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Molecular dynamics simulation for polyethylene crystallization: Effect of long chain branches

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ABSTRACT

The influence of long branches on crystallization behavior has been studied by means of molecular dynamics simulations. Using two systems: polyethylene (PE) with long branches (LCB-PE) and PE without long branches (linear-PE) with the same molecular weight, we have examined the crystallization behavior of the two systems by molecular dynamics simulation. This paper explains the influence of long branches on the isothermal crystallization process and the non-isothermal crystallization process with similar initial interchain contact fraction (*ICF*) in terms of final *ICF*, crystal regions, crystallinity, concentration of tie chains and energy. It is found that the crystallization process is classified as two stages: the nucleation stage and the crystallinity of molecular chains. From the perspective of potential energy and non-bond energy, LCB-PE has lower energy than linear-PE in the nucleation stage while the energy of linear-PE is lower than that of LCB-PE in the second stage. In short, the long branched chains inhibit the crystallization process. **Polyolefins J (2021) 8: 73-84**

Keywords: Molecular dynamics; crystallization; long branches; nucleation; tie chains.

INTRODUCTION

As a kind of semi-crystalline polymer, polyethylene (PE) has been widely used in chemical, clothing, packaging, food and other fields [1] due to its excellent physical properties (such as good chemical resistance, electrical insulation and so on) as well as outstanding mechanical properties (like processibility, toughness, impact strength, slow crack growth resistance and so on). From a physical point of view, the properties of PE depend on the chain structure, including chain length distribution, branch content (BC), branch length (BL) and branch distribution. For the sake of developing high-performance PE, it is very necessary to bring to light the relationship between structure and performance. There are few studies on the influence of the long branches on the crystallization behavior since it is very hard to characterize long branches in experi-

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ments. Based on its inherent ability to track the smalltime scale features, molecular dynamics simulations (MD) are becoming a powerful method in the studies of branch effects on a molecular level in recent years. Some researchers have made a lot of research about short branches on crystallization behavior of PE in the past period of time. In the 1990s, some works about short branches on copolymers crystallization behavior have been done by Mandelkern et al.[2-5]. Studies indicated that with increasing of branch content, crystallinity and lamellar thickness presented a tendency of decrease, while the influence of branch length was inapparent. He found the evolution process from folded chain crystal to bundled crystal when the BC increased to a critical value, and lamellar thickness also reduced with the increasing of BC [6]. A sequence of precisely branched PE with branches regularly distributed along the main chain was synthesized by Wagener et al. [7-13] lately. The morphology of PE was also influenced by BL, where small branches (methyl and ethyl) are contained in the crystal, while branches equivalent to or greater in mass than propyl are not included in the crystal. The influence of branch length on the mechanical behavior of blown films produced by the linear low density polyethylene (LL-DPE) was investigated by Wilkes et al. [14]. Results showed that the increase of short chain branch length is in favor of the enhancement of breaking strength of these products. Short branched chains are reported to have an inhibitory effect on melting temperature. Kim and Phillips [15] found that the melting temperatures of heterogeneous copolymers are always higher than those of homogeneous copolymers.

The effect of branched chains on the macroscopic performance of PE crystallization can be explored by experiments. Due to the great power to describe microstructure changes at the molecular level, computer simulation has been applied to investigate the impact of branches steadily. The impacts of BC, BL, and branch distribution on the crystalline morphology of LLDPE of a series of single-chain structure models were studied using molecular dynamics simulation by Zhang et al. [16, 17]. In the nucleation stage, branches played the part of the nucleating agent and in the crystal growth stage, branches acted as a defect and branch with length exceed 10 cocrystallized with the

main backbone. Ramos et al. [18] explored the role of short branches on the formation of crystal regions in the process of cooling dilute solutions of ethylene/ α olefins copolymer using Langevin molecular dynamics simulations. Consistent with the experimental results, the crystallization temperature decreased with the increase in the number of branches. Sanmartín et al. [19] discovered that a considerably higher number of nuclei with smaller sizes were formed in the case of systems with branches, and the crystallinity decreased as the length of the branch increased. Choi et al. [20] conducted that when the BC reached a certain value of about 38.5, the global orientation order parameter decreased and increased markedly at a branch content of 47.6. Tukur [21] and Li [22] also studied the influence of short branched chains on molecular conformations. Alamo et al. [23] studied the crystallizing regions of the polymers which have the same carbon atoms. The results indicated that the crystallization rate decreased continuously from a linear to a diblock in the star copolymer. In the crystallization process of a single PE chain, three crystalline states were found in previous research work. [24] It was found that the critical BC to form lamellae crystal is 20 branches per 1000 backbone carbons. Moreover, the crystallization kinetics is not affected by BL which only affects the final morphologies [25]. In the molecular dynamics simulation study of bimodal polyethylene (BPE), it was discovered that branch distribution also has an influence on crystallization kinetics. The crystallinity of the chains with branches placed on the long chains was lower than the case of branches placed on the short chains. The BPE model with branches distributed on the long chains was more likely to form tie chains compared with the model with branches distributed on the short chain. In the nucleation process, BL showed great delay effect [26].

Crystallization process of PE with short branches has been explored in depth through the combination of experiments and simulations, while studies of long branches on crystallization are relatively few. In the homopolymerization of ethylene, long-chain branches were produced by using constrained-geometry catalysts (CGCs) developed by Dow Chemical. [27] The LCBs could be produced when dead polymer chains containing a vinyl-ended group are merged into the backbone of growing polymer chains. The viscoelastic behavior of these resins was changed due to the presence of LCBs [28-30]. A sequence of PE samples having long-chain branch density (LCBDs) of a 0.03-1.0 branch per 10000 carbons and long-chain frequencies (LCBFs) of 0.22 branch per polymer molecule were prepared by Kolodka et al. [31] in a slurry polymerization. The viscosity was increased and shear thinning was enhanced significantly due to the increasing LCBF. After that, Zhu et al. [32] synthesized polyethylene which has high molecular weight and narrow polydispersity index with about 30% long branches by using a compound nickel catalyst. Subsequently, the simulation of long branched chain gradually increased. Beigzadeh et al. [33] developed a Monte Carlo model for the polymerization of ethylene with long branches using dual-site catalyst systems, and a mathematical model that could characterize the microstructure of polyolefin with long branches in a semi-bath reactor using two single-site catalysts was developed by Mehdiabadi et al. [34]. Subsequently, Soares et al. [35, 36] studied the appearance of long branches in ethylene polymerization with a combination of catalysts using Monte Carlo simulation. Baig et al. [37] presented a progressive Monte Carlo algorithm for the atomistic simulation of polyethylene with long and short branches which can simulate chain models with quantities of molecular structures. Khonakdar et al. [38] proposed an idea of predicting the influence of long branches on molecular weight and its polydispersity index via rheological studies and the presence of long branches greatly influenced the rheological behaviors. The impact of branches on the topological performance of entangled polymer systems was explored by Jeong et al. [39] via an improved connectivity-altering Monte Carlo algorithm. The results showed that the polymer melts with long branches have obviously more compact overall chain conformations in comparison with the linear polymers.

Although some studies have been made on the synthesis of polyethylene with long branches, the principal function of chain branching is vague as before. In particular, there are few studies on the influence of the long branches on crystallization behavior. In the present study, we followed with interest the impact of long branches on the crystallization of polyethylene. Molecular dynamics simulation was used to explore the isothermal crystallization and non-isothermal crystallization behavior of linear-PE and LCB-PE on the premise of the same molecular weight. The impact of long branches on the crystallization kinetics of polyethylene with similar initial *ICF* was also elucidated in terms of final *ICF*, crystallization rate, crystallinity, tie chains and energy of the two systems. The presence of long branches helps to form more nuclei in the nucleation stage, while it is unfavorable for the merge of nuclei. LCB-PE has more tie chains and low crystallinity, and the long branches restrict the chain motion comparing to linear chains. The existence of long branches is favorable for the first stage while unfavorable for the second stage.

MODEL DEVELOPEMENT AND ANALYSIS METHODES Simulation details

The modeling polyethylene used in the simulation was (1) 20 linear PE chains in all-*trans* conformation with the same chain length (1000 CH₂ units) named as linear-PE; (2) 20 PE chains containing long branches, the main chain contains 750 CH₂ units while the long branches contain 250 CH₂ units, named as LCB-PE. The total units of the two systems are both 20000 CH₂ units with boundary conditions.

The Dreiding II force field [40] was used in this work. Choi [41] discussed the effects of this force field on the folding process of polymer chains and found that the choice of force fields is very important for polymers with a high degree of crystallinity. The total energy E_{total} consists of two parts: the kinetic energy $E_{kinetic}$, which is relevant to crystallization temperature; the potential energy $E_{potential}$, which includes bond potential energy (bond-stretching, bond-bending, and torsional energies) and non-bond potential energy (12-6 Lenard-Jones potential van der Waals energy). The total potential energy can be expressed as: $E_{potential} = E_{stretch} + E_{bend} + E_{torsion} + E_{vdw}$.

Molecular dynamics simulation was carried out using Materials Studio. The integration of the motion equations was performed through the velocity Verlet algorithm with a time step of $\Delta t = 2$ fs. The canonical Andersen NVT ensemble was performed to maintain the temperature of the system. As the temperature used in this simulation work was higher than experimentally observed crystallization temperature the normalized temperature was used [24-26]. The normalized temperature was calculated as $T^*=k_{_B}T/\varepsilon$, where $k_{\rm B}$ is the Boltzmann constant ($k_{\rm B} = 8.3145 \times 10^{-3}$ kJ mol⁻¹ K⁻¹) and ε is the Van der Waals interaction parameter ($\varepsilon = 0.8301$ kJ mol⁻¹). The interpenetration process was simulated at $T^* = 8.0$ for 2000 ps at first. Eleven initial structures were extracted from the trajectory at 20 ps, 30 ps, 40 ps, 50 ps, 70 ps, 100 ps, 150 ps, 300 ps, 500 ps, 1000 ps and 2000 ps. All eleven structures would be used as initial conformations of isothermal crystallization and non-isothermal crystallization process. The simulation of isothermal crystallization was performed at $T^* = 4.0$ for 3000 ps, while non-isothermal crystallization was performed with the sample quenching from $T^* = 8.0$ to $T^* = 3.0$ at a decline rate of $\Delta T^* = 0.25/\text{ns.}$

Analysis methods

Interchain contact fraction (ICF)

To quantify the entanglement density of PE chains, interchain contact fraction (*ICF*) was introduced. It is defined as:

$$ICF = \frac{\sum N_{inter}(r_1)}{\sum N_{iotal}(r_1)}$$
(1)

Here $N_{inter}(r)$ is the number of interchain atoms around certain atom at distance r, and $N_{total}(r)$ is the number of total atoms $(N_{total}(r) = N_{inter}(r) + N_{intra}(r))$ around the same atom. The distance r_1 ranging from 0.48 to 0.52 nm was chosen. Both numerator and denominator were counted by the computer.

Site order parameter (SOP) and crystallinity (X_{j})

To quantify the amount of order in the models, SOP was proposed to calculate the local order parameter of orientation vectors around a specific atom [42]. The SOP of atom k is expressed as follows:

$$SOP_{k} = \frac{\left\langle 3\cos^{2}(\psi) - 1 \right\rangle}{2} = \frac{3}{2} \left\langle \left(\vec{e}_{i} \cdot \vec{e}_{j}\right) \right\rangle_{R} - \frac{1}{2}$$
(2)

where i and j stand for any two orientation vectors in the domain within the radius of 0.55 nm around the site. For a system consisting of N sites, the order parameter of the system is calculated by averaging SOP_k of all sites in the system:

$$SOP = \frac{1}{N} \sum_{k=1}^{N} SOP_k$$
(3)

It is convenient to calculate the crystallinity of a polymer system by the ratio:

$$X_c = \frac{N_{cv}}{N} \tag{4}$$

where N_{cv} is the number of sites with an *SOP* higher than a critical value (~ 0.7) and N is the number of total sites [42].

Nuclei or crystal domain

Atoms are selected from the ordered regions with $SOP_k > 0.7$. These orientation vectors are considered to be enclosed by the same nucleus when the distance between the atom is less than 0.68 nm and the average cosine of the angle between any two orientation vectors is larger than 0.82 [43]. Then different clusters are specified, which overall, constitute the entire crystal-line domain.

Trans state population

The *trans* state population was determined for the percentage proportion of CH_2 units with the dihedral angle between $180^{\circ}\pm15^{\circ}$ in the whole system. While N_i is the number of CH_2 units with the different *trans* dihedral angle in the whole system.

$$P_i = \frac{N_i}{\sum N_i} \tag{5}$$

RESULTS AND DISCUSSION

The nucleation and crystallization kinetics of linear-PE and LCB-PE with the same molecular weight were studied. *ICF*, *trans* state population, crystallization rate, crystallinity, tie chains and energy of the two systems were also taken into account.

Different ICF of linear-PE and LCB-PE

The two systems underwent an interpenetration process of 2000 ps at $T^* = 8.0$. In order to study the influence of long branches, the *ICF* of the two systems

at different moments was calculated. Eleven initial conformations were extracted from trajectory at 20, 30, 40, 50, 70, 100, 150, 300, 500, 1000 and 2000 ps. Intensive points were extracted because of the rapid change of structures at the early stage of interpenetration process. All of them would be acted as initial structures of the isothermal crystallization process and non iso-thermal crystallization process.

Figure 1 indicates the variation of the ICF of the two systems with the collapse time (t) in the interpenetration process. As can be seen from curves, the trend of the two curves is almost the same. At first, the ICF of the two systems rises sharply to a high value, and then decreases slightly and tends to stable eventually. The ICF of the two systems is almost identical in the end, which is about 0.65. It is worth noting that the *ICF* of linear-PE is higher than that of LCB-PE when the collapse time is about 20-300 ps. It is indicated that linear-PEs with more carbon atoms in the backbone can penetrate each other more easily at a short notice. With the increase of collapse time, the differences between the two systems in the interpenetration process decrease gradually. It is indicated that the long branches have little effect on the ICF of the system after equilibration.

More detailed information about the degree of entanglement was exposed by analysis of conformations with different collapse time. As shown in Figure 2, four conformations of the two systems at 300 ps and 2000 ps were extracted. It can be seen that the conformations of the two systems are irregular when the



Figure 1. Interchain contact fraction (*ICF*) of the two systems at different collapsing time (t) at $T^* = 8.0$.



Figure 2. Conformations of linear-PE and LCB-PE at $T^* = 8.0$ when the collapse time is 300 ps and 2000 ps.

(d) 2000 ps, LCB-PE

(c) 2000 ps, linear-PE

collapse time is 300 ps, indicating that the interpenetration process has not reached equilibrium. For LCB-PE, long chain branches are mainly wrapped in the outside of backbone, causing lower *ICF* than linear-PE. Conformations of linear-PE and LCB-PE showed stable spherical shapes at 2000 ps. At this moment, long chain branches of LCB-PE are distributed in both inside and outside of the conformations, indicating the interpenetration process reached equilibrium.

Influence of LCBs on nucleation process

Number of nuclei in multidomain system

In the present simulations, we obtained the number of nuclei which was a function of simulation time for the two systems in the isothermal crystallization process. The number of nuclei at $T^* = 4.0$ is indicated in



Figure 3. Evolution of number of nuclei for linear-PE and LCB-PE in the isothermal crystallization process.

Figure 3. It is observed that the number of nuclei of LCB-PE is more than that of linear-PE at almost any moment. It can be seen that the crystallization process can be classified as the nucleation stage and the crystal growth stage. In the nucleation stage, the two systems have more nuclei before 1800 ps. While in the crystal growth stage, the number of nuclei of the two systems is reduced significantly after 1800 ps, and the two systems have three crystallization regions eventually. The number of nuclei in the former stage is more than that of the latter stage and mergence between the crystals does not appear in the former stage while in the latter stage. It shows that long chain branches are favorable for the previous stage and unfavorable for the latter stage. In the latter stage, the degree of reduction of nuclei for linear-PE is more obvious than that of LCB-PE. Mergence may take place easily for linear-PE when small nuclei meet, while the presence of long chain branches hinders the integration of nuclei.

Chain orientation evolution

The change in the dihedral angle from gauche to *trans* conformations is also crucial to deformation in polymer systems. Figure 4 shows how the *trans* state population evolves as a function of time at $T^* = 4$ for linear-PE and LCB-PE. First, the *trans* state population increases as time goes on. Additionally, LCB-PE has higher *trans* state population than linear-PE before 2400 ps. This is indicated that LCB-PE will take longer to rotate to *trans* formations. And at the end, linear-PE has higher *trans* state population than LCB-PE has higher *trans* state population than LCB-PE will take longer to rotate to *trans* formations. And at the end, linear-PE has higher *trans* state population than LCB-PE has higher trans the population than LCB-PE has higher trans tra



Figure 4. Evolution of *trans* state population for linear-PE and LCB-PE in the isothermal crystallization process.



Figure 5. Three snapshots of 1800 ps (a), 2100 ps (b) and 3000 ps (c) for linear-PE. Different colors represent different crystal regions.

PE.

Images of nucleation in multidomain system

Images of nucleation in the non-isothermal crystallization process were also explored. Figure 5(a-c) shows three snapshots at 1800 ps, 2100 ps, 3000 ps of linear-PE and Figure 6(a-c) shows three snapshots at 1800 ps, 2100 ps, 3000 ps of LCB-PE. Six snapshots extracted by MATLAB software indicate the mergence behavior of crystal regions and final crystal regions. In the nucleation stage, there are six crystal regions for linear-PE when the simulation time is 1800 ps. Two large domains emerged in the middle of the snapshots: one is situated in the upper region and the other in the lower region. When the difference between the stem directions between them is small, reorganization and ordered structures are triggered. In short, the mergence between the crystal regions is relatively easy for linear-PE. Crystal regions become larger and larger and a large and two small crystal regions appeared finally. Compared with linear-PE, the mergence behavior of LCB-PE is more difficult. Six crystal regions appear for LCB-PE when the simulation time is 1800 ps. As time goes on, two large crystal regions do not merge each other, while small crystal regions merge into large crystal regions, causing the reduction of crystal regions at 2100 ps. The presence of long branched chains inhibits the process of crystal growth. The mergence behavior between crystal re-



Figure 6. Three snapshots of 1800 ps (a), 2100 ps (b), and 3000 ps (c) for LCB-PE. Different colors represent different crystal regions.

gions for LCB-PE becomes more difficult compared with linear-PE. At the final stage, two large crystal regions merge into a crystal region and there are two small crystalline regions around it containing very few atoms. The number of atoms contained in the final crystal region was also studied. The two systems contain three crystalline regions eventually, but crystal regions of linear-PE contain 8780 atoms while crystalline regions of LCB-PE contain 7720 atoms. This means that the presence of long branches inhibits the nucleation process eventually.

Influence of LCBs on chain folding process

Crystallinity is a critical parameter to characterize the performance of the polymer. Some mechanical properties and physical properties of the polymer are related to it closely. Xc is according to the two-phase model: the crystalline regions and the non-crystalline regions.



Figure 7. Crystallinity curves for linear-PE (black) and LCB-PE (red) with the similar *ICF* in the isothermal crystallization process.

Isothermal Crystallization Process

Isothermal crystallization behaviors of linear-PE and LCB-PE at $T^* = 4.0$ with similar *ICF* were explored in this section. As is shown in Figure 7(a-b), the crystallization process is divided into two stages: the nucleation stage before 1500 ps and crystal growth stage after 1500 ps. In the nucleation stage, crystallinity of LCB-PE and linear-PE is almost the same. The presence of long branches leads to more crystalline regions compared with linear-PE. Because each crystal region is not very large, the overall crystallinity and atoms in the crystal regions are close to that of linear-PE.

After about 1500 ps, the crystallinity of linear-PE exceeds that of LCB-PE significantly which indicated that long chain branches were excluded from the lamellae, causing a more difficult mergence behavior. The insertion of long chain branches can not only hinder the crystal growth stage, but also destroy the regu-



Figure 8. Crystallinity curves of linear-PE (black) and LCB-PE (red) with the similar *ICF* in the non-isothermal crystallization process.



larity of polyethylene. It proves that the existence of long branches makes a great impact on the isothermal crystallization process.

Non-Isothermal Crystallization Process

In order to study the influence of long branches on the non-isothermal crystallization process, crystallinity of the two systems with similar ICF was calculated every $T^* = 0.5$. From Figure 8, it is indicated that linear-PE begins to crystallize first and after that the crystallinity of linear-PE is always greater than that of LCB-PE. When the temperature is $T^* = 6.0-7.0$, crystallinity of the two systems increases rapidly which shows that a large number of crystals began to form. Crystallinity of the two systems increases slowly when the temperature continues to decrease, which indicates that crystals regions began to merge. Compared with linear-PE, LCB-PE has lower nucleation temperature and crystallinity when the ICF of the two systems is similar. The presence of long branches hinders the growth of crystals. Due to the high content of long branches, the difference in the final crystallinity of the two systems is significant.

Influence of LCBs on tie chains formation

Nilsson et al. [44, 45] developed a Monte Carlo simulation method for modeling tie chains and trapped entanglements in lamellar semi-crystalline polymers. The model predicated that the impact of the amorphous thickness was greater than that of the crystal thickness on the molecular continuity between adjacent crystals.



Figure 9. Tie chains of the two systems with similar *ICF* in the isothermal crystallization process.

After that, they extended the model to include the simulation of the semi-crystalline structure of branched PE in a more realistic manner. It showed that a retarding increase appeared in the inter-lamellar connection concentration with increasing branch content.

Semi-crystalline polymers are composed of crystalline regions and amorphous regions. In the crystal region, the molecular chains fold regularly while in the amorphous region, the molecular chains arrange irregularly and crystalline regions are connected to each other by amorphous regions. The structure of a semi-crystalline polymer such as polyethylene can be viewed as a sandwich with alternating layers of crystalline and amorphous regions on a limited length scale. Tie chains are used as a measure of crystallinity and the concentration of tie chains decreases with increasing crystals regions in the crystallization pro-



Figure 10. Potential energy and non-bond energy of the two systems with similar ICF at the isothermal crystallization process.

cess. In order to understand crystallization process of the two systems with similar *ICF*, tie chains were calculated in the non-isothermal crystallization process. It can be seen from Figure 9 that LCB-PE has more tie chains than that of linear-PE at almost any moment, indicating that LCB-PE has more atoms belong to crystal regions. This is consistent with the higher crystallinity of linear-PE.

Influence of LCBs on energy

The crystallization process of polymer is different from that of a low molecular weight material. The structure of the polymer is mainly related to the aggregation morphology of the chains. Non-bond energy (van der Waals force) plays a very significant role in the crystallization process of polymers, and it refers to intermolecular interactions. To explain above observations in the simulation process, potential energy and non-bond energy were analyzed in the isothermal crystallization process when the ICF of the two systems was similar, and energy curves are presented in Figure 10. At the beginning of the simulation, the energy decreases with time. It shows that the potential energy and non-bond energy follow a two-step reduction trend throughout the simulation process. Based on the above analysis, we got some conclusions.

The two-step reduction process can be divided into two stages. For linear-PE, potential energy and nonbond energy decrease more slowly than LCB-PE at the first stage and become rapidly at the second stage. So, potential energy and non-bond energy of LCB-PE are lower than those of linear-PE at the first stage while potential energy and non-bond energy of linear-PE are lower than those of LCB-PE at the second stage. At the first stage, low energy is favorable for the formation of more crystal regions for LCB-PE. At the second stage, low energy causes increased crystallinity. Compared with LCB-PE, potential energy and non-bond energy of linear-PE is low at 3000 ps, which reveals that the final crystalline state of linear-PE is more stable and crystal structure is more compact. Ultimately, lower energy resulting in higher crystallinity. All of these indicate that the existence of long branches is unfavorable for the final crystallinity.

CONCLUSIONS

The entanglement distribution for the two systems was explored by using *ICF* analysis. The *ICF* at different collapsing time was calculated and the *ICF* of the two systems reached about 0.65 eventually. Conformations at different time were extracted from the trajectory of interpenetration. In the early stage of collapse, long branches are distributed outside of the cluster and with the increase of collapse time, long branches enter the interior of the cluster gradually. Finally, long branches are distributed in the cluster uniformly. Isothermal/non-isothermal crystallization kinetics of the two systems with similar *ICF* were also studied. The influence of long branches on the crystallization kinetics was discussed from the aspects of crystal regions, crystallization, tie chains and energy.

It can be seen that the crystallization process can be classified as the nucleation stage and the crystal growth stage in the isothermal crystallization process of the two systems and LCB-PE has more nuclei than linear-PE in two stages. The presence of long branches helps to form more nuclei in the first stage, but it is unfavorable for the merge of nuclei. The evolution of the two systems with similar ICF was traced by calculating the crystallization and tie chains. And it was found that LCB-PE has more tie chains than linear-PE at almost any time. Crystallinity of linear-PE is higher than that of LCB-PE slightly in the first stage while linear-PE has higher crystallinity than LCB-PE in the second stage. Due to the high content of long branches, the difference in the final crystallinity of the two systems is significant. In the non-isothermal process, the crystallinity of linear-PE is always higher than that of LCB-PE. All of these indicate that the presence of long branches hinders the chain motion, causing lower crystallization compared with linear-PE.

From the aspect of energy, in the isothermal crystallization process, potential energy and non-bond energy of LCB-PE are lower than those of linear-PE in the first stage while linear-PE has lower energy than LCB-PE in the second stage. All of these indicate that the existence of long branches is unfavorable for the final crystallinity.



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