Research Article

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Molecular dynamics simulation of nonisothermal crystallization of a single polyethylene chain and short polyethylene chains based on OPLS force field

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Abstract: Molecular dynamics simulations on the non-isothermal crystallization of a single polyethylene chain and short polyethylene chains based on the all-atom model and optimized potentials for liquid simulations-all atom (OPLS-AA) force field are conducted in this article. Four all-atom single chain models with different chain lengths (C1000, C2000, C3000, and C4000) and four all-atom short chain models with the same chain length and different number of chains (2C500, 4C500, 6C500, and 8C500) are constructed. The collapse process at a high temperature of 600 K and the nonisothermal crystallization process with different cooling rates at the temperature range of 600–300 K are simulated. Roles of chain length, number of chains, cooling rate on the potential energy, van der Waals (V_{dw}) energy, radius of gyration, root mean square deviation, and crystallinity are explored. By comparing with the existing results obtained by the united atom model, the validity and accuracy of this study are proved. Results show that in the collapse process, the chain length is the major factor, whereas the cooling rate has the greatest influence during the nonisothermal crystallization process. As the cooling rate decreases, a “platform” appeared in the V_{dw} energy curve, which has a profound impact on the crystallization.

Keywords: molecular dynamics, polyethylene crystallization, OPLS-AA force field, all-atom model

1 Introduction

Polyethylene is widely used in industry, medical treatment, transportation, and packaging because of its good mechanical properties, easy to be processing, and the low cost. The research on the structure and performance of polyethylene has always been a research hotspot. The physical properties of polyethylene mainly depend on its crystallization process and final conformation. Therefore, it is of great significance to study the crystallization of polyethylene.

To date, many studies on the molecular dynamics simulation of polyethylene crystallization have been reported. Roe and Rigby (1,2) applied molecular dynamics simulation to the crystallization of short-chain polyethylene. They used the spherical “segment” to simulate a CH_2 unit and constructed a chain molecular model. Kavassalis and Sundararajan (3,4) constructed molecular dynamics simulations of a series of short chains (30, 60, 100, 150, 200, 250, 500, 750, and 1,000 CH_2) to study the collapse and crystallization of polyethylene. They treated the methylene group as a unit through the united atom (UA) approximation. They found that folding could only occur when the chain length is greater than 150 CH_2 . Fujiwara and Sato (5–8) studied the crystallization process of a single polyethylene chain (500 CH_2) and short polyethylene chains (100 C20) at gradual cooling. They used the UA model. They also proposed the calculation methods of global order parameters and local orientation parameters to reflect the crystallinity. They pointed out that the preliminary results on the rotation of the chain showed that the UA approximation was not enough, and the addition of hydrogen atoms was necessary. Liao and Jin (9) simulated the collapse crystallization process under 300 K by constructing a UA model with a length ranging from 600 CH_2 to 4,000 CH_2 . They found that when the chain length exceeds 1,200 CH_2 units, the process was divided into three stages: subglobule formation, subglobule growth, and subglobule coalescence into one globule.

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Muthukumar and Welch (10–13) simulated the crystallization process of a polyethylene chain with a chain length of 2,000 CH₂ units by UA Langevin dynamics. They found that the baby nuclei appeared in the initial stage of crystallization, and then the baby nuclei grew into layered crystals, and finally spontaneously selected into a lamella structure with a certain balanced lamella thickness. Gao et al. (14–17) simulated the crystallization behavior of polyethylene chains under isothermal and nonisothermal conditions by constructing a polyethylene chain with the length of 1,000–10,000 CH₂ units. They used UA models. They observed that there are three states in crystallization: (1) nucleation controlled state, (2) competitive state of crystal growth process and new nuclei formation, and (3) crystal growth controlled state. In the final conformation of their simulation, it can be observed that C4000, C5000, and C10000 still form effective crystals at 600 K, which is unreasonable compared with the experimental melting point temperature of 405.65 K obtained by Zhou et al. (18). Ramos et al. (19) reviewed the influence of various characteristics on the rheological properties, glass transition, and crystallization of polyethylene based on computer simulation in the molten state. Olsson et al. (20) compared the tensile deformation of semicrystalline-layered polyethylene based on the all-atom model and the coarse-grained model. They concluded that under the method of the coarse-grained UA model, the H–H and C–H interaction forces are missing, and the critical resolved shear stress are seriously underestimated, leading to a large amount of chain slippage and crystal reorientation, which means that the two modeling methods are quite different. Hence, the addition of hydrogen atoms is indispensable.

In general, the molecular dynamics simulation of polyethylene crystallization at this stage mainly focuses on the UA model and the coarse-grained model. As pointed by the pioneers (5–8,20), the accuracy of these models were not enough. Therefore, it is very important to use the all-atom model to simulate the polyethylene crystallization.

In this study, the all-atom model and optimized potentials for liquid simulations-all atom (OPLS-AA) force field were used to simulate the process of collapse and nonisothermal crystallization of a single polyethylene chain and short polyethylene chains. Roles of chain length, number of chains, and cooling rate on the energy and conformation were analyzed. Results were compared with the published literatures in which UA models were used.

2 Model and method

2.1 Model and force field

In our study, we analyzed the crystallization process of polyethylene chain by molecular dynamics simulations. Four all-atom single-chain models with different chain lengths (C1000, C2000, C3000, and C4000) and four all-atom short-chain models with the same chain length but different chain numbers (2C500, 4C500, 6C500, and 8C500) were constructed listed in Table 1.

As we did an all-atom molecular dynamics simulation, the all-atom force field was necessary. The OPLS-AA force field was used in our simulation. In the OPLS-AA force field, the total potential energy is mainly composed by nonbonded $E_{\text{nonbonded}}$, the bond stretching E_{bond} , the angle bending E_{angle} , and the torsion E_{torsion} . Their expressions are as follows (21):

$$E_{\text{bond}} = \sum_i k_{b,i} (r_i - r_i^0)^2, \quad (1)$$

$$E_{\text{angle}} = \sum_i k_{\theta,i} (\theta_i - \theta_i^0)^2, \quad (2)$$

$$E_{\text{torsion}} = \sum_i \left[\frac{1}{2} V_{1,i} (1 + \cos \varphi) + \frac{1}{2} V_{2,i} (1 - \cos 2\varphi) + \frac{1}{2} V_{3,i} (1 + \cos 3\varphi) \right], \quad (3)$$

$$E_{\text{nonbonded}} = \sum_i \sum_{j>i} \left\{ \frac{q_i q_j e^2}{r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\}, \quad (4)$$

where $k_{b,i}$ is the elastic constant of the bond stretching; $k_{\theta,i}$ is the elastic constant of bond angle bending; $V_{1,i}$, $V_{2,i}$, and $V_{3,i}$ are the elastic constants of the dihedral angular distortion term; r_i and r_i^0 represent the bond length of the i -th bond and its balance bond length; and φ is the angle of the dihedral angle.

Table 1: Models used in the simulation

A single chain model	Short chain model
C1000	2C500
C2000	4C500
C3000	6C500
C4000	8C500

2.2 Site order parameter (SOP) and crystallinity

Crystallinity is one of the most important parameters for semicrystalline polymers. How to quantify crystallinity is also very important in the simulation of nonisothermal crystallization of polyethylene. This study uses the SOPs proposed by Xiang et al. (22). SOP_k is obtained by calculating the average order parameters of any pair of direction vectors existing in the domain with k site as the center and radius of 0.55 nm:

$$SOP_k = \frac{\langle 3 \cos^2(\phi) - 1 \rangle}{2} = \frac{3}{2} \langle \vec{e}_i \cdot \vec{e}_j \rangle_R - \frac{1}{2}. \quad (5)$$

The sites with a value greater than 0.7 are divided into crystallization zones, and the proportion of the number of sites in the crystallization zone to the total number is calculated. The crystallinity is calculated as follows:

$$X_c = \frac{N_{cv}}{N}. \quad (6)$$

where N_{cv} is the number of sites whose SOP_k is higher than the critical value 0.7, and N is the total number of sites.

2.3 Problem definition

The collapse process at a high temperature of 600 K and the nonisothermal crystallization process with different cooling rates at the temperature range from 600 to 300 K were simulated. The collapse process was carried out to obtain the simulated conformation close to the real one, but we also investigated it. Figure 1 shows the temperature as a function of time in our simulation. First, the temperature was held at 600 K for 2,000 ps. During this period, we studied the collapse process of polyethylene chain/chains. This operation promises the system to reach a dynamic equilibrium state. Second, the temperature was changed from 600 to 300 K at the cooling rates of 20, 50, and 100 K·ns⁻¹, respectively, which means the cooling process lasts for 15,000, 6,000, and 3,000 ps, respectively. During this period, we studied the crystallization process of polyethylene chain/chains. We also explored the roles of chain length, number of chains, and cooling rate on the energy and the conformation.

The simulation was conducted using GROMACS software (www.gromacs.org). The leap-frog algorithm was used to integrate the equations of motion of all atoms. The velocity-rescale NVT ensemble (canonical ensemble) was used to

Figure 1: Temperature as a function of time in our simulation.

keep the temperature of the system stable. The cutoff technical was used to accelerate the calculation. Parameters used in the simulations were as follows: the integration step was 0.002 ps and cutoff radius was 0.9 nm. For the single polyethylene chain, the initial state was constructed with all-trans extended conformation. For the short polyethylene chains, the initial state was constructed with several parallel all-trans extended conformations. The models were listed in Table 1. The box used in the simulation was very large and no boundary conditions were set, which means the polyethylene chain/chains in the simulation was in a vacuum.

3 Results and discussion

3.1 Collapse process of polyethylene chain/chains

The temperature was held at 600 K for 2,000 ps. The chain conformations were observed during this period. Figure 2 shows the conformational changes in the collapse process of C4000 and 8C500. In Figure 2, 0 ps shows the initial states. As shown in Figure 2a, in the collapse process of a single polyethylene chain with long length (C4000), the extended chain crumples to lead a random coil. There are some subglobules (14) in the internal part, and they subsequently coalesce into a single amorphous coil. In the collapse process of short polyethylene chains with short length (8C500) as shown in Figure 2b, the chains fold from the extended state gradually and crumple into a random coil. The subglobules are not observed.

Figure 2: Snapshots of the chain conformation in collapse process at 600 K: (a) C4000 and (b) 8C500.

Figure 3 shows the chain conformation in the collapse process with different chain lengths and different number of chains. As shown in Figure 3a, the subglobules are not observed in the short chain length cases (C500 and C1000), whereas they appear in the long chain cases (C2000, C3000, and C4000). Figure 3b shows the chain conformation of short chain (C500) with different number of chains. The subglobules are not observed in the short chain systems.

From Figures 2 and 3, we find that the chain length has a major effect on the chain conformation in the collapse process. The single long chain goes through subglobules (local collapse) and then develops into global collapse, whereas the short chain systems only experience global collapse. The appeared subglobules are closely related to the chain length. This is consistent with

Figure 3: Chain conformation in collapse process at 600 K: (a) a single polyethylene chain with different chain lengths and (b) short polyethylene chains with the same chain length and different number of chains.

the conclusion of Kavassalis and Sundararajan (3,4) and Liao et al. (9) where UA models were used. As reported by Liao et al., subglobules formed only when the chain length is more than 1,200 CH₂ units. In our simulation as shown in Figure 3a, subglobules are not observed in the case of C1000, but they formed in the case of C2000.

Figure 4 shows the change of potential energy, van der Waals (V_{dw}) energy, radius of gyration (R_g), and root mean square deviation (RMSD) as a function of time. From Figure 4a, it is obvious that the potential energy is mainly dependent on the system size. When the total amount of carbon atoms is the same, the final stable value of the potential energy of the single long chain is very close to that of the short chain systems. Compared with the short chain systems with the same system size,

Figure 4: The evolution of energy and configuration parameters for the simulated models at 600 K: (a) potential energy, (b) V_{dw} energy, (c) R_g , and (d) RMSD.

the single long chain fluctuates relatively larger before reaching stability, and the time to reach stability is longer. With the increase of chain length, this situation becomes more obvious. Similar results are evident in Figure 4b with V_{dw} energy. The V_{dw} energy of single CH_2/CH_3 was calculated for the last 500 ps. The value for C1000, C2000, C3000, and C4000 are 1.83241, 2.10565, 2.15586, and 2.23168 $\text{kJ}\cdot\text{mol}^{-1}$, respectively, whereas the value for 2C500, 4C500, 6C500, and 8C500 are 1.8118, 2.07449, 2.21159, and 2.2445 $\text{kJ}\cdot\text{mol}^{-1}$, respectively, which means the V_{dw} energy of single CH_2/CH_3 for single long chain is slightly larger than that of corresponding short chain systems. From Figure 4c, it is clear that the variation of R_g is closely related to the chain length and has little relationship with the number of chains. As the chain length increases, the time for R_g to reach the stability increases. For the short chain systems with different number of chains, their curves are almost identical. It can be also found that there are humps in the R_g curves in a single chain system (C1000, C2000, C3000, and

C4000). This is due to the chain collapse caused by the longer chain length, which then expands and collapses again. This is similar with the observation of Kavassalis and Sundararajan (3) in C1000 case at 600 K where UA model was used. According to Figure 4c, as the chain length increases, the greater the fluctuation of the R_g curve, the longer it takes to contract. Similar results are also apparent in Figure 4d with RMSD. RMSD is a parameter, which reveals the position change between the current conformation and the initial conformation. RMSD is also an important characterization to judge whether the simulation is stable (23).

The curves of potential energy, V_{dw} energy, R_g , and RMSD in Figure 4 show that the simulated models become stable after the dynamic simulation for 2,000 ps at 600 K. During this collapse process, the chain length plays an important role on the energy and conformation change. With the increase of chain length, the system needs longer time to reach stability. The number of chains has little effect on the conformation parameter of R_g and RMSD.

3.2 Nonisothermal crystallization of polyethylene chain/chains

The temperature was changed from 600 to 300 K at the cooling rates of 20, 50, and 100 K·ns⁻¹, respectively. The energy evolution and the structure formation were observed during this period. The final conformation of the simulated models was analyzed, which is shown in Figure 5. It can be found that the final conformation becomes more ordered and regular with the decrease of the cooling rate. In addition, with the increase of the chain length and the number of chains, the size of crystal becomes larger. This trend is consistent with the observation of Gao et al. (16) where isothermal crystallization was studied by using the UA model.

The evolution of potential energy and V_{dw} energy for the simulated models with different cooling rates are shown in Figures 6 and 7, respectively. The cooling rates have some effects on the potential energy and the V_{dw} energy. It can be seen from the figures that the potential energy and the V_{dw} energy have almost a linear relationship with the temperature at the cooling rates of 50 and 100 K·ns⁻¹. This linearity became less obvious at the cooling rate of 20 K·ns⁻¹. This is particularly clear in the V_{dw} energy curves, which are shown in Figure 7a. From Figure 7a, it can be seen that there is a “platform” in the process of cooling. It has been proved by many researchers (3,24) that the V_{dw} energy is one of the main driving forces of crystallization. We believe that this “platform” is related to the crystallization. We will discuss it later.

The evolution of R_g and RMSD for the simulated models with different cooling rates are shown in Figures 8 and 9, respectively. As shown in Figure 8, R_g decreases rapidly and then keeps steady during the cooling. It can be found that when the temperature is high, the fluctuation of R_g is stronger. At this time, the potential energy is high, and the movement of polyethylene chain is more active. It is easy to observe that the decrease of R_g , generally, turns from severe to flat at the temperature of about 435 K, which is consistent with starting temperature of the “platform” of V_{dw} energy. During the range of temperature at which the “platform” of V_{dw} energy takes place, the fluctuation of R_g is still large, which means the chain is still in the greater adjustment. As R_g gradually tends to be stable, the conformation is also gradually stable. This can be also reflected from the RMSD curves in Figure 9. As shown in Figure 9, the slower the cooling rate, the higher the value of RMSD. It can be seen that the more the system is adjusted from the initial random coil, the more regular the crystal conformation and the higher the crystallinity. The cooling rate has a great influence on RMSD.

Figure 5: Final conformation for the simulated models at 300 K with different cooling rates: (a) 20 K·ns⁻¹, (b) 50 K·ns⁻¹, and (c) 100 K·ns⁻¹.

We now consider 6C500 and 8C500 as examples to study the “platform” in V_{dw} energy curves. Figure 10 plots the V_{dw} energy curves with different cooling rates. As can

Figure 6: The evolution of potential energy for the simulated models with different cooling rates: (a) $20 \text{ K}\cdot\text{ns}^{-1}$, (b) $50 \text{ K}\cdot\text{ns}^{-1}$, and (c) $100 \text{ K}\cdot\text{ns}^{-1}$.

Figure 7: The evolution of V_{dw} energy for the simulated models with different cooling rates: (a) $20 \text{ K}\cdot\text{ns}^{-1}$, (b) $50 \text{ K}\cdot\text{ns}^{-1}$, and (c) $100 \text{ K}\cdot\text{ns}^{-1}$.

be seen that the starting temperature of the “platform” of V_{dw} energy of 6C500 and 8C500 is about 420 and 435 K, respectively. To 8C500, the ending temperature of the “platform” of V_{dw} energy is about 360 K. This value shifts to the higher temperature with the increase of cooling rate. In all, as the number of chains decrease, the “platform” of V_{dw} energy shifts to low temperature. Similar results can be also observed when changing the chain length.

Figures 11 and 12 show the snapshots of the chain conformation in cooling process for 6C500 and 8C500, respectively. In the cooling interval of 450–350 K, the conformation of polyethylene chains change from a random coil to a relatively regular conformation, which means that this temperature range is favorable for crystallization.

Figure 13 gives the comparison of crystallinity for different systems at the cooling rate of $20 \text{ K}\cdot\text{ns}^{-1}$. Because

Figure 8: The evolution of R_g for the simulated models with different cooling rates: (a) $20 \text{ K}\cdot\text{ns}^{-1}$, (b) $50 \text{ K}\cdot\text{ns}^{-1}$, and (c) $100 \text{ K}\cdot\text{ns}^{-1}$.

Figure 9: The evolution of RMSD for the simulated models with different cooling rates: (a) $20 \text{ K}\cdot\text{ns}^{-1}$, (b) $50 \text{ K}\cdot\text{ns}^{-1}$, and (c) $100 \text{ K}\cdot\text{ns}^{-1}$.

Figure 10: The evolution of V_{dw} energy as a function of temperature with different cooling rates.

the scales of C1000 and 2C500 are small, the crystallinity curves fluctuate greatly, the curves are not shown here. It can be found in Figure 13 that for the single chain system, in the initial stage of crystallization, the longer the chain length, the faster the crystallization rate; for the short chain system, in the later stage of crystallization, with the increase of number of chains, the crystallization rate and crystallinity increase. As shown in Figure 13b, with the increases of the number of chains, the crystallization temperature of the system gradually increases. These tendencies are consistent with the conclusion of Gao et al. (14–17). In their study, they pointed out that the long chain has an advantage in the early stage of crystallization, whereas the short chain has an advantage in the later stage of crystallization. Moreover, by comparing with Figures 10 and 13, it can be found that the temperature related to the rapid change of crystallinity is consistent with the temperature corresponding to the

Figure 11: Snapshots of the chain conformation in cooling process for 6C500: (a) $20 \text{ K}\cdot\text{ns}^{-1}$, (b) $50 \text{ K}\cdot\text{ns}^{-1}$, and (c) $100 \text{ K}\cdot\text{ns}^{-1}$.

Figure 12: Snapshots of the chain conformation in cooling process for 8C500: (a) $20 \text{ K}\cdot\text{ns}^{-1}$, (b) $50 \text{ K}\cdot\text{ns}^{-1}$, and (c) $100 \text{ K}\cdot\text{ns}^{-1}$.

Figure 13: Comparison of crystallinity for different systems at the cooling rate of $20 \text{ K}\cdot\text{ns}^{-1}$: (a) a single chain system and (b) short chain system.

“platform” of V_{dw} energy. Therefore, it is obvious that the V_{dw} energy has a great impact on the crystallization process of the polyethylene chain.

From Figures 10–13, the temperature of the “platform” in the V_{dw} energy curve has a profound influence on crystallization. By comparing with the experimental melting temperature obtained by Zhou et al. (18), the crystallization temperature obtained in our study is better than the crystallization temperature obtained in the study of Gao et al. (14–17) where the isothermal crystallization was studied by using the UA model.

4 Conclusion

In this study, molecular dynamics simulations on the nonisothermal crystallization of a single polyethylene chain and short polyethylene chains based on the all-

atom model and OPLS-AA force field were conducted. The collapse process at a high temperature and the non-isothermal crystallization process with different cooling rates were simulated. The conclusions were drawn as follows.

1. Crystallization temperature obtained based on the all-atom model and OPLS-AA force field is more accurate than that of the UA model. In the process of collapse, the formation of subspheres, the hump formed in the R_g curve, and the crystallization curves of long and short chains in the nonisothermal crystallization process are consistent with the study of the UA model, but in terms of details and temperature, especially crystallization temperature, the all-atom model does a better job.
2. In the collapse process, the chain length has the most profound effect on the system, and the number of chains has little effect. In the nonisothermal crystallization process, the chain length and chain number

have a certain influence on the energy evolution and crystal formation; the system size and the cooling rate have the greatest influence. When the cooling rate is low, there will be a “platform” in the V_{dw} energy curve. Within this temperature range, the polyethylene chain changes from a random coil to a relatively regular conformation. As the number or length of the chain decreases, the starting temperature of the “platform” shifts to a low temperature. Moreover, at low cooling rates, long chains have an advantage in the early stage of crystallization, whereas short chains have an advantage in the later stage of crystallization. The scale of the system affects the crystallization temperature. As the number of atoms increases, the crystallization temperature of the system also increases. As the cooling rate decreases, the final conformation becomes more orderly and regular.

It is also worth mentioning that the cooling rates used here is much larger than that used in experiments. This is determined by the timescale of molecular simulation. However, we believe the results obtained in this study are also valuable. In future studies, we will further refine and reduce the cooling rate to explore the factors and mechanisms of the nucleation and crystal growth.

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