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Isothermal crystallization of a single polyethylene chain induced by graphene: A molecular dynamics simulation

Li-zhi Wang [a,b,*], Li-li Duan [b]

[a] School of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, China
[b] College of Physics and Electronics, Shandong Normal University, Jinan 250014, China

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ABSTRACT

Molecular mechanisms of the nucleation and growth of polyethylene molecule are investigated by molecular dynamics simulations. Our simulations show that the temperature is an important factor for single polyethylene chain crystallization on graphene. From the crystallization process and the particle number distribution of CH_x groups along *z*-axis, it is find the polymer crystallization have two steps, i.e., adsorption and orientation, the two steps are found to be highly cooperative process.

1. Introduction

Polymer crystallization is one of the most arresting phenomenons in materials science and condensed-matter physics [1,2], because polymer crystallization controls the structural formation processes and the final properties of crystalline polymer. The interfaces play a key role in polymer crystallization. CNTs have been investigated extensively in the theory simulations and experiments. Wei conducted molecular dynamics (MD) simulations of the alkane chain crystallization around the SWCNT [3,4]. The orientation structure of alkane chains formed depend on CNT chirality, and long alkane molecules adsorb easily on the CNT surface. Yang et al. carried out the isothermal crystallization process of a single polyethylene (PE) chain on SWCNT and found the stems of the ordered structure to be aligned parallel to the axis of SWCNT [5]. Li and his groups used CNTs to induce polymer crystallization experimentally and found the shish-kebab structure [6,7]. Recently, Ramanathan et al. report the creation of the polymer nanocomposites with functionalized graphene sheets, which provide superb polymer–particle interaction [8]. Rafiee et al. compare the mechanical properties of polymer nanocomposites with graphene platelets, single-walled carbon nanotubes, and multi-walled carbon nanotubes additives. They find the superiority of graphene platelets over carbon nanotubes [9]. Kalaitzidou et al. report the exfoliated graphite nanoplatelets may serve as a reinforcing agent to produce multifunctional polymer composites, and they find the thermal conductivity of the polymer matrix is enhanced [10]. These properties indicate graphene's great potential equal to or better than CNTs. Inspired by the novel function of graphene, we explore the crystallization process of a single PE chain on graphene substrate with MD simulations.

Most of the experiments have been successfully interpreted by use of Lauritzen–Hoffman (LH) theory [11], but the polymer crystallization still have many controversies in view of the molecular level [12–16]. MD simulations can provide the molecular level description for the interfacial interactions. Graphene as a new nucleating agent have been used in multifunctional polymer nanocomposites. If we want to design favorable microscopic and macroscopic structures of crystalline polymers, we need to know much more about the molecular mechanism of polymer crystallization on graphene substrate.

The purpose of this study is to clarify the mechanisms of the structural formation of a single PE chain on graphene substrate at the molecular level. In this study, we investigate how graphene induces crystallization of a single PE chain with MD simulations. In particular, our concern is to investigate temperature effects for a single PE chain crystallization on graphene substrate.

2. Model and simulation method

Polyethylene is chosen as the model polymer, which consists of a linear chain of 500 CH_x groups. In the beginning, the polymer

* Corresponding author at: School of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, China. Fax: +86 0535 6672002.
E-mail address: yantailizhi@126.com (L.-z. Wang).

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chain is randomly distributed on graphene (62.49 × 98.4 Å) surface. According to previous literature [17], we obtain the random configuration at high temperature (750 K) by MD run of 300 ps, which confirm that the PE chain has relaxed completely. Then we carry out 4000 ps MD simulations at various temperatures (440, 470 and 500 K). Fig. 1 shows the initial randomly distributed configurations of a single PE chain on graphene surface. In order to observe spatial arrangement of PE chain clearly, we eliminated the hydrogen atoms in the image although they are remained in the calculations.

The MD simulations are carried out using the Discover module in Materials Studio [18], and the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) are used as the atomic force field [19]. The recent simulations work show that the interatomic interactions are described using the second-generation COMPASS force field due to its high accuracy in predicting the properties of polymeric materials [20]. Wu and Xu validated COMPASS force field for predicting the properties of highly cross-linked polymer networks were in better agreement with experiment than previous calculations of these properties using DREIDING force field [21]. In addition, Tack and Ford showed that density prediction of thermosetting polymer using COMPASS is better than that using the cff91 force field [22]. The COMPASS force field potential is represented as follows [23]:

$$E_{total} = E_{valence} + E_{cross\text{-}term} + E_{nonbond} \tag{1}$$

where $E_{valence}$ is the valence energy, $E_{cross\text{-}term}$ is the cross-term interacting energy, and $E_{nonbond}$ is the nonbond interacting energy. Details of the force field can be found elsewhere [23]. The detail about every term is expressed as follows:

$$\begin{aligned} E_{valence} = & \sum_b [K_2(b-b_0)^2 + K_3(b-b_0)^3 + K_4(b-b_0)^4] \\ & + \sum_\theta [H_2(\theta-\theta_0)^2 + H_3(\theta-\theta_0)^3 + H_4(\theta-\theta_0)^4] \\ & + \sum_\phi [V_1[1-\cos(\phi-\phi_1^0)] + V_2[1-\cos(2\phi-\phi_2^0)] \\ & + V_3[1-\cos(3\phi-\phi_3^0)]] + \sum_\chi K_\chi \chi^2 + E_{UB} \end{aligned} \tag{2}$$

$$\begin{aligned} E_{cross\text{-}term} = & \sum_b \sum_{b'} F_{bb'}(b-b_0)(b'-b_0') + \sum_\theta \sum_{\theta'} F_{\theta\theta'}(\theta \\ & - \theta_0)(\theta'-\theta_0') + \sum_b \sum_\theta F_{b\theta}(b-b_0)(\theta-\theta_0) \\ & + \sum_b \sum_\phi F_{b\phi}(b-b_0)[V_1\cos\phi + V_2\cos 2\phi + V_3 \\ & \times \cos 3\phi] + \sum_{b'} \sum_\phi F_{b'\phi}(b'-b_0')(b'-b_0')[F_1\cos\phi \\ & + F_2\cos 2\phi + F_3\cos 3\phi] + \sum_\theta \sum_\phi F_{\theta\phi}(\theta-\theta_0)[V_1 \\ & \times \cos\phi + V_2\cos 2\phi + V_3\cos 3\phi] + \sum_\phi \sum_\theta \sum_{\theta'} K_{\phi\theta\theta'} \\ & \times \cos\phi(\theta-\theta_0) \times (\theta'-\theta_0') \end{aligned} \tag{3}$$

$$E_{nonbond} = \sum_{i>j} \left[\frac{A_{ij}}{r_{ij}^9} - \frac{B_{ij}}{r_{ij}^6}\right] + \sum_{i>j} \frac{q_i q_j}{\varepsilon r_{ij}} \tag{4}$$

where b and b' are the bond lengths, θ is the two-bond angle, ϕ is the dihedral torsion angle, χ is the out of plane angle, q is the atomic charge, ε is the dielectric constant, r_{ij} is the $i-j$ atomic separation distance. b_0, $K_i(i = 2–4)$, θ_0, $H_i(i = 2–4)$, $\phi_i^0(i = 2—4)$, $V_i(i = 1–3)$, $F_{bb'}$, b_0', $F_{\theta\theta'}$, θ_0', $F_{b\theta}$, $F_{b\phi}$, $F_{b'\theta}$, $F_i(i = 1–3)$, $F_{\theta\phi}$, $K_{\phi\theta\theta'}$, A_{ij}, and B_{ij} are the system dependent parameters implemented into Discover module of Materials Studio. During our simulation, the time step is 1 *fs* and the cutoff distance is 9.5 Å. the *NVT* ensemble has been used during the simulations with undefined boundary conditions, which implies that the simulated volume is actually infinite. The *NVT* ensemble with undefined boundary conditions is appropriate for conformational searching of the system. We apply the Anderson method to control the temperature of the system [24,25].

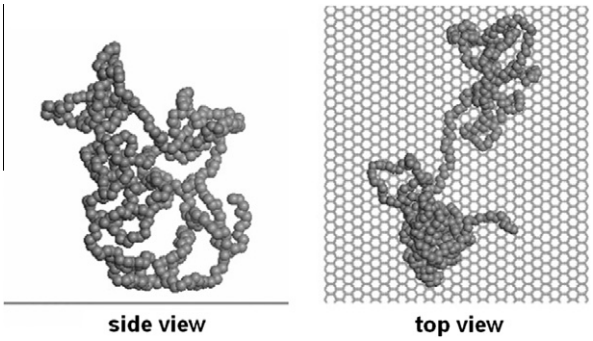

Fig. 1. Initial molecular model of polyethylene on graphene substrate.

3. Results and discussions

In order to understanding of the crystallization behavior of PE chain, we discuss the crystallization process of a single PE chain on graphene substrate. Using the initial configuration of polymer and the graphene shown in Fig. 1, we perform MD simulations to observe the isothermal crystallization process at various temperatures. We show, in Fig. 2, the snapshots of configuration of the graphene-induced polymer chain isothermal crystallization for $T = 500$ K at various times ($t = 500$ ps, 1000 ps, 2000 ps, and 4000 ps). The crystallization process is a molecular transformation from a random coil to a chain-folded crystalline. Analyzing the crystallization process, the process can be summarized as two steps, i.e., adsorption step and orientation step. First, when the PE chain is placed near the graphene substrate, the chain begins to attach to the substrate surface due to strong adsorption of graphene substrate. Second, with more and more CH_x groups adsorbed onto graphene substrate, the PE chain adjusts its configuration and forms the ordering structure. With the progress of adsorption, the molecular order in the adsorbed layer gradually grows. Thus, the adsorption step and the orientation step are found to be highly cooperative process. The process visually displays the nucleation and growth mechanism of a single PE chain on graphene substrate.

Temperature is very important in polymer chain crystallization. Snapshots of the final chain configuration at various low temperatures are shown in Fig. 3. This figure indicates that the stem length becomes longer as the temperature increases. This temperature dependence is probably caused by the fact that the polymer chain can be easily trapped in the metastable state at lower temperature. The molecular crystallization is found strongly dependent on temperature. Because of the chain needs enough kinetic energy to overcome the energy barrier and adjust its configuration in the crystallization process. To observe Fig. 3, we also find multilayered structure at lower temperatures and single layer structure at higher temperatures. Fig. 4 shows the time evolution of total potential energy of PE/graphene system. From Fig. 4, it can be seen that the total potential energy of PE/graphene system have a little decreasing slop after 2000 ps, which implies that the simulation time of 4000 ps is long enough for our systems to reach equilibrium.

Fig. 5 shows the particle number distribution $\psi(z)$ of CH_x groups from the graphene substrate surface at various temperatures. $\psi(z)$ is the number of CH_x groups over the z-axis in a slab between z and