Chain folding in polymer melt crystallization studied by dynamic Monte Carlo simulations

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The morphological metastability of spontaneous crystallization from the melt of short-chain semiflexible homopolymers was studied through dynamic Monte Carlo simulations of a lattice multiple-chain system. Frictional hindrance for the sliding diffusion of the chains in the crystallites was employed to enhance the metastability of folded-chain crystallites, and distinguish the polymer crystallite from its mesophase, though their phase transitions have the similar driving forces. The integral folding of short chains in the crystallites and the constant linear crystal growth rate were identified with the actual polymers. In addition, the roughness of the local growth front accompanied with the occasional reversals and jumplike advancing was observed, which cannot be explained by current models. The crowding of the dangling ends on the fold surface seems to be the main reason for suppressing the lateral growth front, and the mechanism of chain folding was proposed. Its implications to the special behaviors of polymer melt crystallization, such as the semicrystalline state, the effect of the chain rigidity and molecular weight to crystal growth, the reversible premelting, and molecular segregation are briefly discussed. © 2001 American Institute of Physics. [DOI: 10.1063/1.1389860]

I. INTRODUCTION

Polymer melt crystallization is a typical first-order phase transition but usually generates folded-chain crystallites from the supercooled melt due to kinetic preference.1 The limited thickness of lamellar crystallites has been classified as morphological metastability in order to be distinguished from the classical metastability such as polymorphism.2 However, up to now, the mechanism of chain folding, i.e., the details of the kinetic pathway of polymer crystallization, is still not clear.3

The intrinsic difficulty of long-flexible-chain crystallization has been justified by the appearance of crystal growth only at large supercoolings.4 It implies a kinetic barrier for the long-chain molecules to cross the large gap of conformational entropy between the disordered state and the ordered state. Current conflicting models regarding the molecular pathway of polymer crystallization can be divided into the entropy-barrier models, such as the Sadler-Gilmer model,5 and the energy-barrier models, such as the Lauritzen-Hoffman model.6 All of them were developed from the crystallization models of small molecules rather than direct observations of the more complicated polymer system, since molecular level observation of crystal growth is experimentally difficult, if not impossible, for actual polymers. In this respect, molecular simulations are useful extensions of experiment. The simulations of polymer crystallization from dilute solution have identified the nucleation-growth mechanism,7 the convergence in lamellar thickness, and interfacial roughness at the growth front.8–10 However, a spontaneous phase transition from polymer melt has not received a great deal of attention, except for the preliminary investigation of copolymer crystallization.11

Recently, with recognition of the similarity in the molecular driving forces between polymer crystallization and its mesophase formation from the melt, the dependence of the equilibrium melting point upon the driving force, chain length, content of random comonomer, and content of diluentlike small molecules or noncrystalline polymers in polymer mixture was predicted by classical lattice statistics, and then verified quantitatively using dynamic Monte Carlo simulations of the lattice chain model.12 Only three molecular parameters, corresponding to the chain rigidity, the interchain attraction for close packing, and the mixing energy with solvent, were employed to drive phase transitions between the equilibrium states. The lattice model is further applicable in studying the pathway details of the large conformational change during crystallization.

According to the well-known Ostwald’s stage law, a transformation from one stable state phase to another will progress through metastable states whenever such states exist. The morphological metastability of actual polymer crystallization may be enhanced by an activation energy barrier based upon the details of molecular structure. In most common chain polymers, the longitudinal mobility of the chains in the crystallites has been believed to be an essential barrier not only for the thickening growth of the metastable lamella13,14 but also for the ultradrawability of synthetic fibers.15 In other words, the metastability of chain folding will be enhanced by the difficulty of chain motion in the crystallites. As a typical example,16 polyethylene has been found to contain high longitudinal mobility in the hexagonal phase under high pressure (a mesophase called condis crystal17), where the lamellae are extended-chain crystals (ECC) because of a fast thickening growth immediately fol-
lowing the advancing of the lateral front of the lamellae, so the profile of growth front is wedge-shaped or leaf-shaped; while under atmospheric conditions, polyethylene chains contain low longitudinal mobility in the orthorhombic phase and the lamellae are folded-chain crystals (FCC). A local sliding diffusion of chains exists in the micrelaxation model of previous simulations. The longitudinal mobility in the crystallites is easily realized by introducing an activation energy barrier for sliding diffusion of chains in the ordered region. Thus, the metastable FCC can be simulated, and the polymer crystallite can be distinguished from its mesophase by this way, even though their phase transitions have the similar driving forces. The pathway details of the new phase evolution in the supercooled melt can be studied.

In this paper, after an introduction of the simulation techniques, the spontaneous disorder-order phase transitions of semiflexible short-chain polymers with full or partial longitudinal mobility in the ordered region are studied to identify the integral folding behavior of some short-chains polymers during melt crystallization. Then, in the same way, a system containing no longitudinal mobility in the ordered region is generated to study the basic molecular pathway of polymer crystallization from the melt.

II. SIMULATION TECHNIQUES

Dynamic Monte Carlo simulation employs a micrelaxation model to relax the chain conformation on the lattice space with volume exclusion and periodic boundary conditions. The employed micrelaxation model is a single-site jumping accompanied with a local sliding diffusion, which is terminated by the elimination of the nearest sharp kink conformation along the chain. A schematic picture of this model can be found in Fig. 1 of Ref. 19. This model is highly efficient in relaxing the local chain conformation through the sliding diffusion, especially during a disorder-order phase transition. Here the bond, connecting the monomers along the chain, can either stay on a grid line or on a diagonal line in the cubic lattice space. The coordination number is thus 9 + 8 + 9 = 26, which is high enough to describe the short-range interactions without a restriction of the limited dimension of the discrete lattice space for phase transitions in the condensed state.

A typical sample system was generated through presetting 1920 fully ordered chains, each containing 16 monomers in a 32x32x32 cubic box. The occupation density is thus high, at 0.9375, to simulate the condensed state of polymers. In the illustrations of this paper, the chain length and the size of lattice box are subject to change, but the occupation density will be kept in the same value. Then, the extended chains are allowed to relax down to the equilibrium state of coils under athermal conditions, through the micrelaxation model with a random-choice algorithm for the sampling. According to this algorithm, when a monomer is selected through a random choice of the lattice sites, then the algorithm looks for a neighboring void randomly, when a void is selected, then the algorithm looks for a neighboring monomer. So the events of evolution are homogeneous in the lattice space. The unit of evolution time, one Monte Carlo step (MCS), is defined as one random-choice at each lattice site on average. The scaling laws for the chain size and the chain dynamics have been checked as shown in Fig. 1. The “unperturbed” coil size and the Rouse-model chain motion identify the athermal sample system corresponding to a melt state of short-chain polymers.

The athermal condition of the melt usually means an infinitely high temperature. Beyond this condition, three interaction parameters for the nearest neighboring bonds are taken into consideration. Referring to the fully ordered state as the ground state, the first parameter is defined as the energy change $E_c$ for each noncollinear connection pair of the consecutive bonds along the chains; the second one is the energy change $E_p$ for each pair of nonparallel packed bonds on the lateral directions; and the third one is the frictional hindrance $E_f$ working from each parallel-packed bond around the lateral directions of each bond in sliding diffusion. The energy change for mixing a pair of monomers and a pair of voids is omitted due to the high occupation density. The revised METROPOLIS importance sampling method is employed in which each step of micrelaxation is accepted with a probability of $\min[1, \exp(-\Delta E/kT)]$, and the energy barrier is defined as

![FIG. 1. Static and dynamic properties of the athermal lattice chains in 32 x32x32 cubic lattice box with an occupation density of 0.9375. (a) Mean square end-to-end distance $\langle r^2 \rangle$ vs chain length. The solid line with a slope of 1.0 refers to the scaling law of chain size in the “unperturbed” state of coils. (b) Mean-square displacement vs evolution time for 16 mers. The triangles are for the four inner monomers, the circles are for the mass center, and the crosses are for the monomers relative to the chain mass center. The solid lines with the slope 1.0 and 0.5, respectively refer to the scaling laws of the corresponding mean-square displacements for Rouse-model of chains (see Ref. 20 for the details).](image-url)
where, \( c \) is the change in the number of noncollinear connections of the bonds along the chain, \( p \) is the change in the number of nonparallel packing of the bonds excepting the consecutive bonds along the chain, \( n \) is the number of bonds performing local sliding diffusion along the chain, and \( f(i) \) is the number of bonds packing in parallel around the respective \( i \)th bond in sliding diffusion. Since the parallel packing of the bonds represents the close packing of local chains in the crystalline state,\(^{12} \) the frictional hindrance of sliding diffusion will apparently occur in the ordered region but not in the disordered region. Therefore, it represents the longitudinal mobility of chains in the lamellar crystallites and depends exactly upon the perfection of the local-ordered region.

The activation energy barrier can be regarded as a kinetic factor of acceptability in the classical METROPOLIS sampling. In the equilibrium melt before a phase transition occurs, the frictional energy barrier is very low due to the fully disordered state, and contributes to the sampling in both directions of jumping, i.e., a small change in the rate of state flow. So the detailed balance condition for the validity of the METROPOLIS sampling method still holds. During the phase transition, the detailed balance condition will not hold any more, and the activation energy barrier may terminate the phase transition in any potential metastable state. Recently, the kinetics of crystal growth of the Lennard-Jones system simulated by dynamic Monte Carlo simulations has been proved in agreement at large time scale with that of molecular dynamics simulations.\(^{21} \) Therefore, this sampling method is applicable in studying phase transition with an artificial time scale. During phase transition, the sequential states generated by this sampling method can supply helpful information about the molecular pathway of the new phase evolution, and the polymer crystallite can be distinguished from its mesophase by adding an activation energy barrier for the sliding diffusion of chains in the ordered region.

By changing the form of Eq. (1), three reduced parameters can be adjusted, \( E_p/E_c \) represents the intrinsic driving force of the phase transition, \( E_f/E_c \) represents the longitudinal mobility of the chains in the crystallites and \( E_c/(kT) \) represents the system temperature. A stepwise increase in the value of \( E_c/(kT) \) from zero with step length 0.02 represents a cooling process from the melt. The disorder parameter, which is defined as the mean fraction of noncollinear conformations along the chains, can be calculated for the sample system after 300 MCS relaxation at each step of temperature. In the fully ordered state, the disorder parameter is zero, while in the disordered state, such as for the athermal chains, it nears to one.

Figure 2 clearly illustrates spontaneous disorder-to-order phase transitions on the cooling curves with three typical \( E_p/E_c \) values. The finite-size effect of the lattice box seems not to be apparent for this kind of phase transition.\(^{12} \) Variations in the value of \( E_p/E_c \) for the nonpolar polymers can be commonly regarded as due to the difference in chain rigidity, since the nonpolar interchain interaction does not deviate too much. Therefore, \( E_p/E_c = 0 \) means a rigid chain, and \( E_p/E_c = 0 \) a flexible chain. As an example of the semiflexible chain system, \( E_p/E_c = 1.0 \) was fixed in the following sections to investigate the details of the isothermal phase transition.

III. RESULTS AND DISCUSSION

A. Phase transition with longitudinal mobility of chains in the ordered region

With a small frictional setting (\( E_f/E_c = 0.1 \)) and with zero frictional setting (\( E_f/E_c = 0 \)) for the longitudinal mobility of chains in the ordered region, the isotherm behavior of the melt can be traced using the disorder parameter after jumping from the athermal state to the crystallization temperature near the onset of phase transition on the cooling curve. As shown for both cases in Fig. 3, a delay before the disorder-order phase transition indicates an incubation period for nucleation. In principle, every moment of the sample system during the isothermal annealing process can be stored in the computer for detailed analysis with graphics software. Nevertheless, the state of system was recorded at 1000 MCS intervals. During the morphological evolution of both cases,
a wedge-shaped or leaf-shaped profile for the growth front can be observed. This agrees with the morphological characteristics of polyethylene crystallites under high pressure. Compared to the smoothness of growth front that has a sharp interface, the gradual decrease of crystallite thickness on the front is regarded as the roughness. Here, due to the thickening growth, the roughness may not be a native characteristic of the growth front of polymer crystallites. More observations for the sample system with no longitudinal motion of chains in the ordered region will be reported in Sec. III B.

In the crystalline region, the consecutive collinear conformations along the chain result in extended stems. The distribution of stem length can be estimated from the sample system to represent the thickness distribution of the lamellae, as in conventional small-angle x-ray scattering measurements. For the sample system with no hindrance of sliding diffusion, the stem length directly approaches the chain length (16 units), and is not stable at any intermediate length, which would be indicative of chain folding, as shown in Fig. 4(a). Extended-chain crystals (ECC) morphology is immediately generated during phase transition. A snapshot of lamellar crystallites can be found in the previous paper [see Fig. 2(b) of Ref. 12].

For the sample system with a partial hindrance of sliding diffusion in the ordered region, there is a maximum of monomer population corresponding to a stem length in the vicinity of half a chain length (about 8 units) during the phase transition at a proper temperature, as shown in Fig. 4(b). This implies that the metastable once-folded chains can stabilize the crystal thickness. The lamellar morphology of the crystallites can be directly observed. For a longer chain system (32 mers), a metastable lamella containing twice-folded chains (with a stem length of about 10 units) can even occur when crystal growth and isothermal annealing at a proper crystallization temperature. It then thickens to once-folded chain crystals (with a stem length of about 15 units), as is clearly shown in Fig. 4(c). These observations agree well with the integral folding behavior of polyethylene and poly(ethylene oxide) short-chains which contain partial longitudinal mobility in the crystallites.

Here, longer periods or higher temperatures in isothermal annealing will favor further thickening, and may make the chains fully extended. However, since the overall frictional hindrance for the sliding diffusion of the stems increases with lamellar thickness, further thickening is not favored, and may even be completely inhibited in the nonintegral folding. For the case of long-chain molecules, the metastable thickness of lamellae may be approached due to a balance of these contradictory tendencies. This conjecture needs to be verified in future simulations for a long-chain system with larger frictional hindrance for sliding diffusion in the crystallites. Regardless, the simulation results of short-chain polymers have clearly demonstrated that the occurrence of ECC or FCC, i.e., the morphological metastability of chain folding, depends upon the longitudinal mobility of the chains in the ordered region.

The fold surface structure of the once-folded chain crystals is worth studying. From Fig. 5, where only sharp-folded chains are drawn and viewed along the direction of stems, one can see that the sharp folds do not cover the whole surface. This implies that the lamellar thickness can be stabilized by only partial amounts of regularly folded chains. The distribution of fold directions seems rather random, and sectorization does not occur. This result is quite different from the experimental observations of the single crystals grown from dilute solution or from the surface of the thin

FIG. 4. Distribution of monomers vs stem length at some evolution time points (the numbers denoted with the curves ×1000 MCS) for the multiple-chain system in 32×32×32 cubic box with an occupation density of 0.9375. Solid lines connecting the discrete data points are drawn with a displacement of 300 along the vertical axis for clarity. (a) For 16 mers with the setting \( E_f/E_c = 0.1 \) and \( E_r/(kT) = 0.2163 \); (b) for 16 mers with the setting \( E_f/E_c = 1.0 \), \( E_r/E_c = 0.1 \) and \( E_r/(kT) = 0.198 \); (c) for 32 mers with the setting \( E_f/E_c = 1.0, E_r/E_c = 0.1 \) and \( E_r/(kT) = 0.174 \).
A film of polymer melt. A possible reason may be the small length of chains, the small size of the crystallites, or a difference in the crystal growth mechanism, since in the dilute solution, or on the surface of the melt, the dangling ends are obliged to fold back immediately at the growth front. Further observations using longer chains, higher annealing temperatures, and larger crystallites are expected in the near future to identify the reason.

B. Phase transition without longitudinal mobility of chains in the ordered region

If \( E_f / E_c = 0.3 \) was set, a bond with sliding diffusion in the fully ordered region will have a frictional hindrance of \((26 - 2) \times 0.3 = 7.2\), two consecutive bonds along both directions of the chain being deducted from the coordination number, with a sampling acceptability of only \(\exp(-7.2) \approx 0.0007\). In other words, the longitudinal motion of this bond is almost impossible in the fully ordered region. Crystal growth without the longitudinal mobility of chains in the crystallites will be less complicated than the cases in the preceding section.

Due to the long incubation period of nucleation and the limitation of hardware calculation, it is difficult to simulate the spontaneous crystallization under very small supercoolings. The highest testing temperature at which spontaneous nucleation occurs before 50,000 MCS is \( E_c / (kT) = 0.180 \). Under this isothermal condition, the grown lamella is thin and metastable with a thickness of about 5 units, as shown by the thick lines in Fig. 6(a) for a 32 mer system in 32-sized cubic box without any sliding diffusion in the ordered region. The profile of lateral growth front still shows wedge-shaped or leaf-shaped, i.e., the roughness as in Sec. III A. However, the advancing fronts contain horizontal lines to form an approximate lozenge shape as an example in Fig. 6(b). The advancing rate of each horizontal line is not homogeneous, as a comparison result of Figs. 6(b) and 6(c). If the observa-
model to describe the mechanism of crystal growth in the melt may be the “Erstarrungsmodell” (the solidification model).24 A large number of chains will pass through the lamella without folding back immediately.25 However, these dangling ends require more transverse space on the fold surface than the corresponding stems in the crystalline region. Crowding on the fold surface is a natural result. To keep the crystal flat, some sharp fold ends are necessary to coexist with the dangling ends, and supply them the free transverse space above the fold surface.26 During advancing of the lateral growth front, if enough sharp fold ends cannot be found immediately from the melt, the dangling ends will invade the grow front due to the crowding on the fold surface, as an illustration in Fig. 6(a). They can suppress the front gradually, unless an adequate number of sharp fold ends occur after local melting and reorganization. This kind of rearrangement may involve several layers of the growth front and appear as the observed local surface reversal and intermittent advancing (see for instance, Fig. 6). This kind of process might not necessarily be rate determining step, but should be essential even for the fastest growth of lamellar crystallite from the melt with large supercooling.

It is possible to generate the sharp fold ends by the local rearrangement on the growth front. In the polymer melt, there is a correlation hole for monomer packing with respect to the other chains.27 This means that the first neighbor of a monomer contains a high probability of belonging to the same chain. At the growth front, two packed monomers belonging to the same chain form a closed loop, and a sharp fold end can be simply generated by tightening this loop through sliding diffusion. After the closed loops have formed an adequate number of sharp fold ends, the lateral growth front can be further advanced. Thus, the dangling ends with the opened loops will remain as the main component above the fold surface of the lamella, and may contribute to the apparent reversible premelting on the fold surface of some polymer crystallites.28

The depth of the correlation hole will depend upon the chain flexibility. For the case of rigid chains, a closed loop will not be generated with high probability, and forming a sharp fold is also difficult due to chain rigidity. This may be the reason for the small growth rate and ill-formed lamellae of some rigid-chain polymers.29

Chain entanglements in the melt or the structural defects of actual polymer chains, such as the short branches, will slow up or even block up the tightening of the closed loops, and hence, the lamellar growth. The long loops and cilia on the fold surface may not further crystallize for a similar reason. So the semicrystalline state is a natural result of polymer melt crystallization.

The short chains will generate small closed loops, which can be tightened faster than the large closed loops generated by long chains, so the crystal growth of short chains is usually faster than the long chains. However, under small supercoolings, the folding of short chain in the reversal region of thicker crystallites is less stable than that of the long chain due to the high mobility of the chain ends. The shorter chains will be gradually excluded from the growth front. This might
be the reason for molecular segregation of polymer crystallization.

IV. SUMMARY

The metastable state of spontaneous melt crystallization of short-chain polymers has been simulated by introducing an activation energy barrier for sliding diffusion of chains in the ordered region, which distinguishes polymer crystallite from its mesophase even though they contain the same kinds of driving forces for disorder-order phase transitions. The morphological metastability of chain-folded lamella, especially the integral folding of short chains, and constant linear crystal growth rate are identified with the actual polymers. Current models cannot describe the detailed observations, such as the roughness of the lateral growth front accompanied with the local reversal and intermittent advancing. Crowding of the dangling ends on the fold surface seems to be the main reason for suppressing of the growth front. The mechanism of chain folding and its implications to the special behaviors of melt crystallization of chainlike molecules are thus discussed.

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