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The crystallization of low-density polyethylene: a molecular dynamics simulation

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Abstract

Three models (star-shaped, H-shaped, and comb-shaped polyethylenes) are used to study the crystallization behavior of low-density polyethylene at the molecular level by means of molecular dynamics simulation. It is shown that, for the three types of polyethylene corresponding to the models, the neighboring sequences of *trans* bonds firstly aggregate together to form local ordered domains, and then they coalesce to a lamellar structure. In the process, the branching sites are rejected to the fold surface gradually. The driving force for the relaxation process is the attractive van der Waals interaction between the chain segments. Furthermore, it is found that the number of the branch sites and the length of the branch play an important role in determining the formation of the lamellar structure. The longer the length of the branch and the fewer the number of the branch sites, the more perfect lamellar structure can be formed.

Keywords: Molecular dynamics simulation; Polyethylene; Long branching

1. Introduction

Polyethylenes are usually divided into three classes: low density polyethylene (LDPE) [1], linear low density polyethylene (LLDPE) [2], and high density homopolyethylene (HDPE) [3]. Although it is believed that LLDPE would replace LDPE in film applications because of its superior properties, LDPE still has a large share of the market due to its greater process ability [4–6]. LDPE has a highly branched structure, i.e. it has a central backbone from which many branches are appended, these branches have branches, and those branches have branches, etc. The lengths of all of these branches are broadly distributed, so it becomes difficult to determine lengths of the branches and the spacings between them. Thus it is very difficult to systematically investigate the relationship between the structure and property of LDPE by experiment. Recently, a number of polymers with well-defined structures that serve as models for polyethylene with long chain branching were synthesized and characterized experimentally [7]. The structures were some with a single long branch (‘stars’), some with exactly two branch points (‘H’ types, etc.), and some with several long branches randomly distributed along the backbone (‘combs’). In the experimental literature, how the branching structure controls chain dimensions is discussed. However, to our knowledge, the information about the crystallization of the polyethylene with well-controlled structure and long chain branching has not been reported yet.

Nowadays, the polymer models with well-controlled structures can be easily built by using simulation software, and the structural formation process of polymer chains can be investigated at the molecular level by means of molecular dynamics (MD) simulation method. Several MD simulations [8–11] starting from a single chain model have given us some insights into the microscopic process of polyethylene crystallization, the features of crystal morphology, and the influence of temperature on crystallization. Kavassalis and Sundararajan [8] studied the lamellar formation of a single linear polyethylene chain collapsed from an all-*trans* conformation and a rotational isomeric state conformation. Fujiwara and Sato’s simulations showed that the orientationally ordered structure of a single linear polyethylene chain with 500 CH_2 units was formed at a low temperature both by gradual stepwise cooling and by quenching from a random configuration at a higher temperature [9,10]. The effect of molecular weight on the collapse mechanism of a single chain and on the dimension of the formed lamella was simulated [11].

Recently, we studied the roles of branch, branch distribution, branch contents, and branch length in the crystallization

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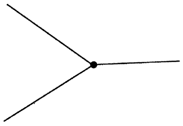
of the LLDPE by MD simulation of several single chain models [12,13]. In Ref. [13], the simulations were performed on two series of copolymer chain models with precisely controlled methyl branching and with branches of different lengths, respectively, to study the roles of branch content and branch length in co-polyethylene crystallization. For the latter models, each chain has only one branch and the branch length is up to 16 carbon atoms. Then we may be asked, when the chain has more than one branch and the branch length is much longer than 16 carbon atoms, what will happen to the co-polyethylene crystallization? In this paper, based on the simulations just mentioned above, MD simulations of three types of single chain models (star-shaped, H-shaped, and comb-shaped polyethylenes) are performed to investigate the crystallization behavior of low-density polyethylene.



star-shaped

H-shaped

comb-shaped

Fig. 1. The schematic representing the three models of the polyethylene with well-controlled structure and long branching.

2. Model and method

Three single chain models with well-controlled structure, each with 600 CH_2 units but different long chain branches, were created by the Polymer Build Model of *Cerius*^{2} software. One has a single long branch with 200 CH_2 units (star-shaped), the second has four branches with two branch sites at the end of the backbone (H-shaped), and the third has four long branches with four branch sites randomly distributed along the backbone (comb-shaped). For the H- and comb-shaped models, each branch contains 50 CH_2 units. It should be noticed that the branch sites in the comb-shaped model are randomly selected, for the ordering processes and the results can depend sensibly on the way they are chosen [12]. In Ref. [7], the silicone atoms are used as the branch sites. Following Ref. [7], we also select the silicone atom as a branch site and a $\text{—}CH_3$ unit is connected to a silicone atom to insure silicone has four valence bonds. This replacement should have effects in the segregation of the branch sites out of the crystalline domain. However, we found that even though the branch site has a carbon atom, it is also expelled from the crystalline phase as a defect [13]. So, compared with the carbon, the effects of silicone in the segregation may be ignored. The schematic representations of the chain models (whose structures are similar to those shown in fig. 1 of Ref. [7]) are depicted in Fig. 1, where the black balls represent the branch sites (silicone atoms).

By using the Amorphous Builder of *Cerius*^{2} software, the random coils of the three models are created, and then the random coils are annealed 10 cycles from $T = 300$ to 1000 K and cooled to 300 K at intervals of 50 K per 0.1 ps to overcome local minimum energy barriers, respectively. At the end of each cycle, the structure is relaxed by minimization. From the fully relaxed structures, the canonical Nosé–Hoover molecular dynamics simulations are performed, where the integration time step is set to 0.001 ps, the temperature is set to $T = 300$ K, and a relaxation constant for the heat bath variable is 0.1 ps. The cutoff distance for the van der Waals interaction is 10.5 Å. The duration of the simulation for each model is 3 ns.

The Dreiding II force field [14] from the *Cerius*^{2} software package is used for the atomic force field. Following Ref. [8], the united atom approximation is adopted to simplify the calculations. The total potential energy E_{total} consists of four parts: (1) the bond-stretching energy E_{stretch} for two adjacent united atoms, (2) the bond-bending energy E_{bend} among three adjacent united atoms, (3) the torsion energy E_{torsion} among four adjacent united atoms, and (4) the 12-6 Lennard–Jones potential E_{vdw} between two non-bonded atoms. The total potential energy E_{total} can be expressed as:

$$\begin{aligned} E_{\text{total}} &= E_{\text{bond}} + E_{\text{vdw}} = E_{\text{stretch}} + E_{\text{bend}} + E_{\text{torsion}} + E_{\text{vdw}} \\ &= \frac{1}{2}K_{\text{b}}(R - R_0)^2 + \frac{1}{2}K_{\theta}(\theta - \theta_0)^2 + \frac{1}{2}K_{\phi}[1 \\ &\quad - d\cos(3\phi)] + D_0\left[\left(\frac{\sigma}{r}\right)^{12} - 2\left(\frac{\sigma}{r}\right)^{6}\right] \end{aligned} \tag{1}$$

where R is the bond length between two adjacent atoms, R_0 the equilibrium bond length, θ the bond angle between three adjacent atoms, θ_0 the equilibrium bond angle, ϕ the dihedral angle formed by four consecutive atoms, and r the distance between two non-bonded atoms.

3. Results and discussion

3.1. The relaxation process of the polyethylene chains with long chain branching

As radius of the gyration matrix, R, defined in the *Cerius*^{2} software, can characterize the overall shape and orientation of a polymer chain. So we employ the radius of gyration to describe the orientation changes of the three models during crystallization. The diagonalization of the R matrix gives its principal values R_x^2, R_y^2, R_z^2 (eigenvalues) and the corresponding orientations (eigenvectors) in the Cartesian frame. The radius of gyration (R_g) and its three Cartesian components (R_{gx}, R_{gy}, and R_{gz}) are defined as:

$$R_g^2 = \frac{1}{n}\sum_{i=1}^{n}\left\langle(\mathbf{r}_i - \mathbf{r}_c)^2\right\rangle \tag{2}$$

$$R_{gx}^2 = \frac{1}{n}\sum_{i=1}^{n}\left\langle(x_i - x_c)^2\right\rangle \tag{3}$$

$$R_{gy}^2 = \frac{1}{n}\sum_{i=1}^{n}\left\langle(y_i - y_c)^2\right\rangle \tag{4}$$

$$R_{gz}^2 = \frac{1}{n}\sum_{i=1}^{n}\left\langle(z_i - z_c)^2\right\rangle \tag{5}$$

where $\mathbf{r}_i = (x_i, y_i, z_i)$ is the position vector of the ith atom, $\mathbf{r}_c = (x_c, y_c, z_c)$ the position vector of the center of mass, x_i, y_i, and z_i the position of the ith atom, x_c, y_c, and z_c the position of the center of mass, $\langle\ldots\rangle$ denotes the ensemble average, and the relation $R_g^2 = R_{gx}^2 + R_{gy}^2 + R_{gz}^2$ holds.

For the three models the variations of R_g with simulation time are similar, for brevity, we only take the comb-shaped chain as an example to discuss the relaxation process of the polymer. The time evolutions of R_{gx}, R_{gy}, and R_{gz} for the comb-shaped chain are shown in Fig. 2. As divided by the dot line in Fig. 2, before about 360 ps, R_{gx} increases while R_{gy} decreases with the evolution of the simulation time; and after about 360 ps, R_{gx}, R_{gy}, and R_{gz} fluctuate around a corresponding mean value, respectively. Comparing the values of R_{gx} with those of R_{gy} and R_{gz}, it is easily seen that the values of R_{gx} are larger. This indicates that during the relaxation process, the random coil becomes more and more anisotropic before 360 ps, and after 360 ps an anisotropic structure (the lamellar structure as shown in Fig. 3) is formed. This process can be visually captured by displays of the conformations of the random coils at different simulation time in Fig. 3, where the black balls represent the silicone atoms. From Fig. 3, it can be seen that with the time evolution, the neighboring sequences of *trans* bonds firstly aggregate together to form local ordered domains, and then they coalesce to a lamellar structure. In the process, the branching sites are rejected to the fold surface gradually. This result is very similar to that obtained from the simulations starting from the random coil of LLDPE models [12,13].

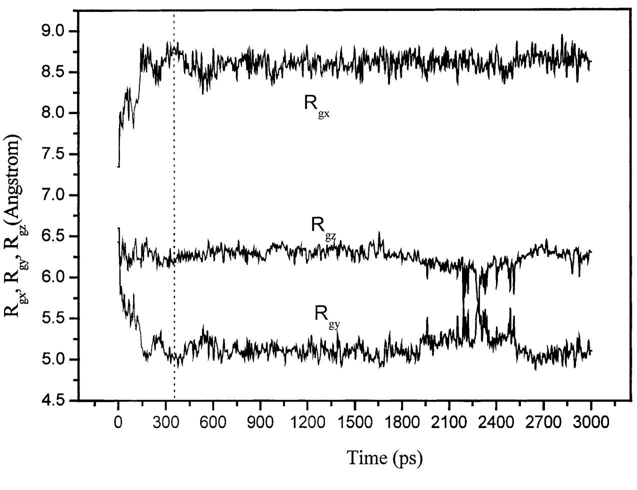


Fig. 2. The three Cartesian components R_{gx}, R_{gy}, and R_{gz} of the radius of gyration (R_g) versus simulation time for the comb-shaped chain.

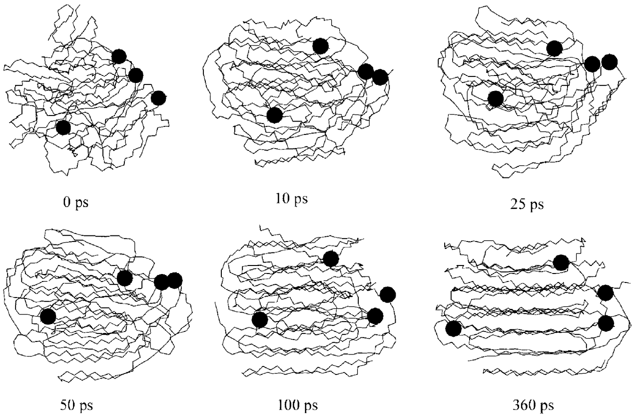


Fig. 3. The collapse process of comb-shaped, at 300 K, where the black balls represent the branch sites (silicone atoms).

Now let us discuss the variations of the potential energy with the time for the comb-shaped chain. Fig. 4 shows the time evolution of the total potential, the van der Waals, and the bond energies. It is shown that as the relaxation proceeds, the bond energy is repulsive (positive), while the van der Waals energy is attractive (negative). The total potential energy decreases during this time due to the significant decrease of van der Waals energy. So it is obvious that the attractive van der Waals interaction between the chain segments is the driving force for the collapse process as discussed in our previous paper [12].

3.2. The morphology of the lamellar structure

The conformations obtained from the random coils at 3 ns are shown in Fig. 5, where the black balls represent silicone atoms. It can be seen that the lamellar structure is formed by the co-crystallization of the long-branch with the main chain and the branch sites are located out of the crystal region. Comparing the three conformations, we can find that the lamellar structure of the star-shaped polyethylene is more perfect than those of the H- and comb-shaped, which can be characterized by the average values of R_g for the three chains as listed by boldface in Table 1. As mentioned above, the shape of the polymer chain can be described by means of the gyration tensor (matrix). The eigenvalues of the matrix give the principal values of R_x^2, R_y^2, R_z^2, and R_{gx}, R_{gy}, R_{gz} are the three components of the radius of gyration, which are used to describe the principal axes for a prolate sheroid. The long axis of the spheroid represents the ordered direction of the lamellar structure, in this paper, x is the long

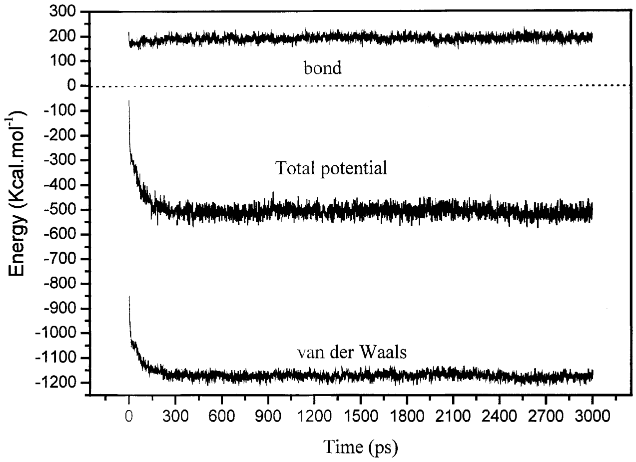


Fig. 4. Time evolution of the bond, the van der Waals, and the total potential energies of the comb-shaped chain.

Table 1

Table. 1 The time averages of the radius of gyration (R_g) and its three Cartesian components R_{gx}, R_{gy}, and R_{gz} for the three well-controlled polyethylene models, the time interval is the last 500 ps of each simulation

Type	R_g (Å)	R_{gx} (Å)	R_{gy} (Å)	R_{gz} (Å)
Star-shaped	12.18	**9.47**	4.69	5.91
H-shaped	11.70	**8.77**	5.17	5.76
Comb-shaped	11.83	**8.65**	5.08	6.27

axis of the prolate spheroid of the polyethylene chain. So the value of R_{gx} may be used to estimate the lamella thickness roughly. The larger the R_{gx} is, the thicker the lamella. In Table 1, it is shown that the value of R_{gx} for the star-shaped (9.47 Å) polyethylene with one site and a branch of 200 carbons is larger than those of the H- and comb-shaped, while the values of R_{gx} for H-shaped (8.77 Å) with two sites and four branches of 50 carbons is slightly larger than that of comb-shaped (8.65 Å) with four sites randomly distributed and four branches of 50 carbons. The average lengths of crystalline stems (simply estimated from the average number of units in each stem, which is calculated as the total number of the chain units divided by the number of stems) are about 40 Å for the star-shaped polyethylene and about 35 Å for the H- and comb-shaped. From these facts, it may be concluded that there are two factors affecting the formation of the lamellar structure for the polyethylene with well-controlled structure and long chain branching: one is the number of branch sites; another is the length of the branch. The longer the length of the branch and the fewer the number of branch sites, the more perfect lamellar structure can be formed. But it should be noted that their delicate balance might have important effects.

To investigate the way the branch chain and the main chain packed into the lamellar structure, we show the snapshot of the crystal-core of the comb-shaped model at 3 ns in Fig. 6, where Fig. 6a is the side view and Fig. 6b is the top view. It can be clearly seen from Fig. 6b that the branches and the main chain together form a lamellar structure with deformed hexagonal symmetry and the stems in the outer layer of the structure have a tilted configuration. This result is similar to that obtained from the simulations of linear polyethylene [8,9].

In our previous simulation, we studied the roles of different branch lengths in the crystallization of the co-polyethylene by using models with one branch containing carbon atoms

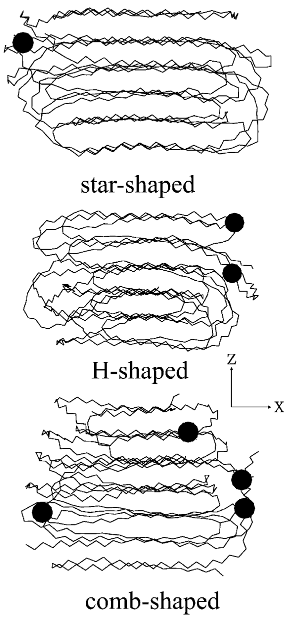


Fig. 5. The conformations of the three well-controlled polyethylene models at 3 ns.

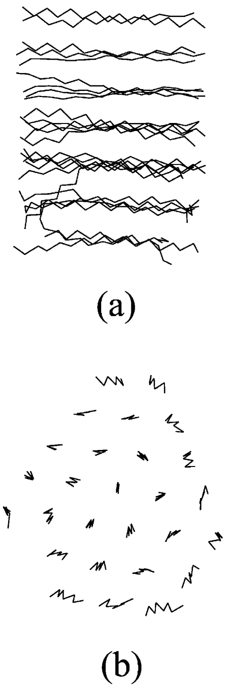


Fig. 6. The snapshot of the crytal-core of the comb-shaped chain at 3 ns; (a) is the side view and (b) is the top view.

from one to 16 [13]. It showed that the critical chain length for side-chain crystallization is 10 carbons, and in the co-crystallization the side chain is packed in a manner similar to linear polyethylene. This result is confirmed by the present simulation of the models with more branches containing more carbon atoms.

4. Conclusions

In this paper, we obtain some microscopic insight into the crystallization process of the polyethylene with well-controlled structure and long branching. During the relaxation process of the random coils, a lamellar structure is formed and the branching sites are rejected to the fold surface gradually. The driving force for the relaxation process is the attractive van der Waals interaction between the chain segments. It is also found that there are two factors affecting the formation of the lamellar structure for the well-controlled polyethylene: one is the number of branch sites; another is the length of the branch.

Acknowledgements

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References

[1] Fawcett WE, Gibson RO. J Chem Soc 1934:386.
[2] Karol FJ. J Macromol Symp 1995;8–9:563.
[3] Ziegler. K. Brennstoff Chem B-C 1954;35:321.
[4] Mendelson RA. Trans Soc Rheol 1965;9:53.
[5] Mendelson RA, Bowles WA, Finger FL. J Polym Sci, Part A-2 1970;8:105.
[6] Ghijsels A, Ente JJSM, Raadsen J Int Polym Process 1992;7:44.
[7] Hadjichristidis N, Xenidou M, Iatrou H. Macromolecules 2000;33:2424.
[8] Kavassalis TA, Sundararajan PR. Macromolecules 1993;26:4144.
[9] Fujiwara S, Sato T. J Chem Phys 1997;107:613.
[10] Fujiwara S, Sato T. J Chem Phys 2001;114:6455.
[11] Liao Q, Jin X. J Chem Phys 1999;110:8835.
[12] Zhang X-b, Li Z-s, Lu Z-y, Sun C-c. J Chem Phys 2001;115:3916.
[13] Xiu-bin Zhang, Ze-sheng Li, Zhong-yuan Lu, Chia-chung Sun. Macromolecules 2002; 35:106.
[14] Mayo SL, Olafson BD, Goddard III WA. J Phys Chem 1990;94:8897.