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Two mechanisms of polymer chain crystallization within nanoglobule

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ABSTRACT

In molecular dynamics (MD) simulation, the crystallization behavior of a polymer nanoglobule was studied as a function of temperature. The crystallinity in the nanoglobule was determined by using the site order parameter method [*Macromolecules,* 2008, 41: 6733]. The isothermal crystallization kinetics was determined at different temperatures and the rate of crystallization, K_c, and the Avrami exponents, n, were determined as a function of temperature. The typical bell-shape curve of the crystallization rate vs. temperature was observed to be asymmetric and very different from the symmetric bell-shaped behavior seen in bulk crystallization. This can be attributed to a lower chain diffusion activation free energy near the surface of the nanoglobule than in bulk. The obtained Avrami exponents n are non-integer and vary with temperature, ranging from close to $n = 1$ at the lowest investigated temperatures and reaching $n = 4$ for the highest investigated crystallization temperatures. A detailed morphological and statistical analysis of the MD snapshots and trajectories suggests that at least two kinds of crystallization environments and corresponding mechanisms are active: one in the (~3 nm) surface layer and one in the inner part of the nanoglobule. The two crystallization mechanisms were used in an approximate binary model providing a satisfactory prediction of the observed overall Avrami exponents.

1. Introduction

Crystallization in polymer systems is an important process in polymer science and technology [1,2]. Crystallization and the kinetics of crystallization are not only important for bulk materials but are also of great importance for nano-materials [3–7]. The kinetics of polymer crystallization is important during the polymer processing stage and for the ensuing morphology of the semi-crystalline material.

Different from crystallization of small molecules, polymer crystals are usually formed via chain folding [8]. Several theories or models [9–18] were proposed for explanation of the thermodynamics and kinetics of polymer crystallization, among which the nucleation and growth theory developed by Lauritzen and Hoffman [18] (LH) is mostly known. This model introduced the classical image of polymer crystallization in two steps: the nucleation step and the crystal growth step.

A large number of experimental studies on polymer crystallization kinetics [19–22] is available. It was found in experiment that the experimental data obey the Avrami equation [23] and the Avrami exponent usually is not an integer [24,25] indicating that the nucleation/crystallization mechanism is not always easy to be established in a unique way from the Avrami analysis and that additional or complementary information must be obtained to determine the microscopic mechanism of the observed kinetic crystallization behavior.

Molecular dynamics (MD) is a powerful tool in exposing the microscopic mechanisms. Many MD studies made efforts in polymer crystallization [9,12,13,26]. But to our knowledge there are almost none of the studies related to the crystallization kinetics, which needs the plot of the crystallinity, f_c, of simulated system versus time. The f_c is a fraction of particles in the crystalline phase vs. total particles in the system, not the order of the orientation function usually used in MD studies. Recently we proposed the site order parameter (SOP) that we can use to calculate the crystallinity of the polymer chain system at any moment [3]. Thus SOP provides a chance to describe crystallization kinetics of polymer system. After an recently elementary study on nano-particle crystallization [27], in the present study, we use the SOP approach to further study the crystallization behavior in a polymer nanoglobule.

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2. Methodology

2.1. MD simulation

Molecular Dynamics (MD) simulations were performed using a GPU enabled molecular dynamics program (GMD) developed and implemented on a single GPU by Liu et al. [28]. The GMD simulations were performed for a polymer globule containing 1200 linear chain molecules, each chain consisted of 300 CH_2 united-atoms (in total 360,000 particles). The globule was placed in the middle of a cubic box with the linear size of the box set to two times the radius of the globule so that an empty space is reserved to maintain zero pressure. The force field parameters used for simulation were derived from the Dreiding II force field [29]. The Dreiding force field is widely used for polyethylene (PE) [3,30–33] for which the hexagonal crystalline structure of PE chains is obtained in simulations. By virtue of giving lower barrier heights from the *gauche* conformation to the *trans* conformation, it leads to a faster crystallization process which results in a considerable saving in CPU time.

NVT-ensemble MD simulation runs were performed using an integration time step of 0.002 ps. The Nose-Hoover thermostat algorithm with a relaxation time of 0.1 ps was used. First an MD simulation was performed at 1000 K for 15 ns to get an equilibrium melt state [3]. The temperature used here was thus normalized by 1000 K. The normalized temperature was denoted as T_n. The simulation of crystallization of each system was performed for 16 ns at 15 temperatures, $T_n = 0.40$ to 0.68 with a step of $T_n = 0.02$.

2.2. Site order parameter (SOP)

Recently, we developed a method to calculate the crystallinity of a polymer system from MD simulations based on the *Site Order Parameter* (SOP). The SOP of the kth site is calculated as follows:

$$\mathrm{SOP}_k = \frac{3}{2}\left\langle \left(\vec{e}_i \cdot \vec{e}_j\right)^2 \right\rangle_R - \frac{1}{2} \tag{1}$$

where the average $<(\ldots)>_R$ is defined over the first interaction shell with radius R surrounding the central particle k. $\vec{e}_i$ and $\vec{e}_j$ are the unit vectors of particle i and particle j, respectively. Here unit vector of particle i stands for the unit vector pointing from particle $i-1$ to particle $i+1$. For the entire system that contains N particles, the order parameter of the system is calculated by averaging SOP of all particles in the system, viz.

$$\overline{P} = \frac{1}{N}\sum_{k=1}^{N} \mathrm{SOP}_k \tag{2}$$

In our recent work [3], we proposed to calculate the crystallinity of a polymer from the SOP, according to

$$f_c = \frac{N_{cv}}{N} \tag{3}$$

where N_{cv} is the number of particles with SOP $>$ SOP_{cv} which are then assigned be in the crystalline state and N is the total of number particles. Yu et al.[3] found that the critical value $\mathrm{SOP}_{cv} = 0.7$ is reasonable to be the watershed between the crystalline phase and the non-crystalline phase because this SOP value corresponds to the transition point of the density curve of crystallization process.

3. Results and discussion

3.1. Crystallization kinetics of the polymer nanoglobule at different temperatures

The overall isothermal crystallization kinetics can be conveniently monitored by following the fraction of crystalline material as a function of time. We calculated the fraction of crystalline material in the globule as a function of time using Eqs. (1)–(3) for all crystallization temperatures. The results for $T_n = 0.40$, 0.50, 0.60 and 0.68 are shown in Fig. 1. The crystallization curve has in each case three stages: the induction or nucleation stage, the crystal growth stage and the perfectioning stage. During the nucleation period nuclei are created and as expected the length of the induction stage depends on temperature; the higher the crystallization temperature the longer the induction period. The crystallization stage is the part of the curve that shows the larger increase with time in the crystalline fraction and finally the perfectioning stage is characterized by the crystallinity increase with time at a smaller rate than in the crystallization stage. Although the four crystallization curves for the nanoglobule in Fig. 1 are all S-shaped they are very different from the behavior in bulk. In general, as shown in many experiments, the S-shaped curve for bulk crystallization is symmetric with respect to the inflection point of the crystallization curve. However, in the case of nanoglobule crystallization shown in Fig. 1, the time from the inflection point of the crystallization curve to the plateau is much longer than that from the start of the experiment to the inflection point, which leads to an asymmetric curve. The broadening and asymmetry behavior is found here a specific feature in the crystallization of nanoglobule.

The rate of crystallization K_c, which is defined as a rate of the crystallinity increment in the crystal growth stage, can be obtained from the slope of the crystal growth stage of the crystallization curves (as in Fig. 1) and the temperature dependence of K_c is shown in Fig. 2. The crystallization rate increases with temperature to about $T_n = 0.60$ and then decreases towards higher temperature, giving an asymmetric bell-shaped temperature dependence. Crystallization at temperature below the maximum crystallization rate ($T_n < 0.60$) is called “cold crystallization” and that at higher temperature ($T_n > 0.60$) is called “hot crystallization”. Usually the temperature dependence of the crystallization rate in bulk experiment has a more symmetric bell-shape than the temperature

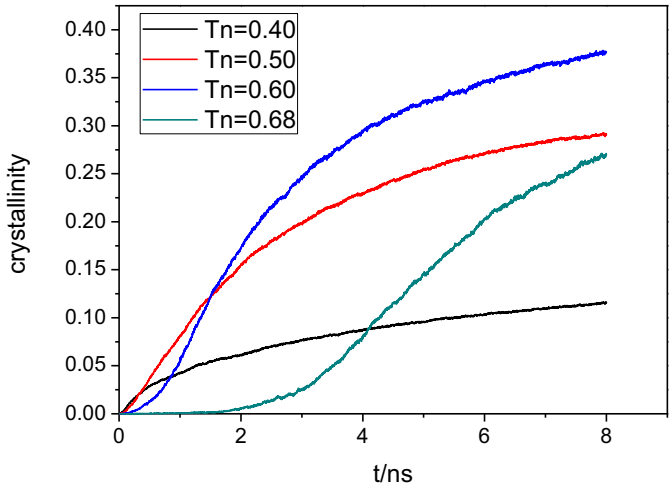

Fig. 1. Crystallinity as a function of time of the large globule consists of 360,000 CH_2 united atoms.