Role of Block Junctions in the Interplay of Phase Transitions of Two-Component Polymeric Systems

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ABSTRACT: Block junctions are the topological constraints of connecting two homopolymers of different species to form diblock copolymers, which make the phase transition behaviors of diblock copolymers deviate from that of parallel polymer blends. We performed dynamic Monte Carlo simulations of these two parallel polymeric systems to compare their behaviors in the interplay of phase transitions. The results showed the lowered melting point of one component in symmetric diblock copolymers, as well as their enhanced critical segregation strength for demixing prior to crystallization. Furthermore, prior microphase separation in symmetric diblock copolymers produces a template for parallel stacking of lamellar crystals, which is of practical importance in the barrier properties of polymeric materials. Our observations may facilitate a better understanding to the phase transition behaviors of copolymer systems.

INTRODUCTION

Hierarchical microstructures in multicomponent polymeric materials are fabricated conventionally via two basic types of phase transitions, i.e., liquid—liquid phase separation and liquid—solid crystallization. The interplay between these two types of phase transitions makes the complex phase transition behaviors with profound mechanisms.1 The classical lattice statistical theory, like the well-known Flory—Huggins theory,2 takes account of the site—site mixing interaction B between two components as the driving force for phase separation in multicomponent polymeric systems. Recently, by taking account of the bond—bond anisotropic attraction $E_p$ as the driving force for crystallization in one polymer component, the lattice statistical theory has been developed to predict the equilibrium melting points.3,4 Simultaneous employment of these two kinds of driving forces allows us to study the interplay of corresponding phase transitions, by means of the mean-field theory and dynamic Monte Carlo simulations.5

Under the thermodynamic conditions designed by the mean-field theory, molecular simulations have offered us many insights into the profound mechanisms in the interplay of polymer phase transitions.6 On the one hand, liquid—liquid demixing could be induced purely by the component-selective crystalline-order interactions, which explains the melt incompatibility between isotactic and atactic polypropylenes.7 In addition, for such blends near the melting points, thermal fluctuations toward crystalline order will significantly enhance liquid—liquid demixing.8 On the other hand, polymer crystal nucleation could be triggered by the prior liquid—liquid demixing in polymer solutions.9 In addition, the interfaces between two incompatible components in polymer blends will enhance crystal nucleation,10 while such an effect occurs only with poor enough solvent in polymer solutions.11

Up to now, we mainly focused our attention on the interplay of phase transitions in intermolecular multicomponent polymeric systems, like in polymer solutions and in polymer blends. Macromolecules can form intramolecular multicomponent systems, such as block copolymers, gradient copolymers, graft copolymers, and random copolymers. In the latter cases, the block junction connecting two components on each macromolecule serves as a topological constraint to the segmental molecules of each component performing phase transition behaviors. Therefore, understanding the role of block junctions becomes a key issue in the study of phase transition behaviors of various copolymers.

It is well-known that the microphase separation of diblock copolymers appears much more difficult than the macrophase separation of binary polymer blends. Such a difficulty can be attributed to the fact that block junctions raise the entropy penalty by stretching each polymer chain over interfaces, and meanwhile raise the surface-free-energy penalty by making the nanoscale distributions of interfaces. The Fredrickson—Helfand theory can predict the critical segregation strength for the microphase separation of symmetric diblock copolymers with a definite chain length,12 which has made the Hartree correction to the Leibler’s mean-field theory.13 Such a prediction has been verified by the molecular simulations of symmetric diblock...
copolymers as reported by Fried and Binder, as well as by the Monte Carlo simulations of diblock copolymers for phase diagrams by Matsen and his collaborators. In these simulations, only the mixing interaction $B$ has been employed. How the block junctions affect the interplay of phase transitions in diblock copolymers is still unclear.

In this report, we performed dynamic Monte Carlo simulations to address the interplay issue. We will compare the behaviors of phase transitions between two parallel cases separately corresponding to symmetric polymer blends and symmetric diblock copolymers. Our results show that block junctions will shift down the melting point of one component, and raise up the critical segregation strength for the occurrence of demixing prior to crystallization. In addition, prior demixing in diblock copolymers facilitates parallel stacking of lamellar crystals, which is of practical importance in integrating the properties of functional polymeric materials.

The paper is organized as follows. After the introduction, we make a brief description of the simulation techniques. Then, we report the simulation results about the melting points and the crystal morphology influenced by the block junctions, accompanied by some discussion. The conclusions will be summarized at the end.

**SIMULATION TECHNIQUES**

The lattice model has been the basic tool in our understanding of the multicomponent systems as well as of their phase transition behaviors. The Flory–Huggins lattice theory calculates the mixing entropy of chainlike macromolecules. The lattice model has been widely applied in the Monte Carlo simulations of polymers as well.

In a lattice box with its linear size of 64, we assumed that a polymer chain consecutively occupied the lattice sites, with each monomer on one site and with the chain length counted by the number of monomer sites. Each component in the symmetric polymer blends was constructed by 16-mers, while each block in the symmetric diblock copolymers was formed by 16-mers as well. The occupation density was fixed at 0.9375, since a small amount of vacant sites played the role of free volume to relax polymers. The microrelaxation model allowed each monomer to jump into its vacant neighbor, with partial sliding diffusion along the chain if necessary. Polymer chains relax with periodic boundary conditions. Double occupation and bond crossing were forbidden in order to mimic the volume exclusion of polymers. The unit of time evolution was defined as the Monte Carlo cycles (MCs), each containing the number of trial moves equal to the total amount of monomers in the sample systems.

The conventional Metropolis sampling algorithm was employed, with the potential energy change in each step of microrelaxation

$$\Delta E = \beta B + \rho E_p + c E_c = \left(\frac{B}{E_c} + \frac{\rho E_p}{E_c} + c \right) E_c$$

where $E_c$ is the bending energy for each pair of bonds consecutively connected along the chain, $E_p$ is selective to the crystalline component, and $B$ is the mixing interactions between two components; $\beta$, $\rho$, and $c$ are the net amounts of interactions corresponding to the related energy parameters, respectively. In practice, we set $E_p/E_c$ as the driving forces for crystallization of one component (the value for another component was kept as zero), $B/E_c$ for variable segregation strength (in the literature, the definition of segregation strength is conventionally $\chi N$, where $\chi$ is the well-known Flory—Huggins interaction parameter containing $B$, and $N$ is the chain length), and $E_c/kT$ for variable system temperatures ($k$ is the Boltzmann’s constant and $T$ is the temperature).

We first put fully ordered 32-mer chains in the lattice box and then relaxed them under athermal conditions into random coils, for two parallel samples with and without block junctions at the middle of the chain, respectively. Afterward, we cooled down the homogeneous mixing states of polymer blends and diblock copolymers to low temperatures, to observe spontaneous crystallization and phase separation.

**SIMULATION RESULTS AND DISCUSSION**

**Meting Points Influenced by the Block Junctions.** In principle, if the overshooting for primary crystal nucleation can be effectively avoided on cooling, the onset point to initiate polymer crystallization will be very close to the thermodynamic equilibrium melting point. We tentatively measured such an onset point as the melting point. To this end, we introduced a template of crystalline layer by freezing part of fully ordered
chains upon athermal relaxation in the preparation process of two parallel samples. This template will induce either crystallization or liquid—liquid demixing on cooling, and avoids primary nucleation for both types of phase transitions. The same procedure has been applied in our previous simulations of polymer solutions for the study of the interplay of phase transitions

The cooling curves of crystallinity are separately shown in Figure 1a,b for two series of parallel samples with fixed $E_c / E_{e}$ values but various segregation strengths. By comparisons between two parallel samples, one can immediately recognize that diblock copolymers exhibit lower onset values of template-induced crystallization than parallel polymer blends. In addition, the cooling curves can be separated into two groups according to their sensitivity to the segregation strengths: in polymer blends, those curves with $B / E_{e} < 0.1$ meet with each other, while in diblock copolymers, those curves with $B / E_{e} \geq 0.1$ meet with each other, although not so densely as in the parallel group of polymer blends.

We read the onset temperatures of the template-induced crystallization on the cooling curves, from the intersection between two extrapolation lines drawn separately from the regions before transition and upon fast transition. This onset temperature can be tentatively regarded as the equilibrium melting point. The results for the melting points of both series of samples with various driving forces for crystallization as well as for liquid—liquid demixing are summarized in Figure 2.

In Figure 2, two groups of curves in Figure 1 make different slopes of the melting points in their linear dependence on the segregation strength. Let us first look at the group of high segregation strengths. The almost constant melting points, i.e., the overlapping of cooling curves in Figure 1, imply that liquid—liquid demixing occurs before crystallization. According to the theoretical phase diagrams, prior demixing in immiscible polymer blends will yield the same bulk concentrations for polymer crystallization and hence results in constant melting points.10 Nevertheless, the prior demixing in diblock copolymers generates a vast amount of nanoscale-spaced interfaces. At the interfaces, polymers are forced to contact with another component. Again, according to the theoretical phase diagrams, the melting points of the diluted polymers at the interfaces will be raised with the increase of segregation strengths;10 therefore, the melting points of diblock copolymers with prior demixing are still slightly sensitive to the segregation strengths.

In Figure 2, the groups of low segregation strengths exhibit a parallel shifting down of the melting points of diblock copolymers from those of polymer blends. In other words, the melting points are suppressed by the block junctions. In addition, the block junction shifts up the critical segregation strengths for the occurrence of liquid—liquid demixing prior to crystallization, from zero to 0.1 as indicated by the transitions in the slopes of two groups. Since crystallization of diblock copolymers drives phase separation as well, those penalties of conformation entropy and surface free energy for microphase separation still exist here, which suppress the melting points and raise the critical segregation strength for prior demixing. In other words, the observed shifting for demixing driven by $E_p$ interactions can be attributed to the same effects of block junctions as for demixing driven by $B$ interactions. Indeed, the critical segregation strengths for the occurrence of demixing in the latter case have been shifted up in symmetric diblock copolymers ($\chi N \approx 10.5$),12 in comparison to the parallel polymer blends ($\chi N = 2$).

In Figure 2, one can also see that the critical segregation strength for prior demixing appears insensitive to the strength of driving forces for polymer crystallization ($E_p / E_{e}$ values),
implying independent contributions of two types of driving forces for phase transitions.

**Crystal Morphology Influenced by the Block Junctions.**

Polymer crystallization prefers to form lamellar crystals due to a kinetic preference of chain folding. In large spatial-temporal scale of reality, the lamellar crystals can stack together to form spherulites. In the present molecular simulations, however, the spatial-temporal window is so narrow that we could not observe spherulite growth except for lamellar crystal growth initiated by primary nucleation. Primary nucleation generates randomly oriented lamellar crystals in the crystallizable component of polymers. Therefore, both polymer blends and diblock copolymers generate only random stacking of lamellar crystals in conventional crystallization from the homogeneous mixing states. Even in immiscible polymer blends, the phase-separated polymers generate random stacking of crystals in the bulk phase as well. In contrast, microphase separation of diblock copolymers can yield an ordered lamellar array with nanoscale resolutions, which makes spatial confinement to the subsequent polymer crystallization and thus templates the crystalline phases in a nanoscale ordered pattern.21

Previous molecular simulations of polymer crystallization confined in lamellar microdomains have demonstrated that, at high temperatures, perpendicular orientations of polymer crystals are preferred due to the confinement effect of block junctions.22 This behavior implies that block junctions may help our harvest on the lamellar crystals with a long-range parallel stacking.

To demonstrate the above-discussed case, we performed the parallel simulations of isothermal crystallization for diblock copolymers with and without prior demixing, respectively. We chose high temperatures in order to observe a significant incubation period for primary crystal nucleation in the spontaneous slow isothermal crystallization. The purpose of this choice is twofold: on the one hand, a long incubation period allows the formation of a perfect pattern of microdomains in the prior demixing; on the other hand, the high temperature secures the preferences of perpendicular orientations of polymer crystals in the parallel-stacked microdomains. The time-evolution curves of crystallinity and demixing parameters upon isothermal crystallization in two designed samples are shown in Figure 3. One can clearly see from Figure 3a that the diblock copolymers with B/Ec = 0.2 contain no prior liquid—liquid demixing, although the initiation of crystallization needs a long incubation period; while
CONCLUSIONS

We pushed forward our investigations from polymer blends to diblock copolymers, in order to address the role of block junctions in the interplay behaviors of phase transitions. The simulation results showed that the block junctions shift down the melting points and shift up the segregation strengths for the prior occurrence of liquid—liquid demixing in diblock copolymers. In addition, the block junctions allow prior microphase separation to help parallel stacking of lamellar crystals, which provides us a promising path to fabricate a periodic layer structure for integrating some important properties of functional polymeric materials. Overall, our observations provide useful insights into the complex phase transition behaviors of copolymer systems.

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