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Variable trends of chain-folding in separate stages of strain-induced crystallization of bulk polymers

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ABSTRACT

We performed dynamic Monte Carlo simulations of isothermal crystallization of bulk polymers at a high temperature, which was induced by a homogeneous stretching with a constant strain rate over a wide range of strains. We observed that the crystallites exhibit variable trends of chain folding in three sequential regions of strains, revealing hierarchical mechanisms of strain-induced polymer crystallization: in the first region, sporadic stretched segments initiate intermolecular crystal nucleation with less chain folding at higher strains; in the second region, massive less-stretched segments perform crystal growth with more chain folding at higher strains; in the third region, those folded chains extend via a melting-recrystallization process, again with less chain folding at higher strains. Different trends of chain-folding between crystal nucleation and growth appear intrinsic and ultimately lead to shish-kebab crystals. Our observations provided a molecular-level rationale to understand various experimental phenomena upon the processing for oriented semi-crystalline polymers.

1. Introduction

Most of useful semi-crystalline polymers are oriented in order to gain higher mechanical strength, such as flow-induced skin-layer formation upon plastic molding, strain-hardening upon rubber stretching, biaxial stretching or blowing upon thin-film processing, and fibrous-structure formation upon fiber spinning and plastic necking [1]. The fabrication of oriented semi-crystalline polymers can be either strain-induced crystallization upon a stretching of amorphous polymers [2–13], or strain-induced melting-recrystallization upon a stretching of semi-crystalline polymers (cold-drawing) [14–22]. Therefore in both industrial and academic meaning, evolution of microscopic polymer structures upon strain-induced crystallization is an important issue.

Early thermodynamic considerations used those final crystallization states to predict a critical strain for the transition from folded-chain to extended-chain crystals upon strain-induced crystallization below the melting point [23–25]. However, the preferences of polymer crystal orientations should be dominated by primary nucleation of strain-induced crystallization. Flory first adopted fringed-micelle nucleation to describe the formation of oriented fibrous crystallites [26]. Keller and Machin believed that those extended-chains form fibril nuclei first and then induce an array of folded-chain lamellar crystals [27]. Yeh and Hong argued that a certain amount of chain-folding may also exist in the fibril nuclei [28]. The different trends of chain-folding between crystal nucleation and growth appear essential for the formation of shish-kebab crystals, which deserves further investigation.

Upon further stretching into higher strains after polymer crystallization, i.e. upon the cold-drawing of semi-crystalline polymers, two stages of structural evolution have been extensively investigated. In the first stage, usually referred to yielding, the mosaic slips of crystalline folded-chain blocks dominate morphology transformation upon yielding [14,15,29–32]; in the second stage, usually referred to necking, the blocks of folded chains transform into oriented fibrous structures via a melting-recrystallization process [16,17,21,22,33,34]. So far, the molecular-level scenario [35] for the strain-induced melting-recrystallization process remains in a mystery, which deserves further investigation as well.

Recently, we developed a new scheme in our dynamic Monte Carlo simulations to stretch homogeneously a bundle of bulk polymers at high temperatures, and observed a sudden reduction in the preferences of chain folding of new crystallites, implying a transition of strain-induced crystal nucleation from intra-molecular to inter-molecular mechanisms [36]. A combination of Flory's theories on the melting-point depression of random

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copolymers and on the melting-point up-raising of stretched polymers can predict well the onset strains of random copolymers observed in our simulations [37]. There have been several other molecular simulations, focusing on various aspects of strain-induced polymer crystallization, such as shish-formation in polymer flows [38–40], separate effects of shear rate and strain on crystallization [41], crystal nucleation at high strains [42,43], temperature dependence of nucleation rates [44], plastic deformation [45] and fiber formation [46]. However, molecular simulations covering over a wide range of strains for the whole strain-induced crystallization process, from the early stage of crystal nucleation to a late stage of post-growth stretching, have not yet been studied. In this report, following the previous simulation approach, we observe the evolution of polymer structures over a wide range of strains at a high temperature. The results will demonstrate that, although crystal nucleation favors the mechanism of intermolecular fringed-micelle nucleation by consuming those highly stretched segments in the melt, subsequent crystal growth maintains its habit of chain-folding by consuming those less stretched segments, and further stretching extends those folded-chains via a melting-recrystallization process. Thus, the chain-folding nature of strain-induced crystallization provides us a rationale to understand the hierarchically mechanisms of strain-induced crystallization, from local initiation to crystal development and then to the global further stretching.

2. Simulation techniques

We developed a homogeneous stretching of bulk lattice polymers in our dynamic Monte Carlo simulations [36]. As demonstrated in the left part of Fig. 1, we put 1920 chains, each containing 128 monomers with both chain ends separately restricted on the YZ planes at $X = 1$ and $X = 16$, in the $16 \times 128 \times 128$ (XYZ) lattice box with hard-wall boundaries. The occupation density was 0.9375 to mimic a bulk polymer phase, and a small number of vacancy sites played a role of free volume for chain motion. Polymer chains moved in the lattice space via a micro-relaxation model [47], which allowed a monomer jumping from an occupied site to a neighboring vacancy site, occasionally with partial sliding-diffusion along the chain. The bonds were oriented either along lattice axes or along diagonals, so the coordination number of each monomer could be as high as 26 (summed over six axes, eight body diagonals, and 12 face diagonals). Each bond thus contains maximum 13 possible orientations. Both double occupation of monomers on the lattice sites or bond crossing were forbidden to mimic the volume exclusion of polymer chains. The preset fully ordered chains were relaxed for 10^6 Monte Carlo (MC) cycles to reach the random-coil state under athermal conditions (as a time unit, each MC cycle contains the number of trial moves equal to all the monomers. In thermodynamic meaning, the athermal condition corresponds to an infinitely high temperature). Polymer chains with two restricted ends mimic those network chains under affine deformation. We tentatively avoided any entanglement in the initial states, although slipping entanglements can be further added along this approach of investigations in near future. The root mean-square end-to-end distance of 128-mer chains in the random-coil state was around 16 sites, and thus choosing 16 sites as the initial X size of the box could ensure no deformation in the initial state of polymer chains. The athermal random coils were then quenched into a temperature to observe strain-induced isothermal crystallization.

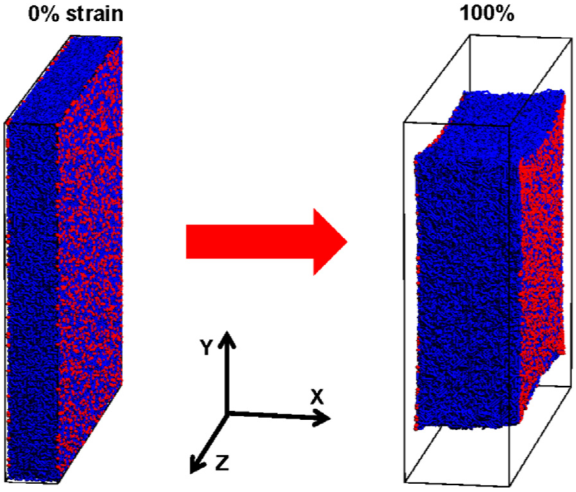

Fig. 1. Snapshots to demonstrate affine deformation of bulk polymers with constant total volumes. The blue cylinders in the box represent polymer bonds, and the red spheres denote the chain ends that are restricted in the boundary YZ planes. The left snapshot was obtained after the relaxation of polymer chains for 10^6 MC cycles under athermal conditions, and the right snapshot was obtained when polymer chains were stretched up to 100% strain at the temperature of 4.5 with the strain rate 6.25%/4000 MC cycles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Polymer coils prepared above were stretched under a high temperature by moving the right YZ boundary step-by-step along X-axis. We first randomly selected one X site, and cut all the chains passing through its corresponding cross-sectional YZ plane into two parts. Then, we shifted the right part for one more X site, and reconnected all the broken bonds at the YZ plane via local sliding diffusion to open the first kink in the left part of the chains. If the sliding diffusion demands for the left chain end leaving away from its YZ boundary plane, this trial event of stretching will be rejected and then be immediately followed with the next trial event at another randomly selected X site. The probabilities of breaking the bonds along the chains were almost equal, except for those near two chain ends, mimicking a homogeneous stretching of bulk polymers. After each successful event of stretching, the system relaxed for a certain period (variable at 1000, 4000 and 10,000 MC cycles, while the Rouse relaxation time of bulk 128mers is around 3200 MC cycles [48]), which defined the strain rate (corresponding to 6.25%/1000 MC cycles, 6.25%/4000 MC cycles and 6.25%/10,000 MC cycles, respectively). New vacancy sites were inserted into the bulk sample with volume expansion upon the stepwise shifting of the right X boundary, which should be expelled as soon as possible under a normal stress upon stretching polymers. Therefore, a strongly centrifugal energy E_a, driving the newly added vacancy sites away from the central X axis of bulk polymers, was introduced to ensure the constant volumes upon affine deformation in the bulk polymer sample, as demonstrated in the right part of Fig. 1.

The conventional Metropolis sampling algorithm was employed at each step of micro-relaxation with the potential energy penalty

$$E = aE_c + pE_p + bE_a \qquad (1)$$

Here, E_c is the potential energy change for non-collinear connection of consecutive bonds along the chain, reflecting the chain flexibility, E_p is the potential energy change for each pair of nonparallel packed bonds, reflecting the molecular driving force for polymer crystallization [48], a is the net change of non-collinear connection pairs of bonds along the chain, p is the net change of nonparallel packed pairs of bonds, and b is the net change of pair contacts between monomers and newly added vacancy sites. In practice, E_p/E_c was fixed at one to allow for a proper flexibility of chains at crystallization temperatures, E_a/E_c was set as 1000 to expel the newly added vacancy sites from the bulk phase during stretching. $kT/E_c = 4.5$ represented a high system temperature for the observation of