed to the decreased body entropy penalty of crystallization as mentioned in the Introduction. A fast crystallization in PET melt containing global oriented chains has been reported in experiments[38] as the well-known strain-induced crystallization.[39]

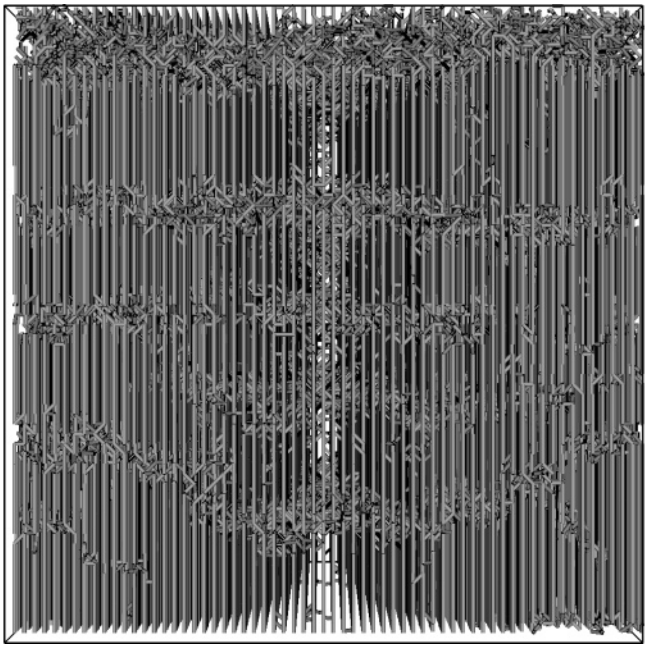

Figure 6. Snapshot of folded-chain crystals formed in the isothermal crystallization from the intermediately relaxed melt at the temperature of $E_c/(k_BT) = 0.25$. All the bonds are shown in cylinders.

The disentanglement in the state right after melting was regarded as a main reason to accelerate the recrystallization at low temperatures.[36] However, Figure 5b shows that even in bulk short chains like 30-mers, which are so short that no entanglement effect could exist in their melt,[40] the crystallization rate is still enhanced in the intermediately relaxed melt. Therefore, the orientational memory seems to be more fundamental than the disentanglement in the acceleration of recrystallization.

The obtained metastable folded-chain crystals of 120-mers are shown in the snapshot of Figure 6. Again, this picture shares the same coordinate directions with Figure 1 as well as Figure 4 and demonstrates the uniform orientations of crystallites dictated by the intermediately relaxed coils which contain the memory of the original orientations of polymer chains.

As revealed in Figure 3, there is a wide distribution of coil sizes in the intermediately relaxed melt of uniform chain lengths. Those highly oriented coils are expected to facilitate the crystallization more, and hence they may play an essential role in the initiation of fast crystallization. To check out whether such a precursor exists in those highly oriented coils, we studied the early stage of isothermal crystallization from the intermediately relaxed 120-mers, in particular at one MC cycle, at the temperature of $E_c/(k_BT) = 0.25$. We searched for those crystalline bonds containing more than 10 parallel neighbors and found 14 chains they belonged to. In the original intermediately relaxed melt, these 14 chains

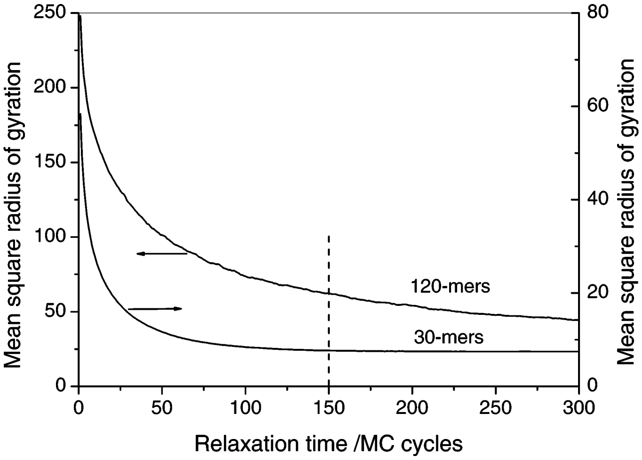

Figure 7. Athermal relaxation curves of mean-square radius of gyration for two species in the bulk extended-chain mixture as indicated. For the details of the mixture, see the text. The vertical dashed line indicates the instance when the intermediately relaxed melt was produced.

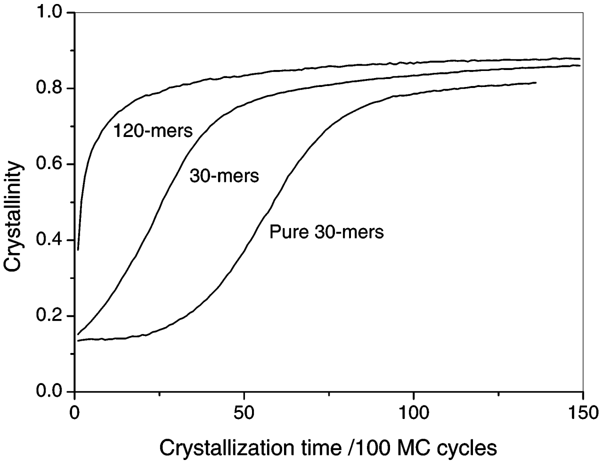

Figure 8. Time evolution curves of crystallinity for two species in the intermediately relaxed mixture and for the relaxed pure 30-mer melt, as labeled nearby in the figure, at the temperature of $E_c/(k_BT) = 0.26$.

have the mean-square radius of gyration at 93.513, which is very close to the average result at 91.044 over all the coils. Therefore, there is no precursor formed by those highly oriented coils in the initiation of fast crystallization. This implies that at the given temperature most of chains are more or less oriented and contribute to the initiation of crystallization. The absence of precursor is actually consistent with the experimental observations that the shish precursor disappears without a long-chain component.[21,22]

Polydispersity of molecular weights seems to be a prerequisite for the formation of shish-kebab crystals.[7] The shish-kebab morphology appears as a consequence of hierarchical crystallization. The absence of a hierarchical crystallization should be attributed to the absence of distinguishable relaxation fractions in the melt, since in the melt of uniform chain lengths there is only a single-peak distribution of coil sizes. This judgment encouraged us to go ahead to investigate the binary blend of different chain lengths.

C. In a Binary Blend of Different Chain Lengths. Since long chains can keep the orientational memory longer than short chains, and the memory offers the priority in crystallization, it will be interesting to see a hierarchical crystallization in the intermediately relaxed binary mixture of different chain lengths. To this end, we construct the initial extended-chain mixture by putting 128 120-mers at first four layers and putting 7680 30-mers at the rest 60 layers in 64^3 cubic lattice. The athermal relaxation curves of coil sizes for different chain lengths are shown in Figure 7. One can see that the long chains indeed relax slower than the short chains. We, therefore, picked out the intermediately relaxed state at 150 MC cycles, where no crystalline order remains and the relaxation of the short-chain component has already been saturated but that of the long-chain component not.

The isothermal crystallization of short chains in the intermediately relaxed mixture appears much faster

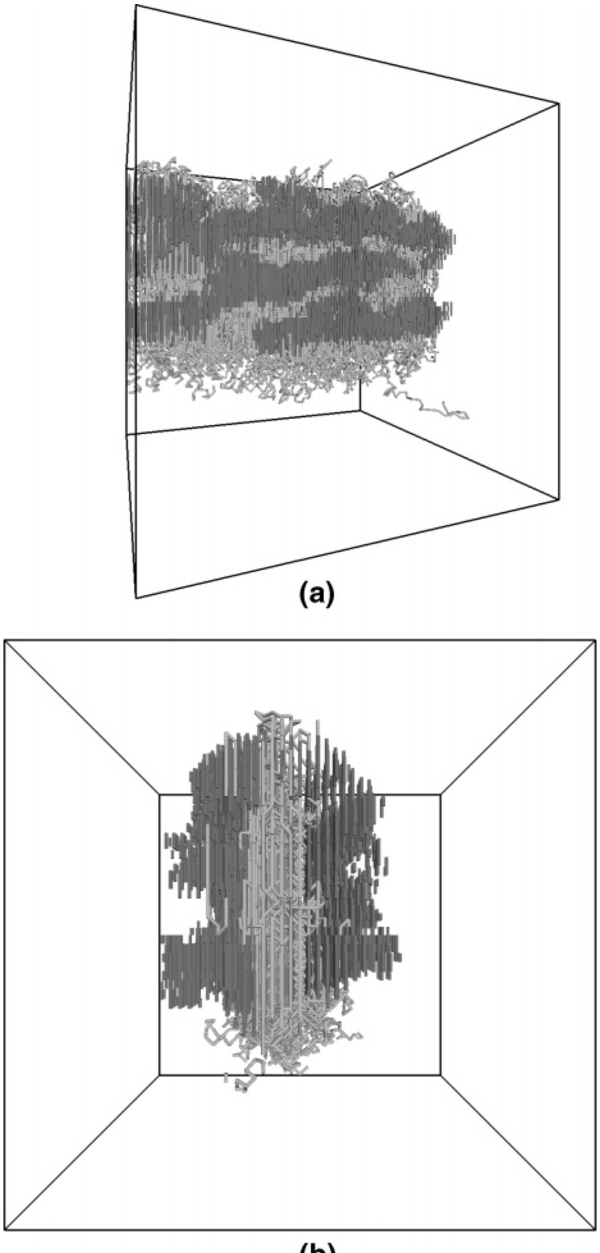

Figure 9. Snapshots of the crystallites at the instance of 100 MC cycles during the isothermal crystallization of the mixture at the temperature of $E_c/(k_BT) = 0.26$. For the long-chain component, all the chains have been drawn in bright gray, while for the short-chain component, only the bonds containing more than 18 parallel neighbors are drawn in dark gray. All the bonds are shown in cylinders. (a) View from the spreading surface; (b) view from the transection.

than that in the relaxed purely short chains, and this acceleration can be attributed to the prior crystallization of the long-chain component, as shown in Figure 8. Figure 9 provides the snapshots at 100 MC cycles of crystallization, demonstrating that the present long-chain crystals facilitate the crystallization of short chains. The long-chain component has a priority in the crystallization, and the short chains just start their crystallization from the lateral side of long-chain crystals by means of epitaxial crystallization. The parallel outgrowth of the multilayer crystals produces kebabs, while the long-chain crystals in prior crystallization act as shish. The growth of kebabs induced by shish in the melt can be regarded as a case of self-nucleation.

The above observations on the binary blend of different chain lengths suggest that the source of precursors is the oriented noncrystalline long-chain component. Since only the orientational relaxation is applied here, it is expected that under a shear/elongation flow of polymer melt the orientational relaxation rather than the stretching of polymer chains decides the precursor formation in the subsequent crystallization. It is obvious that the stretching will select the short-chain component in the priority of orientations due to a less penalty on the conformational entropy of chains, while the relaxation selects the long-chain component to keep the orientational memory longer.

In the practice of self-nucleation techniques, the sluggishness of the long-chain component on melting makes the memory effect of orientations difficult to be separated from the memory effect of self-nucleation. This is simply because both the memories of orientation and self-nucleation depend on the temperature and the time period applied in the thermal treatment. Therefore, the orientational memory can facilitate the sporadic nucleation by changing the amount of athermal nuclei with temperatures, as observed in experiments[41] and considered in theories.[42,43]

IV. Concluding Remarks

It is natural to observe the orientational relaxation after the stretching has made the coil shape far away from the equilibrium. Experimental observations suggested that the occurrence of precursors should be related with the relaxation process. Molecular simulations provide us the possibility to study the details of precursor formation, in particular, the role of orientational relaxation in precursor formation.

We make a summary of our simulation results here. We first observed the athermal relaxation of bulk extended chains. The relaxation appears continuous in the transition and homogeneous among the chains, and its rate depends on the chain length. Then, we found that isothermal crystallization can be accelerated by the orientational memory produced in the above relaxation, as demonstrated in both long-chain and short-chain systems. However, the crystallization did not show any precursor formed by those highly oriented coils in the melt of uniform chain lengths. We repeated the above process in a binary mixture of different chain lengths. In the crystallization of an intermediately relaxed blend, we observed the precursor formed by the oriented long-chain component, which induces the epitaxial crystal growth of the relaxed short-chain component. This mechanism has provided a well interpretation of the formation of shish-kebab crystals in polymer melt. Therefore, our simulations demonstrated that the orientational relaxation makes a selection of the long-chain component to keep the orientational memory longer and hence to let them be the source of precursor formation in the subsequent crystallization. The above results suggested the essential importance of the orientational relaxation and polydispersity in the understanding of the semicrystalline texture produced in flow-induced crystallization.

Further simulations employing a flow field in the melt are under our research schedule. We are going to learn how the stretching cooperating with the relaxation affects the precursor formation in flow-induced crystallization. The results will be reported later.

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