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Strong memory of strain-induced copolymer crystallization as revealed by Monte Carlo simulations

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ABSTRACT

We performed dynamic Monte Carlo simulations of strain-induced crystallization of homopolymer and random copolymers under cyclic loading of strains. We found that since the second loading random copolymers shift down the onset strain of crystallization and raise up the crystallinity, in contrast to homopolymer. We attributed the strong memory to the remaining of sequence-length segregation raised by copolymer crystallization during the first loading of strains. The mechanism is consistent with that for the strong memory of copolymer crystallization under cyclic cooling, as revealed by previous experiments and simulations. Our results showed a new effect of chain-sequence defects on the cyclic loading performance of rubbers.

1. Introduction

It is well-known that natural rubbers contain a relatively high sequence regularity, which benefits its strain-induced crystallization for a good strain-hardening performance. Therefore, how the sequence defects, including those chemical, geometrical and spatial irregularities, affect the strain-hardening performance of synthetic polymer rubbers is worthy of further investigation.

In principle, sequence defects can be treated as non-crystallizable comonomors in statistical copolymers that have been divided into heterogeneous and homogeneous copolymers. For heterogeneous copolymers, a high diversity of comonomer distribution among polymers may lead to phase separation prior to crystallization, as demonstrated by dynamic Monte Carlo simulations of lattice copolymer models [1,2]. In contrast, for homogeneous copolymers, only weak segregation can be reached by very large Flory-Huggins interaction parameters, as estimated by de Gennes [3]. Crystallization of homogeneous copolymers performs sequence-length segregation to facilitate the potential separation between monomers and comonomers [4]. If the sequence-length segregated states remain in the second-round crystallization, a strong memory effect to accelerate copolymer crystallization has been found in both experiments [5] and molecular simulations [6]. This memory has been further evidenced in many other investigations [7–9]. Stretching of the rubber at the temperatures slightly above the crystallization temperature can induce polymer crystallization [10], because the stretching decreases the conformational entropy change of crystallization and raises the melting point for larger supercooling [11]. So far, whether the strong memory of copolymer crystallization exists in the cyclic loading of strains has not yet been investigated.

Recently, dynamic Monte Carlo simulations of strain-induced polymer crystallization have been performed to investigate the crystal nucleation switching from the intramolecular to the intermolecular modes [12], the hierarchical trends of chain-folding upon persistent stretching [13], as well as crystal nucleation combining two chain lengths in their binary mixtures [14]. The simulations even verified the thermodynamic theory of strain-induced crystallization of random copolymers [15]. In this report, we compared dynamic Monte Carlo simulations of strain-induced crystallization of bulk homopolymer and homogeneous random copolymers under cyclic loading of strains. The results will demonstrate a strong memory of strain-induced copolymer crystallization upon cyclic loading, with the microscopic mechanism as the same as the previous proposition for cyclic cooling.

2. Simulation techniques

As usual, we employed a lattice model of polymer chains in our dynamic Monte Carlo simulations, with the crystalline order

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represented by parallel packing of the bonds [16]. 1920 polymer chains were put in a box with cubic cells 16 × 128 × 128 (XYZ) and neutral hard walls as the boundary conditions (polymer chains will leave the lateral boundaries as soon as being stretched), each chain occupying 128 lattice sites that can be assigned to either monomers or comonomers by the probability of preset mole fraction (supposing that comonomer does not bring any parallel-packing interaction of the bonds for crystallization) [1]. The amount of polymers was large enough for us to overlook any effect at the sample surface where the mixing between the chain units and the centrifuged new vacancy sites was set as athermal. Homopolymer held the uniform monomers. For a series of homogenous random copolymers, we separately set the comonomer mole fractions as 0.06, 0.12 and 0.24, with their sequences determined by a random-number generator [1]. The total occupying density was set as 0.9375 in order to mimic the bulk state of polymers, and the rest vacancy sites were treated as free volume for micro-relaxation with single-site jumping jointed with local sliding diffusion [17]. Trial sliding of comonomer into any parallel-packing region of monomer bonds was rejected to mimic the ethylene-based copolymers due to its supposed large side group incompatible to the crystalline region of monomers. After a long-term athermal relaxation for 10^6 Monte Carlo (MC) steps (each MC step as for the time unit is defined as the trial moves equal to all the monomers) to erase the thermal history, the melt was quenched to different temperatures for an isothermal stretching process with X-coordinates extending from 16 to 80, as demonstrated by the snapshots in Fig. 1.

In the Metropolis sampling for each step of micro-relaxation, the potential energy criteria was

$$\frac{\Delta E}{kT} = \left(a + p\cdot\frac{E_p}{E_c} + b\cdot\frac{E_a}{E_c}\right)\frac{E_c}{kT} \qquad (1)$$

where a was the net change of non-collinear bonds, p was the net change of parallel-packing monomer bonds, E_p was the parallel-packing interaction reflecting the crystalline order of monomer bonds, E_c was the energy difference between collinear and non-collinear bonds reflecting the chain flexibility, b was the net change of new vacancy sites expelled from the central X-axis, E_a was the energy change to dispel new vacancy sites in reflecting the normal stress of affine deformation [12], k was the Boltzmann's constant, and T was the temperature. Below we treated the reduced temperature parameter kT/E_c as the system temperature T without any further explanation. For simplicity, we set $E_p/E_c = 1$ to reflect a proper chain-flexibility at the crystallization temperatures, and $E_a/E_c = 1000$ to quickly dispel new vacancy sites away from the central X-axis during the relaxation process of each stretching step. During the retraction process, we set $E_a/E_c = 0$ to let the stretched chains to relax spontaneously the normal stress.

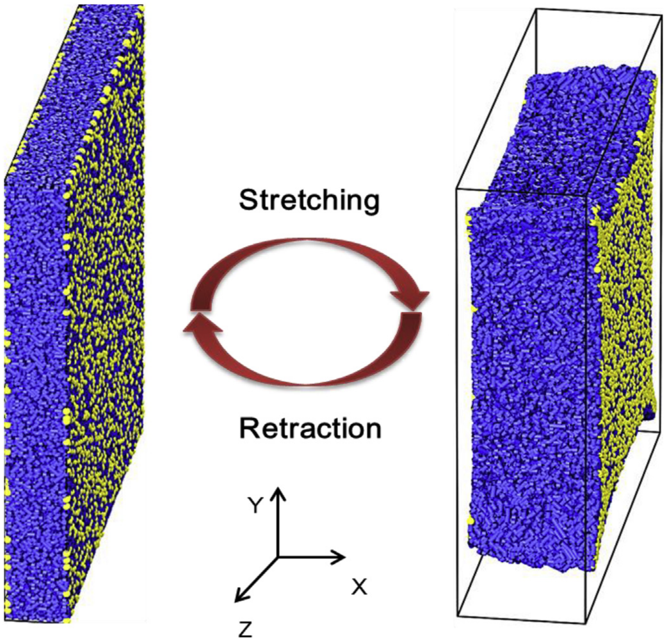

Fig. 1. Snapshots to illustrate the stretching and retraction processes of homopolymer or random copolymers. Both the stretching and retraction processes were carried out at a reduced temperature $T = 4.5$ and a constant strain rate 6.25%/4000 MCs. The strain was estimated on the basis of the initial cell when the length of X-axis was 16. Blue color stands for monomers or comonomers, while yellow color stands for the restricted chain ends on the end planes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

We adopted the stretching process reported in previous simulations of strain-induced polymer crystallization [12], where two chain ends of each polymer were separately restricted in the 2D space of the parallel end planes, and their distances were increased step-by-step to mimic the stretching process under a constant strain rate. During each step of stretching, the sample was stretched at a randomly selected X-coordinate. In details, its right part was shifted towards one more site, and all the broken segments on the selected YZ plane were reconnected by performing a local sliding diffusion along the left part of the chain (terminated by the removal of the first kink). A long-term relaxation was then provided to realize a homogeneous stretching in each step.

In each step of the retraction process, 4000 MCs relaxation was given to all the chain units for the right end-plane to move irreversibly towards the next right plane, where the chain ends were restricted again in the new 2D space. In another word, all the chain ends moved to the next end plane during each step of spontaneous relaxation of stretched polymers. In this way, step by step, a constant strain rate of the retraction process could be realized, as illustrated also in Fig. 1.

3. Simulation results and discussion

3.1. Homopolymer in the first cycle of loading

We start with the first-round stretching and retraction processes of homopolymer at various temperatures from $T = 4.9$ to 5.3. The strain-evolution curves of crystallinity are summarized in Fig. 2a and b, separately for the stretching and the corresponding retraction processes. The crystallinity was defined as the fraction of monomer bonds containing more than five parallel monomer bonds, which monitored strain-induced crystallization as well as the retraction-induced melting.

Fig. 2a reproduces the stretching observations in our previous simulations [12], where one can see larger strains required for the initiation of crystallization at higher temperatures. Fig. 2b demonstrates the melting induced by the retraction process, in which one can see the correspondingly larger strains for crystal melting at higher temperatures. There exists a significant hysteresis of crystallization-melting cycle during the stretching-retraction processes at each temperature. It is interesting to note that at the beginning of retraction, the crystallinity temporarily raises up a little rather than immediately drops down. The observation appears as consistent with the parallel experiments [18–21], probably due to the relaxation of stretched polymer chains which facilitates crystallization.

3.2. Random copolymers in the first cycle of loading

We then observed the first-round stretching and retraction