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A single polymer folding and thickening from different dilute solution

Mao-Xiang Wang *

School of Science, Nanjing University of Science and Technology, Nanjing 210094, China

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ABSTRACT

The primary nucleation and crystal growth of a single chain from different dilute solution are studied by Monte Carlo simulations. The interplay of crystallization and demixing/collapse is conveniently investigated in chain folding. We find the solvent qualities affect the nucleation mechanism, crystal morphology and the thickening process. In good solution the swollen coil allows the stems more extended and facilitates to form thicker crystalline stems. The poor solvent condition is helpful to perform fast nucleation and produce a dense crystal. But to get more reorganization the critical athermal solution is the best choice, where the longitudinal thickening and width contraction of the folded stem is well coupled. Our results may complement the kinetic mechanism of crystal growth beyond the point of lamellar thickening.

1. Introduction

The understanding of polymer crystallization and its theoretical description remains a challenge due to the nucleation theories developed from low molecular weight systems. Especially the lamellar thickness is identified with the critical size of nuclei, not related with the key features of polymers in melts or solutions. Recently molecular dynamics simulations on polymer melt crystallization study the time sequence of chain folding and the cluster contracting [1]. The kinetic mechanism of competition between the formation of stems and the random coil shape of polymer chains is also investigated by S. Stepanow [2]. To avoid the entanglement in polymer melt and consider different coil shape in polymer solution we choose a single chain in different solution to study the kinetic mechanism of crystallization.

For a single isolated polymer, when the solvent quality changes there may exist coil–globule transition and crystallization [3]. So the first single-molecule single crystals are hard prepared and verified through keeping crystals from joining during growth [4]. The interplay of collapse and crystallization not only exists in dilute solution but also even at the nascent stage of polymer crystallization during synthesis. According to Wang–Landau Monte Carlo algorithm, except a direct first-order transition due to strong interaction between monomers [5,6], the normal phase transition of a single polymer chain concerns collapse and crystallization [7,8]. The former is smooth and resembles a second-order phase transition [9] but the latter is a typical first-order transition from a random coil state to a perfectly ordered folded state. Recently Hu finds the structural transformation due to coil–globule transition affects the free-energy barrier for intrachain crystallization [10,11]. Muthukumar reports the initial crystal growth depends on the entropic barriers and explains a new model of polymer crystallization based on the spinodal decomposition description [12,13]. But considering the collapse the coil size may play a more important role in the kinetic pathway of crystallization.

Furthermore, how the crystal grows beyond the size of the critical nucleus is also under intense studies. Lauritzen and Hoffman pioneered the kinetic approach with secondary nucleation from dilute solution and they found the folded chain crystals beyond the critical thickness will not melt and keep stable at the crystallization temperature [14]. Langevin dynamics simulations result that the folding mechanism is established by chain entropy, not by kinetic barriers [15]. But one key issue about the chain folding in dilute solution is the effect of thermal interactions. In poor solvents of PET, the intramolecular association induces the loss in flexibility of polymer chain and changed the end surface energy [16]. This change will influence the chain sliding diffusion necessary for crystal growth. Especially in the globule state the crystal surface is limited and the chain sliding diffusion is difficult so Kavassalis and Sundararajan find the chain folding are unambiguous in homogeneous primary nucleation and subsequent growth of folded chain crystals [17]. Considering the solvent qualities the mobility of segments is changing with the thermal conditions so it is necessary to study the equilibrium crystal growth in different solutions. In this paper using Monte Carlo simulations we will

* Tel.: +86 25 84315592 (office), +86 13675101763 (mobile number).
E-mail address: wangmx@njust.edu.cn.

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investigate the crystallization and the subsequent crystal growth of a single polymer chain in different solutions.

2. Simulations technology

In our dynamic MC simulations, a number of consecutive occupations represent a polymer chain, while the other single voids can be regarded as solvents in solution. In a cubic box with periodical boundary a monomer can jump from an occupied site to a void with a slithering diffusion if necessary [11]. The monomers are allowed along the cubic axes, face diagonals and body diagonals and so the coordination number of each site is $q = 6 + 12 + 8 = 26$. In our lattice model the interaction range of each site includes 1, $\sqrt{2}$ and $\sqrt{3}$ so we will observe the normal phase transition of a single chain. In each step of microrelaxation, the Metropolis sampling is performed with a potential energy penalty:

$$\Delta E = \Delta p E_p + \Delta b B + \Delta c E_c = \left(\Delta p \frac{E_p}{E_c} + \Delta b \frac{B}{E_c} + \Delta c\right) E_c, \quad (1)$$

where E_p is an attractive nearest-neighbor interaction between parallel polymer bonds and it measures the driving force of crystallization. E_c is the bending energy for each pair of bonds connects along with the chain and B is the mixing interaction of the monomers and solvents. Δp, Δb and Δc respectively represents the net number of nonparallel packing of two bonds, the monomer-solvent contacts and the non-collinear connection of bonds. The movable probability is defined as $exp(-\Delta E/KT)$, where K is the Boltzmann constant and T is the temperature. The time unit is the MC cycle that sums trial move of each monomer on an average.

3. Preparation

From the "principle of polymer chemistry" written by Flory [18], when the interaction parameter $\chi > 0$ the size of the coil begins to keep away from the special scaling laws in good solution and the single polymer tend to collapse as in the poor solution. So we assume the $\chi = 0$ as the critical solution in this paper. In our simulations the well known Flory interaction parameter χ can be estimated from $(q-2)B/KT$. When we observe the process of coil–globule transition we find the coil size decreases with the increase of parameter B [19]. So for a single polymer chain with $N = 1024$ segments we choose three distinct collapse states to describe three different dilute solutions: for good solution $B/E_c = -0.2$; the critical solution is $B/E_c = 0.0$ and the poor solution we choose $B/E_c = 0.2$.

In this paper we want to study the kinetic mechanism of crystallization from solution. So in each simulation we will try the best to reduce the effect of supercooling. Thus we will firstly search each onset crystallization temperatures in three solutions. As shown in my previous paper the cooling process from the same athermal equilibrium coil state in different solutions was investigated. We find $B = 0$ really is the boundary for the incubation before crystallization. As $B < 0$ the cooling curves demonstrate an abrupt change in the densities while $B > 0$ there are gradual increase in densities [19].

For the three chosen solutions the evolution of crystallinity and density as a function of temperatures from the same athermal coil state is shown in Fig. 1. We find in the good solution the crystallinity and density performed synchronous changes, which inferred that crystallization is the only force to drive the monomers coming together. But in poor solution there are two obvious changes in density: the first gradual increase and the second abrupt increase. They respectively show the procedure of collapse and subsequent contribution of crystallization. While for the critical solution the curve of density is like in the good solution and

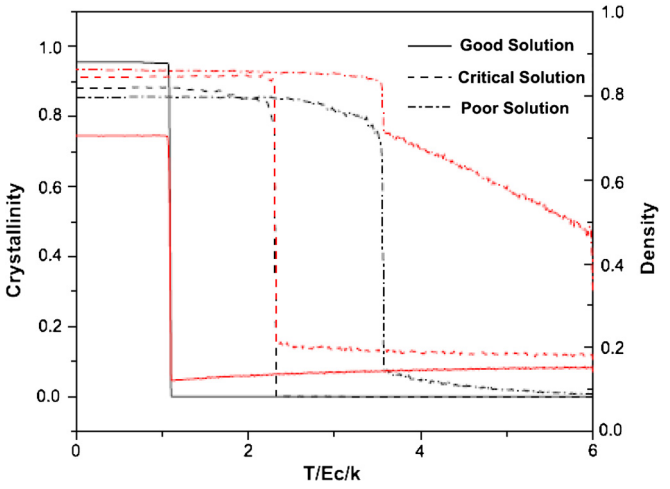

Fig. 1. The evolution curves of crystallinity and density for a single polymer with $E_p/E_c = 1$ from different solutions with $B/E_c = -0.2$, 0.0 and 0.2 respectively corresponding to good, critical and poor solution. The crystallinity is defined as the fraction of those crystallizable bonds containing more than 5 parallel neighbors. The cooling process is the stepwise decrease with the step length of $0.01E_c/k$ and every step 3000 MC cycles. All the results are calculated over 20 observations as an ensemble average.

show the only abrupt change. But it demonstrates a transient gradual increase in the crystallinity like in the poor solution. Although the evolution of density is different there exists only one turning point in the crystallinity curves. These onset crystallization temperatures are respectively: $B/E_c = -0.2$, $T = 1.1E_c/k$; $B/E_c = 0.0$, $T = 2.31E_c/k$; $B/E_c = 0.2$, $T = 3.57E_c/k$. Based on these preparations we will study the effect of solvent qualities on the nucleation and crystal growth of a single polymer chain.

4. Primary nucleation

From the same althermal "coil" state, we perform the parallel simulation of isothermal crystallization from three different dilute solutions at each onset crystallization temperatures. In Fig. 2 one can see that crystallization from the good solution undergoes a significant incubation period for primary crystal nucleation. But for the crystallization in the poor solution it does not need the incubation of primary nucleation and crystallization performs directly like a secondary nucleation due to the prior collapse. In the critical solution we find there is also a shorter incubation period for nucleation and the density of the pre-nuclei is higher than in good solution. Comparing the final densities after crystallization we clearly observe the densities of the crystal increase with the interaction parameter B, in accordance with the demixing of polymer in solution.

On the other hand, the crystallinity does not show the same dependence on the solvent qualities. From Fig. 2 we can see that the crystallinity in good solution is highest but in poor solution is not lowest intuitively. Instead crystallization from critical solution results poorest crystallinity. Where is this situation coming from? Maybe we should observe the crystal growth after primary nucleation in detail to get insight.

5. Crystal growth

The mechanism of chain folded crystal growth of macromolecules has had many refinements since its suggestion by Lauritzen and Hoffman [14]. Recently Crist studies the small crystal formed from one or a few polyethylene-like material and gives the equilibrium growth aspect of folded chain polymer crystals [20]. Through a similar polymer theory including entropy effects