

How Polydispersity of Network Polymers Influences Strain-induced Crystal Nucleation in a Rubber*

Miao-miao Zhang, Li-yun Zha, Huan-huan Gao, Yi-jing Nie and Wen-bing Hu**

Department of Polymer Science and Engineering, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Abstract Network polymers in a rubber or a gel often contain non-uniform chain lengths. By means of dynamic Monte Carlo simulations of polymer mixtures with various compositions of two chain lengths, we investigated how the factor of polydispersity influences their strain-induced crystal nucleation. Under a high temperature and a high strain rate, the stretching of both polymers revealed that crystal nucleation is mainly accelerated by the presence of short-chain polymers; nevertheless, both polymers join together in the nucleation process. Further analysis proved that crystal nucleation is initiated from those highly stretched short segments, which are rich on the short-chain polymers.

Keywords: Crystallization; Rubber; Polydispersity; Molecular simulation.

INTRODUCTION

Strain-induced crystallization raises the strain-hardening phenomenon of natural rubbers. Its discovery was actually the first experimental observation on polymer crystallization, dating back to 1925 when Katz applied X-ray diffraction to monitor the crystalline order upon the stretching of natural rubbers^[1]. In 1947, Flory developed the thermodynamic theory to predict the shifting-up of melting point due to the stretching of polymers^[2]. Since then, experimental investigations on the strain-hardening behavior of natural rubbers have attracted broad attention^[3,4]. Vulcanization commonly generates randomly distributed crosslink in the rubber. In this sense, network polymers are far from uniform. However, the effect of chain-length polydispersity on the strain-induced crystallization has not yet been well studied. This situation is probably related to the fact that characterization and adjustment of chain-length distributions in the rubber are practically difficult.

Recently, a new scheme of dynamic Monte Carlo simulations has been developed to investigate the strain-induced crystallization behaviors of bulk uniform polymers^[5–7]. Upon raising strains, a transition in the preferences from intramolecular to intermolecular crystal nucleation has been observed^[5]. In addition, intermolecular crystal nucleation at a high temperature is initiated by those sporadically distributed and highly stretched segments on polymer chains^[6]. Furthermore, although intermolecular crystal nucleation generates less chain folding at beginning, subsequent crystal growth still generates more chain-folding, and the post-growth stretching extends those folded chains *via* a melting-recrystallization process^[6]. Randomly distributed defects on

* This work was financially supported by the National Natural Science Foundation of China (Nos. 20825415 and 21274061), National Basic Research Program of China (No. 2011CB606100) and Program for Changjiang Scholars and Innovative Research Teams in Universities. The support from Anhui Tong Feng Electronics Corporation is also appreciated.

** Corresponding author: Wen-bing Hu (胡文兵), E-mail: wbhu@nju.edu.cn

Invited paper for the special issue of “Polymer Crystallization”

Received March 26, 2014; Revised April 21, 2014; Accepted April 28, 2014

doi: 10.1007/s10118-014-1495-9

the sequences of copolymers will depress the melting point as well as the onset strain of crystallization, both of which can be predicted well by combining Flory's treatment on the melting-point depression of random copolymers with his treatment on the melting-point shifting-up of strain-induced polymer crystallization^[7].

In this report, along the same approaches of molecular simulations as introduced above, we go further to investigate the effects of chain-length polydispersity on the strain-induced crystal nucleation of polymers. We set up a binary mixture of polymers of two chain lengths sharing the same chemistry. Both the long and short polymers are simultaneously stretched, mimicking to the situation of stretching network polymers with an extreme polydispersity. The results will show that crystal nucleation is accelerated by the mixing of two chain lengths, in particular, the presence of short polymers. We attribute the initiation of crystal nucleation to those highly stretched segments rich on short polymers. This nucleation mechanism will facilitate our better understanding of the practical strain-induced crystallization in the stretched rubbers and gels.

The paper is organized as follows. After Introduction, we made a brief description on the simulation techniques, followed with the simulation results and discussion. The paper ends with a summary of our conclusions.

SIMULATION TECHNIQUE

Dynamic Monte Carlo simulations of lattice polymers have been widely applied in the study of polymer crystallization^[8]. In the box of the XYZ sizes $16 \times 128 \times 128$, we filled some 256-mers as the long-chain component, and some 128-mers as the short-chain component for various long-chain volume fractions. The occupation density was as high as 0.9375 to mimic the bulk mixtures. Polymer chains performed micro-relaxation steps, with monomers jumping into their vacancy neighbor sites, sometimes accompanied with partial sliding diffusion along the chain^[9]. Therefore, small amount of single vacancy sites were necessary for polymer motion, playing the role like the free volume in the bulk polymer phase. Double occupation and bond crossing were forbidden to mimic the volume exclusion of polymer chains. The boundary conditions were simply hard walls upon polymer stretching.

The initial state of the sample with various compositions was prepared as described below. Taking the long-chain fraction 0.5 as an example, we set 480 long chains and 960 short chains with random sequences in the arrays along Z-axis, each chain folds 15 times along X-axis, but the two components were separated by the folding lengths of 16 and 8 monomers along Y-axis, as demonstrated in Fig. 1. The preset ordered state was relaxed over 5×10^6 MC cycles (each MC cycle was defined as the number of trial moves equal to the total amount of monomers) under athermal conditions, although both chain ends were restricted on their original YZ planes. We then obtained the nearly random coils in the homogeneous mixtures of two chain lengths.

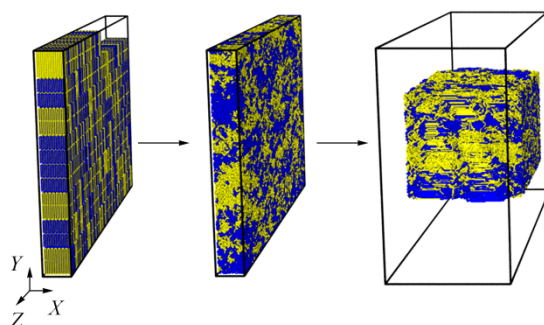


Fig. 1 Snapshots of the preset ordered, the initial relaxed and the final stretched (400% strain) states of the sample with long-chain fraction 0.5

The two ends of each polymer chain are separately restricted on the parallel plates locating at the boundaries of *X*-axis. Those bonds belonging to long chains are colored in yellow, and those bonds of short chains are in blue. (The online version is colorful.)

We step-by-step increased the spacing between two plates at the boundaries of X-axis and kept both chain lengths restricted at their corresponding plates. In details, we randomly selected an X site, and moved all the sites locating on its YZ plane as well as in the right part towards one more X site. We then reconnected all the broken ends on the YZ plane by performing partial sliding diffusion till the first kink got opened along the left part of the broken chain, and relaxed the system for 15000 MC cycles. Therefore, referred to the initial 16-site size on X-axis, the strain rate is 6.25%/15000 MC cycles. If partial sliding diffusion along the left part of the broken chain requests for the chain end leaving away from its plate, this trial step of stretching will be rejected. Each step of stretching introduced many new vacancy sites on that YZ plane. In order to maintain the total volume of the bulk sample, we imposed a centrifugal force field E_a onto those new vacancy sites, which played the role like normal stress upon stretching polymer chains.

The conventional Metropolis sampling algorithm was employed with the total potential energy change in each step of micro-relaxation,

$$\Delta F = cE_c + pE_p + aE_a \quad (1)$$

where E_c was the bending energy for two bonds consecutively connected along the chain, E_p was the parallel-packing energy for two bonds in crystalline order, E_a was the centrifugal energy for each new vacancy site jumping away from the center of the corresponding YZ-plane; c , p and a were the net amounts of corresponding changes. We chose E_c as the reference parameter. We set $E_p/E_c = 1$ as a strong enough driving force for polymer crystallization when the chains were still flexible, $E_a/E_c = 5000$ as a strong enough normal stress for maintaining constant volume, and $kT/E_c = 4.5$ as a high enough temperature for the observation of strain-induced crystallization where k was the Boltzmann constant and T the temperature.

RESULTS AND DISCUSSION

We first observed the strain evolution curves of total crystallinity for the samples with various long-chain fractions when both long and short polymers are stretched together. The results are summarized in Fig. 2. All the crystallinities in the samples with various long-chain fractions are saturated at the level of 0.65, which appears slightly higher than the level of 0.57 as observed in our previous simulations of polymers with uniform chain length 128^[5], implying that the long-chain (256) component can release, to a certain extent, the strong topological restriction at chain ends upon the harvest of crystallinity during strain-induced crystallization. The snapshot of the sample with long-chain fraction 0.5 at the final stretched state (400% strain) has been shown at the right end of Fig. 1.

The onset strain for the initiation of polymer crystallization can be read from the curves in Fig. 2, and the results are summarized in Fig. 3. One can clearly see from Fig. 3 that a small amount of short chains immediately lower the onset strains from the ideal situation of mixtures, implying an acceleration effect on the practical initiation of crystallization.

In order to figure out which component dominates crystal nucleation at the early stage of crystallization, we further observed the crystallinity in each component. Figure 4(a) compares three pairs of strain-evolution curves of crystallinity in two components at the early stage of strain-induced crystallization of samples with different long-chain fractions. One can see that in the sample with long-chain fraction 0.8, the crystallinity of short polymers raises slightly prior to that of the long-chain counterpart, although the long-chain component joins crystallization very soon. This result implies that crystal nucleation could be dominated by the short-chain component.

We further compared the strain evolution curves of orientational order parameters of the corresponding components under parallel situations of Fig. 4(a), as shown in Fig. 4(b). The priority of high orientation in the short-chain component becomes more obvious at the early stage of strain-induced crystallization. Apparently, the high orientation facilitates crystal nucleation in the short-chain component.

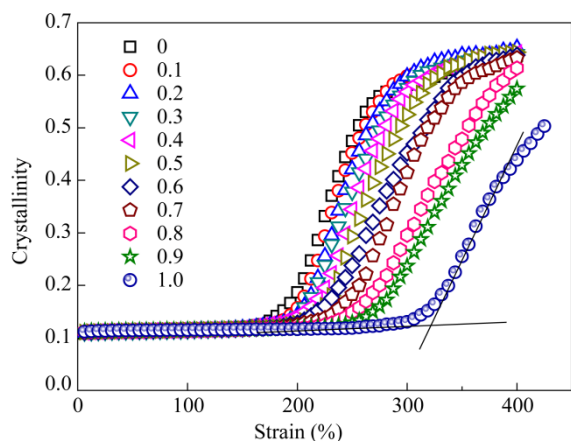


Fig. 2 Strain-evolution curves of crystallinity in the samples with various long-chain fractions as denoted. The crystallinity was defined as the fraction of bonds containing more than five parallel neighbors. The horizontal crystallinity (around 0.1) at beginning can be attributed to the thermal fluctuations of ordering in the melt phase. The onset strain is defined by the crossover of two extrapolations, as drawn in straight lines.

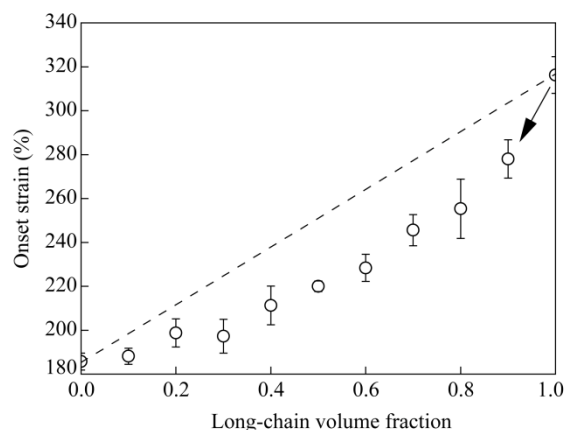


Fig. 3 Onset strains under various long-chain fractions obtained from Fig. 2. Each data point with an error bar was averaged over five independent observations. The dashed line guides the eyes for an ideal situation, and the big arrow indicates the more significant acceleration effect by adding short-chain polymers.

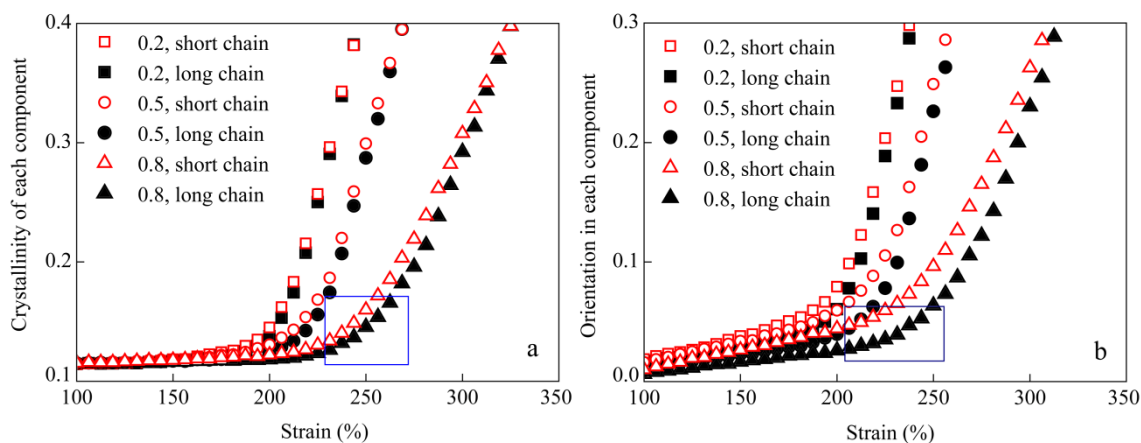


Fig. 4 Strain evolution curves of (a) crystallinity and (b) orientational order parameters separately for two components as denoted in the samples with three typical long-chain fractions (0.2, 0.5 and 0.8). The scales are enlarged in order to monitor the early stage of crystallization. The definition of crystallinity is similar to that given in Fig. 2. The definition of orientational order parameter is as usual as $(3\cos^2\theta-1)/2$ for those bonds with the reference to X -axis. The rectangular frames focus the early differences between two components.

It should be noted that during stretching under the present high temperature and the strain rate, demixing parameters of two components do not indicate any obvious component segregation, even upon crystallization, as demonstrated in Fig. 5. Therefore although crystal nucleation is initiated by the sporadic highly stretched short segments mainly belonging to short polymers, both components actually join together in crystal nucleation as well as crystal growth, in particular when short polymers become the dominant component as demonstrated in the sample with long-chain fraction 0.2 in Fig. 4(a) as well as in the right snapshot of Fig. 1.

In our previous simulations of strain-induced polymer crystallization, we have observed that crystal nucleation is normally initiated from those highly oriented short segments sporadically distributed in the polymer chains^[6]. One may imagine that under the same strains, short polymers could generate a higher concentration of

oriented segments than their long-chain counterpart, resulting in its relatively higher orientation at the early stage of crystallization than the long-chain component, as demonstrated in Fig. 4(b).

In present simulations, we also calculated the strain-evolution curves of concentrations of highly oriented short segments in two chain-length components. The results are summarized in Fig. 6. One can indeed see that the samples with higher long-chain fractions generate a larger difference in the concentrations of highly oriented segments between two components at higher onset strains, implying the priority of the short-chain component in the initiation of crystal nucleation.

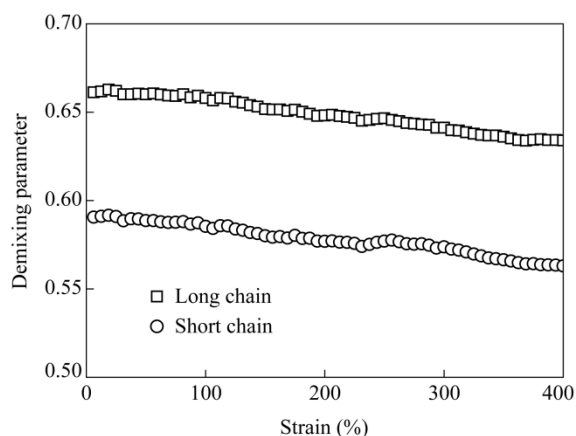


Fig. 5 Strain-evolution curves of demixing parameters of two components as labeled in the sample with 0.5 long-chain fraction

The demixing parameter was defined as the average fraction of monomers of the same species occupying 24 neighbors (26 neighbors on all the axes and diagonals, subtracted two neighbors along the chain) of each monomer in the lattice space.

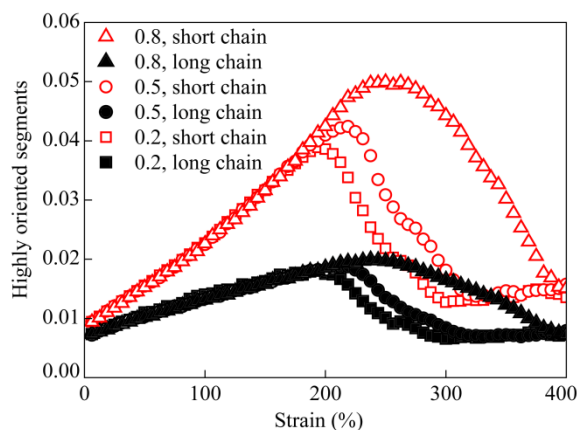


Fig. 6 Strain-evolution curves of the concentrations of highly oriented segments along polymer chains of two components as denoted in the samples with three typical long-chain fractions

The highly oriented segment was defined by the end-to-end distance of consecutive six bonds along the chain larger than four aligned bonds.

Under visual inspection of the snapshots, Figure 7 provides a retrospective observation on the first nucleus, demonstrating that those highly oriented short segments in the short chains generate crystal nuclei at the beginning of crystal nucleation (225% strain), earlier than those on long-chain polymers. This observation evidences the acceleration mechanism of the short-chain component in the initiation of crystallization, as observed in Fig. 3 as well as in Fig. 4.

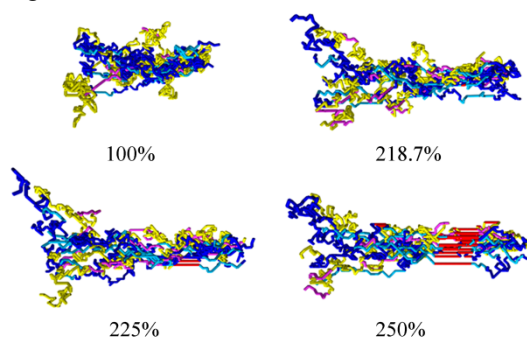


Fig. 7 Snapshots of a bundle of chains in the sample with 0.8 long-chain fraction separately at four strains as denoted

These chains join into the same crystal nucleus in the fourth figure. Those pink bonds are the highly oriented segments in long chains colored originally in yellow; and those sky blue bonds are the highly oriented segments in short chains colored originally in dark blue. The red bonds are the crystalline bonds containing more than five parallel neighbors, in priority transformed from those sky blue bonds.

CONCLUSIONS

We have investigated the effect of chain-length polydispersity on the strain-induced crystal nucleation in rubbers, by means of dynamic Monte Carlo simulations of lattice polymers in the bulk mixtures of two chain lengths. The results showed that the mixing can accelerate crystal nucleation of long chains, as dominated by the short-chain component. We analyzed the microscopic mechanism of strain-induced crystal nucleation, and attributed the source of crystal nucleation to those highly oriented short segments that are rich for short polymers. However, both polymers join together in crystal nucleation and growth. In reality, those chain ends may not necessarily keep in a plane upon affine deformation of the network, but short chains naturally take over higher stress than long chains. Our observations will facilitate our better understanding of the polydispersity effect during strain-induced crystallization in rubbers and gels.

REFERENCES

- 1 Katz, J.R., *Naturwissenschaften*, 1925, 13: 410
- 2 Flory, P.J., *J. Chem. Phys.*, 1947, 15: 397
- 3 Tosaka, M., *Polym. J.*, 2007, 39: 1207
- 4 Zhao, B., Tian, N., Liu, Y., Yan, T., Zhou, W., Li, L., Zhou, Y., Weng, G. and Huang, G., *J. Polym. Sci. Part B: Polym. Phys.*, 2012, 50: 1630
- 5 Nie, Y.J., Gao, H.H., Yu, M.H., Hu, Z.M., Reiter, G. and Hu, W.B., *Polymer*, 2013, 54: 3402
- 6 Nie, Y.J., Gao, H.H. and Hu, W.B., *Polymer*, 2014, 55: 1267
- 7 Nie, Y.J., Gao, H.H., Wu, Y.X. and Hu, W.B., *Soft Matter*, 2014, 10: 343
- 8 Hu, W.B. and Frenkel, D., *Adv. Polym. Sci.*, 2005, 191: 1
- 9 Hu, W.B., *J. Chem. Phys.*, 1998, 109: 3686