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Kinetic Monte Carlo Simulations of Polymer Cold Crystallization

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Abstract We performed kinetic Monte Carlo simulations of a lattice polymer model holding intramolecular and intermolecular activation barriers for polymer diffusion, on the basis of the previous dynamic Monte Carlo simulations of polymer crystallization. We explored the effective parameter sets for two barriers to freeze the amorphous polymers at low temperatures. The subsequent heating process of the frozen amorphous polymers exhibits clear cold crystallization behaviors. We made preliminary investigation on the crystallinity and the morphology of polymer crystallites yielded during the cold crystallization, which appear in consistence with our common experimental observations. Our present work paves the way for molecular simulations of hot and cold polymer crystallization in the whole temperature range between the glass transition temperature and the melting temperature.

Keywords Polymer; Cold crystallization; Monte Carlo

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INTRODUCTION

It is well-known that polymer crystallization kinetics is dominated by a nucleation process, and the nucleation rate is controlled by the free energy barrier for the initiation of nucleation as well as by the diffusion barrier for crystalline units passing through the crystalline-amorphous interface, separately in the high and low temperature regions between the glass transition temperature and the melting point. These two barriers make polymer crystallization rate exhibit a parabolic-like temperature dependence with a maximum in the middle temperature region.^[1,2] Crystallization in the high temperature region upon cooling from the melt is called as hot crystallization, while crystallization in the low temperature region upon heating from the glassy state is named as cold crystallization. Cold crystallization in the low temperature region yields much smaller crystallites with less perfect crystalline structures than hot crystallization, which commonly benefits the industrial processing of polymer materials with a better transparency or a higher toughness, and thus is worthy of investigations. While so far, most of our investigations on polymer crystallization are focusing on hot crystallization dominated by the nucleation barrier,^[1,2] cold crystallization dominated by the diffusion barrier is difficult to study due to the obstacle in precise temperature control to bypass fast crystallization upon cooling into the low temperature region, in particular, by the conventional differential scanning calorimeter (DSC) measurement.

Recently, fast-scanning chip-calorimeter measurement provides a better temperature control for bypassing fast crystallization and expands our investigation of crystallization towards the low temperature region.^[3–5] It is generally believed that crystallization below the glass transition temperature is completely suppressed by the low molecular mobility.^[6] Nevertheless, new experimental observations on the correlation between enthalpy relaxation and polymer cold crystallization were reported,^[7,8] which demands the corresponding molecular simulations for a better understanding of polymer cold crystallization at the molecular level.

Dynamic Monte Carlo simulations of a lattice polymer model have been extensively applied to investigate polymer crystallization.^[9–11] The energy parameters for polymer crystallization include the intramolecular conformational energy E_c between *gauche* and *trans* states as well as the intermolecular compact packing energy E_p between two parallel packed bonds, with each step of micro-relaxation to mimic real polymers moving in continuous space (the so-called dynamic Monte Carlo simulations). As introduced above, in the low temperature region, cold crystallization is dominated by the activation barriers for polymer diffusion. In each step of micro-relaxation, polymer diffusion contains the intramolecular barrier for the conformational change of bond connections as well as the intermolecular barrier for the adhesive interactions of neighboring non-bonded monomers. The intramolecular conformation barrier can be assigned as the activation barrier for the transition from *gauche* state to *trans* state of rotational isomerism on each backbone bond, as illustrated in Fig. 1.^[10] In the lattice model, the conformational change is reflected by the linear and nonlinear connections of consecutive bonds along the polymer chain. On the

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other hand, the intermolecular adhesive barrier can be assigned to the activation barrier for the splitting in each pair of two monomer contacts, as shown in Fig. 1 as well. The conventional Metropolis algorithm for Monte Carlo sampling has been employed, which follows the detailed balance.^[12–14] The kinetic Monte Carlo simulations add the same activation barriers on two opposite directions of micro-relaxation of polymers, which maintains the detailed balance well but lowering the sampling acceptability.^[15,16] With the activation barriers employed equally on two opposite directions of trial moves in each step of micro-relaxation, the diffusion effects in the low temperature region can be introduced for our investigation of polymer cold crystallization.

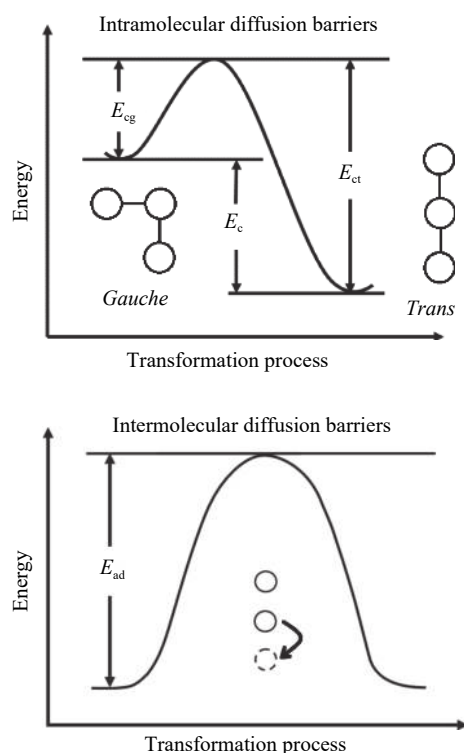


Fig. 1 Illustration of (top) intramolecular potential energy barriers E_{cg} and E_{ct} for conformational transition between a *gauche* state and a *trans* state of rotational isomerism on each backbone bond along a polymer chain, shown as collinear and non-collinear connections between two consecutive bonds, respectively, and (bottom) intermolecular potential energy barriers E_{ad} for each pair of non-bound neighboring monomers that split up on each micro-relaxation move. E_c is the *gauche-trans* energy change.

In this report, we employed the kinetic Monte Carlo simulations to investigate the cold crystallization behaviors of polymers upon heating from the frozen amorphous states. The parameters for the intramolecular and intermolecular energy barriers were explored in a logic sequence for their proper ranges. The results demonstrate that the crystallinity and the morphology features of cold crystallization behaviors are consistent with our common experimental observations. Thus, our simulation approach is conducive to further investigation for better understanding the new experimental observations.

TECHNIQUE DETAILS

We set up a lattice box of $64 \times 64 \times 64$ cubic cells and put 1420 chains, of which each contains 128 monomers with one monomer occupying one lattice site, into the box. A bulk polymer system was thus mimicked with the polymer occupancy density of about 0.6934. The rest vacancy sites were regarded as the free volume for polymer diffusion *via* micro-relaxation. In our dynamic Monte Carlo simulations, we randomly selected a monomer on the lattice polymer chains and one of its vacancy neighbors, and then tried to move the monomer into that vacancy neighbor like those monomers in a real polymer, with a single-site jumping and if necessary, partial sliding diffusion along the polymer chain.^[17] Since the bond could align along either 6 lattice axes, 12 face diagonals, or 8 body diagonals, the lattice coordination number was as many as 26. Double occupation and bond crossing were forbidden on account of the volume exclusion of polymers. Periodic boundary conditions of the lattice box were employed. The polymers in our simulations were nearly random coils with their diameters much smaller than the box sizes, thus the finite size effects for crystallization were not obvious. The unit of simulation time, one Monte Carlo cycle (MCC), was defined as the total amount of trial moves equal to the monomers in the lattice box.

The conventional Metropolis sampling algorithm was employed with the total potential energy change ΔE in each step of micro-relaxation of polymers. As illustrated in Fig. 1, the conformational energy parameters contain both the activation barriers on both sides, E_{cg} and E_{ct} , as well as their net result E_c for maintaining the detailed balance. It is worth mentioning that, when $E_{cg} = 0$, the parameter set should return back to our previous dynamic Monte Carlo simulations only with E_c . As introduced above, E_p is the net packing energy difference between parallel and non-parallel packed bonds which are neighboring in space. The activation barrier for adhesive interactions between two non-bonded monomers, E_{ad} , described the non-bonding monomers around each monomer to hinder the motion of the latter. Therefore, the total potential energy change in each step of micro-relaxation was integrated by these barriers, as given by

$$\Delta E = \Delta E_{cg} + \Delta E_{ct} - \Delta E_c + \Delta E_p + \Delta E_{ad} \quad (1)$$

We used the energy parameter E_c to reduce the dimension of other energy parameters (below simplified as E_{cg} , E_{ct} , E_p , and E_{ad} , respectively, for E_{cg}/E_c , E_{ct}/E_c , E_p/E_c , and E_{ad}/E_c), and thus the reduced temperature kT/E_c was briefly denoted as T . In practice, we counted the numbers of monomers and bonds corresponding to the above energy parameter changes in each step of micro-relaxation, and calculated the total potential energy changes. In detail, for E_{cg} and E_{ct} , we counted the total amount of bond connections changing from non-linear to linear connections, E_{ct} the total amount of bond connections changing from linear to non-linear connections, E_p the net amount of non-parallel-packed bonds, and E_{ad} the total amount of monomer-monomer contact pairs in splitting-up.

RESULTS AND DISCUSSION

In the first step, polymer chains were put with an initially ordered state into the lattice box, and then were athermally relaxed (all energy parameters were set as zero) for a sufficient time period to reach an equilibrium random coil state. This state was used as the initially frozen state for heating up from the low temperature region. The cold crystallization was monitored by the crystallinity in the heating process with the reduced temperature $T = 0.1$ increasing step-by-step with the step length of 0.1 after every 3000 MCCs. Crystallinity was defined as the fraction of crystalline bonds that contain more than 9 parallel neighboring bonds (since each bond could contain parallel neighbors along either the lattice axes or the diagonals as much as 24 bonds after subtracting two bonded neighbors, we arbitrarily chose 9 parallel neighbors of each bond as the demarcation between the crystalline bond and the amorphous bond).

In our previous dynamic Monte Carlo simulations of polymer crystallization, the standard protocols were the parameter sets of $E_c = 1.0$ and $E_p = 1.0$.^[9–11] We started with exploring the suitable parameter range of E_{ad} for the intermolecular activation barrier. To this end, we set $E_{cg} = 0$, $E_{ct} = 1.0$, $E_c = 1.0$, and $E_p = 1.0$, and increased E_{ad} from zero to a large enough value for suppressing any crystallization from the initial amorphous state in the low temperature region. The results are summarized in Fig. 2. One can see that without any adhesive interactions (*i.e.* $E_{ad} = 0$), the crystallization will be initiated as soon as the heating scan was launched at $T = 0.1$. The melting curve beyond $T = 5.0$ could be attributed to the superheating for crystal melting upon fast heating. Cold crystallization occurs only when polymers are frozen in the low temperature region with the larger E_{ad} values above 0.2. However, if the value of E_{ad} becomes too large, for instance, above 1.2, cold crystallization will be almost hindered during the heating process.

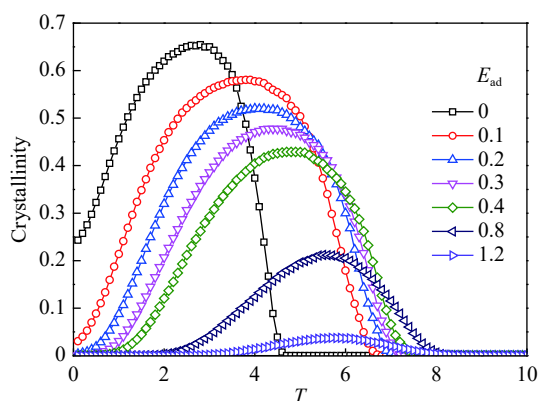


Fig. 2 Heating curves of crystallinity for the bulk polymer sample with various E_{ad} ($E_{ct} = 1.0$, $E_{cg} = 0$, and $E_p = 1.0$). The temperature was increased stepwise from 0.1 with a step length of 0.1 and a step period of 3000 MCCs.)

Next, we explored the suitable parameter range of E_{ct} for the conformational activation barrier. To this end, we set $E_{ad} = 0.2$ and $E_p = 1.0$, and changed the energy parameter E_{ct}

with $E_{cg} = E_{ct} - E_c$. The results for cold crystallization on heating scan are summarized in Fig. 3. One can see that when the conformational barrier becomes high enough, for instance, $E_{ct} = 40$, cold crystallization will be almost insensitive to this barrier height.

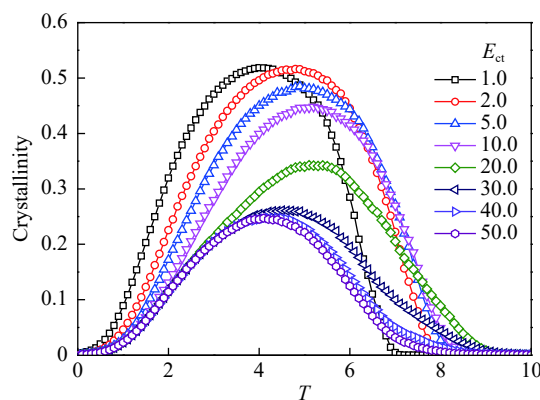


Fig. 3 Heating curves of crystallinity for the bulk polymer sample with various E_{ct} ($E_{ad} = 0.2$, $E_{cg} = E_{ct} - E_c$, $E_c = 1.0$, and $E_p = 1.0$). The temperature was increased stepwise from 0.1 with a step length of 0.1 and a step period of 3000 MCCs.)

Third, we explored the suitable parameter range of E_p for the driving forces of polymer crystallization. To this end, we set $E_{ad} = 0.2$, $E_{ct} = 10$, $E_c = 1.0$, and $E_{cg} = 9.0$, and changed the energy parameter E_p to explore its suitable range for cold crystallization. The results of heating curves are summarized in Fig. 4. One can see that when the crystallization driving force E_p becomes too weak, for example, 0.2, no cold crystallization can be initiated in the heating process, and when E_p becomes too large, for example, 2.0, melting occurs beyond the observation window of temperature due to a too high melting point.

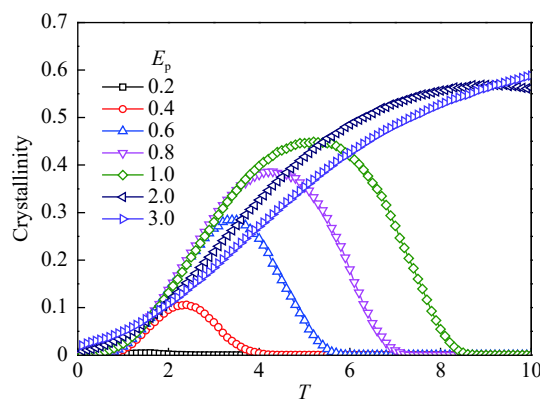


Fig. 4 Heating curves of crystallinity for the bulk polymer sample with various E_p ($E_{ad} = 0.2$, $E_{ct} = 10$, $E_c = 1.0$, and $E_{cg} = 9.0$). The temperature was increased stepwise from 0.1 with a step length of 0.1 and a step period of 3000 MCCs.)

The cold crystallization yields unique crystalline morphology in the low temperature region. We further investigated the variation of polymer mobility in the heating process with the most suitable parameter set $E_p = 1.0$, $E_{ad} = 0.2$, $E_{ct} = 10$,

and $E_{cg} = 9.0$. With these parameter sets, the cold crystallization starts around $T = 1.0$ and its corresponding melting ends around 8.0 in the heating process above. We calculated two quantities at each step of temperature raising: one was the acceptability of trial moves, the other was the largest length of the sliding monomers (denoted as L_m) along the chain. Fig. 5 shows that both the acceptability and L_m rise with the increase of temperature. When the temperature becomes below 4.0 (the saturation of cold crystallization), trial moves of polymer chains are hardly accepted, although the cold crystallization has already been initiated at $T = 1.0$. With the increase of crystallinity, the increase of sliding lengths is significant but not for the acceptability. The latter becomes obviously increased only after cold crystallization is saturated at the temperature 4.0. As the temperature reaches at 8.0 (the end of crystal melting), the acceptability increases slightly slower, and meanwhile L_m becomes saturated as the normal behaviors in the melt phase. Apparently, the initiation of cold crystallization requires very small acceptability and very short range of sliding monomers around $T = 1.0$. This result implies that the crystal nucleation could be initiated even below the glass transition temperature, as observed in the new experiments.^[7,8]

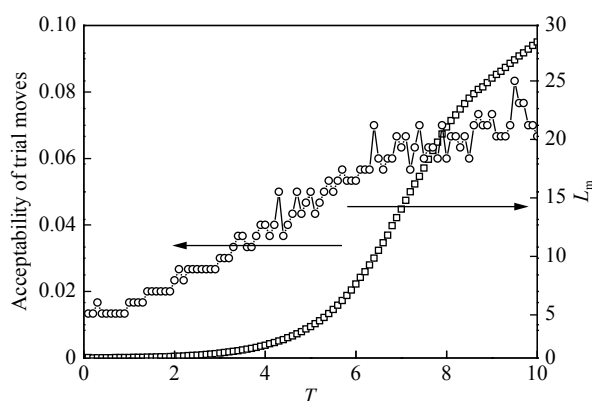


Fig. 5 The acceptability of trial moves and the largest length of sliding monomers L_m along the polymer chain within the time period of each temperature step, for the polymer systems with $E_p = 1.0$, $E_{ad} = 0.2$, $E_{ct} = 10$, $E_c = 1.0$, and $E_{cg} = 9.0$ (The acceptability of trial moves was defined as the fraction of accepted trial moves in the total number of trial moves within 3000 MCCs at each step of temperature. L_m was defined as the maximum number of monomers in each step of sliding diffusion along the polymer chain within the time period of each temperature step.)

The hot crystallization in the high temperature region should be controlled by the nucleation process, as indicated by the incubation period during the isothermal crystallization process. To confirm that hot crystallization can be reproduced as well with two activation barriers, we investigated the isothermal crystallization processes within the time window of 45000 MCCs at high temperatures, with the results for the time evolution curves of crystallinity summarized in Fig. 6. One can clearly see the elongated incubation periods for the time evolution curves of crystallinity at higher temperatures.

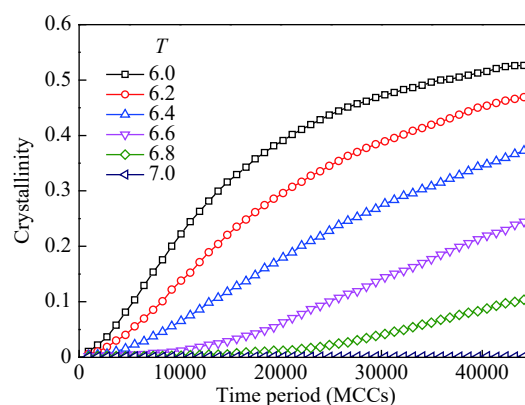


Fig. 6 Time evolution of crystallinity during isothermal crystallization at various denoted temperatures in the high temperature region, for the polymer systems with $E_{ct} = 10$, $E_{cg} = 9.0$, $E_p = 1.0$, and $E_{ad} = 0.2$

We expanded the temperature range of isothermal crystallization and observed the highest crystallinity achieved and the melting temperature within the time window of 45000 MCCs, as the results shown in Fig. 7. Since the time period 45000 MCCs for isothermal crystallization is much larger than 3000 MCCs in each step of heating scan, the maximum crystallinity reaches around 0.6, slightly higher than 0.5 achieved in the heating scan shown above. This can be attributed to the longer crystallization period to harvest a higher crystallinity. On the other side, the melting ends at the temperature around 7.0, slightly lower than 8.0 in the heating scan shown above. This result can be attributed to the incomplete melting during the limited time in each step of heating scan which expands the melting range. The results are consistent with our common experimental observations.

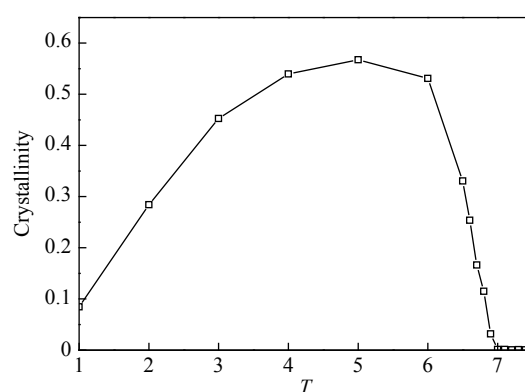


Fig. 7 Crystallinity saturated in the isothermal crystallization of 45000 MCCs at various temperatures for the melt polymer systems with $E_{ct} = 10$, $E_c = 1.0$, $E_{cg} = 9.0$, $E_p = 1.0$, and $E_{ad} = 0.2$

Finally, we compared the crystallite morphology harvested during isothermal crystallization for 45000 MCCs at various temperatures. Fig. 8 demonstrates four snapshots after isothermal crystallization at $T = 2.0$, 5.0, 6.0, and 6.5, respectively. The snapshot at $T = 2.0$ represents the crystallization in the low temperature region, showing many small

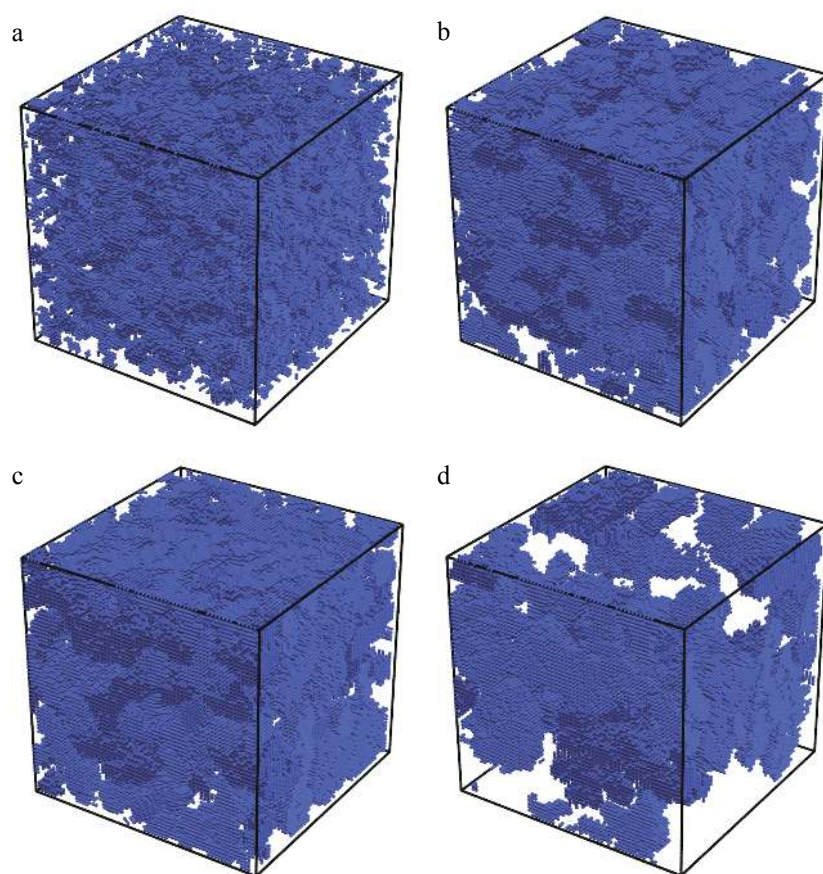


Fig. 8 Snapshots of polymer crystallites in the unit cell harvested at (a) $T = 2.0$, (b) $T = 5.0$, (c) $T = 6.0$, and (d) $T = 6.5$ after isothermal crystallization for 45000 MCCs (The energy parameters are the same as in Fig. 7. Only the crystalline bonds are shown with blue cylinders for exposure of the crystallite morphology.)

crystallites in Fig. 8(a) due to a high density of crystal nuclei although its crystallinity shown in Fig. 7 is still lower than that harvested at $T = 6.5$. The snapshots at $T = 5.0$ and 6.0 shown in Figs. 8(b) and 8(c) represent the crystallization harvesting the highest crystallinity in the middle temperature region. The crystallization at $T = 6.5$ as shown in Fig. 8(d) reflects the low density of crystal nuclei generated at small supercooling with much larger lamellar crystallites due to the spontaneous chain-folding. The total crystallinity harvested with large crystals at this temperature is actually slightly higher than that shown in Fig. 8(a) at $T = 2.0$. The morphology features are consistent with our common experimental observations on the feature of polymer crystal morphology yielded at the low temperatures.

CONCLUSIONS

By introducing both intramolecular and intermolecular activation barriers for polymer diffusion at low temperatures, we performed kinetic Monte Carlo simulations to investigate cold crystallization of bulk polymers in the heating process and the isothermal processes. We explored the suitable ranges for various energy parameters to reproduce the proper cold crystallization behaviors. The results for temperature

dependences of polymer mobility, harvested crystallinity, and morphology are consistent with our common experimental observations on polymer cold crystallization. Therefore, our simulations pave a way for our further study of cold crystallization behaviors in the low temperature region to better understand new experimental observations, as well as the global temperature profile of polymer crystallization kinetics between the glass transition temperature and the melting temperature.

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