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Original article

Simulation of secondary nucleation of polymer crystallization *via* a model of microscopic kinetics

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ABSTRACT

We present simulations of the mechanism of secondary nucleation of polymer crystallization, based on a new model accounting for the microscopic kinetics of attaching and detaching. As the key feature of the model, we introduced multibody-interaction parameters that establish correlations between the attaching and detaching rate constants and the resulting thickness and width of the crystalline lamella. Using MATLAB and Monte Carlo method, we followed the evolution of the secondary nuclei as a function of various multibody-interaction parameters. We identified three different growth progressions of the crystal: (i) Widening, (ii) thickening and (iii) simultaneously thickening and widening of lamellar crystals, controlled by the corresponding kinetic parameters.

1. Introduction

Polymer crystallization usually consists of two steps, nucleation and crystal growth. While nucleation plays a key role, it remains so far a poorly understood process. In part, this is because it is still a big challenge to observe experimentally the nucleation event at a molecular level. Thus, theoretical modeling and computer simulation have been employed to reveal the details of nucleation. Lauritzen and Hoffman (LH) proposed the most widely accepted surface nucleation theory of polymer crystallization. There, the free energy for formation of the first crystalline stem (the secondary nucleus) of the polymer chain on the flat growth surface represents the energy barrier for surface nucleation. To allow for growth, the length of this nucleus along the chain direction has to be slightly longer than the minimum required for stability. Under these conditions, the growth rate of the crystal is maximized [1–3]. In contrast, Sadler and Gilmer (SG) proposed an entropically determined barrier related to the removal of unfavorable chain conformations rather than a barrier due to enthalpy differences [4–6]. In the SG model lamellar thickening is possible without invoking surface nucleation. The entropic barrier increases with lamellar thickness. The results of the SG model can also explain the correlation of growth rate and lamellar thickness with super-cooling, in accordance with some experimental observations. Along this route, Goldbeck-Wood *et al.* [7] and Sommer and Reiter [8–11] considered the molecular kinetics by taking into account interactions between nearest neighbor units. These treatments of molecular kinetics allowed the formation of a rough fold surface of a polymer crystal and agreed in some aspects with experimental results.

However, additional experimental results revealed the existence of meso-phases or intermediate states during crystallization [12,13]. Although secondary nucleation theory and rate-theory are partly successful on explaining the evolution of the lamellar thickness and the velocity of the growth front, they do not provide a detailed picture of nucleation, neither do they explain the role of intermediate states in crystallization.

Hu *et al.* have systematically simulated polymer crystallization in the melt and in a confining environment, using dynamic Monte Carlo simulations of systems of lattice chains [14–17]. They proved that in contrast to the LH model intramolecular crystal nucleation contributes to the nucleation barrier and is responsible for adjacent reentry chain-folding in lamellar crystallites. In their simulations, chain flexibility, interaction between two parallel stems and an energetic barrier for chain sliding were considered. They have revealed a variety of molecular details of the nucleation stage and lamellar growth. Furthermore, Muthukumar *et al.* took into account the entropy of the connecting loops. Based on

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Langevin dynamics simulations of a single polymer chain of high molecular weight, they proposed that crystalline lamellae consisting of folded polymers rather than extended chains are thermodynamically stable [18,19].

Though a large number of works have contributed to the field of polymer crystallization, and particularly nucleation, still many questions have not been answered. For instance, it is not yet clear how anisotropic interactions between chain segments affect polymer nucleation. In this letter, we propose to treat nucleation of polymer crystallization with a model based on microscopic kinetics. We assume that the rate constants of attaching and detaching of a crystalline stem of a polymer chain vary with stem length and the width of the resulting crystalline cluster. We reveal that the formation of secondary nuclei is controlled by multibody interaction parameters.

2. Methods

The microscopic process of crystallization from a melt can be described well by the cluster-growth scheme, which was adopted by Becker and Döring [20], Turnbull and Fisher [21]. A series of cascaded elementary processes is applied to simulate the attachment and detachment of a crystalline unit from a crystalline cluster. Becker and Döring have originally proposed this scheme in 1935 for explaining the gas–liquid phase transition. We now apply this scheme to describe the microscopic kinetics of crystallization. The growth of a polymer crystal results from the processes of attachment and detachment of motifs at the growth surface. Our model considers the basic motif of polymer crystallization to be a short sequence of monomer units. The stem length is determined by the number of crystalline monomer units which they contain. At each site of the crystal, three processes may occur: (1) Extension of a stem by one motif or the initiation of a new stem by attaching a single motif. (2) Simultaneous detachment of a certain number motifs of a crystalline stem. If the stem contains only one motif, it is eliminated once this motif is detached. (3) In cases where the number of attached and detached motifs is balanced, the length of the stem may stay unchanged. The attachment rate constants k^+ and detachment rate constants k^- determine the rules of evolution of the length of a crystalline stem.

In the original three-dimensional version of kinetic Monte-Carlo simulations performed by Sadler, the attachment rate constant k^+ remained unchanged while the detachment rate constant k^- was related to the number of bonds broken when a unit is removed [22]. This means that both rates did not change with the length of the crystalline stem. However, for polymer crystallization, the covalent connection between subsequent units along the chain direction and the consequences of these connections have to be taken into account. We propose that along the direction of chain axis, the probability for attaching an additional crystalline unit to an already attached stem of a given number of crystalline units decreases with increasing stem length, *i.e.*, with increasing number of already crystalline units. This differs from the SG model. In the case of small molecules, k^+ remains constant, along all the spatial directions, with size of the crystal. Besides, similar to the independence of the attachment rate $1/\tau_A$ of the crystal size as observed for small molecules, in the SG model $1/\tau_A$ is also independent of the stem length, width and orientation of crystalline clusters on the crystalline growth front. Accordingly, the kinetics for attaching of an additional crystalline motif along the chain axis is given by the following expression:

$$k^+ = A_1 \times \exp(-b_1 L_c)$$

where b_1 is an entropic term and $\exp(-b_1)$ is the probability of attaching a single motif of a polymer chain onto the crystal growth face. A_1 is a pre-factor of the rate constant of attaching and L_c is the stem length defined by the number of motifs in a chain stem.

The detachment rate constant depends on the cluster size. Crystallization of small molecules can be considered as the special case where $L_c = 1$. Considering all the three dimensions of the nucleus of lamellar polymer crystals (lamellar thickness i_c along c axis, length i_b along b axis and width i_a along a axis) of the polymer lamellae, we assume:

$$\begin{aligned} k^-(L_c, i_b, i_a) &= A_2 \times \exp\left[\sum_{i_c=1}^{L_c} - b_2(i_c, i_b, i_a)\right] \\ &= A_2 \times \exp\left\{\sum_{i_c=1}^{L_c}[-b_{2c}(i_c) - b_{2b}(i_b) - b_{2a}(i_a)]\right\} \end{aligned}$$

$$\begin{aligned} b_{2j}(i_j) &= b_{2j} \times i_j, \ \text{when} \ i_j \le i_j^*, j = a, b, c \\ b_{2j}(i_j) &= b_{2j} \times i_j^*, \ \text{when} \ i_j > i_j^*, j = a, b, c \end{aligned}$$

where b_{2c}, b_{2b} and b_{2a} are enthalpic terms, which represent the surplus enthalpy after attaching a motif along the c axis, b axis and a axis, respectively, compared to the previously attached motif. b_{2c}, b_{2b} and b_{2a} reflect the long-range multi-body correlations among the units. A_2 is a pre-factor of the rate constant for detaching.

The crystal growth was simulated on the growth face consisting of a cubic lattice of size 100 × 100, with each motif represented by a cube. We use $L_c(m, n)$ to represent the length of stem at position (m, n), where m and n indicates the row and column number, respectively. In a simulation cycle, we calculate the attachment rate $k^+(m, n)$ and detachment rate $k^-(m, n)$ of each position according to its surroundings, and generate a random number $\varepsilon(m, n)$ from 0 to K, where K is the maximum possible range for the detachment rate set in advance. The stem length was allowed to change according to the following principles:

$$\begin{cases} L_c(m,n) = L_c(m,n) + 1, \quad \text{if} \ \varepsilon(m,n) \le k^+(m,n) \\ L_c(m,n) = 0, \quad \text{if} \ k^+(m,n) < \varepsilon(m,n) \le k^+(m,n) + k^-(m,n) \\ L_c(m,n) = L_c(m,n), \quad \text{if} \ k^+(m,n) + k^-(m,n) < \varepsilon(m,n) \le K \end{cases}$$

Then, after the time step $t = t + 1$ the system moved to the next cycle and we repeated the above steps. Thus, we can get the evolution patterns of the whole system.

3. Results

The average lamellar thickness with time was simulated using a 2-dimensional model, as shown in Fig. 1. As different lengths of stems were allowed in our model, the stem length was not constant but exhibited a distribution in length. At the beginning of the simulation, stems were independently initiated or removed. Repeating this process caused that at some points some stems

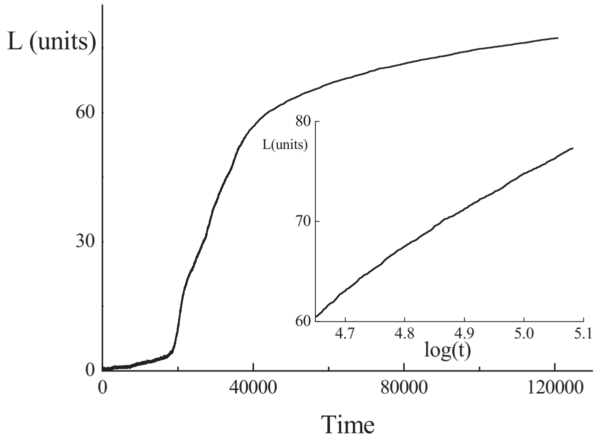

Fig. 1. Variation of chain stem length with time simulated with a 2-dimensional model with $b_1 = 0.095$, $b_{2c} = 0.030$, $b_{2a} = 0.050$. The inset redraws this data using a logarithmic time axis.