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Compatibility of Triblock Copolymers in an A/B/Copolymer Ternary Mixture

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ABSTRACT: Monte Carlo simulations were used to model A/B/triblock copolymer ternary mixtures with a fixed volume fraction (19%) of homopolymer A. The volume fraction of block copolymer was varied from 0 to 66%. The simulation illustrated how two incompatible polymers A and B can be blended with a block copolymer. When homopolymer A forms a dispersed phase, both B−A−B and A−B−A triblock copolymer chains tend to stretch on the interface, and some of them form the interchain association on the interface, so that triblock copolymers are more efficient as compatibilizers than A−B diblock copolymers. Some of A−B−A triblock copolymer chains are not located at the interface, but form polymeric micelles in the matrix phase, while nearly all the triblock copolymer chains are concentrated at the interface. Therefore, B−A−B triblock copolymers are better compatibilizers.

Introduction

Two homopolymers A and B are normally immiscible because the entropy change of mixing is very small.[1] As a result, incompatible blends often exhibit poor mechanical properties. Much effort has been devoted to the compatibilization of two incompatible homopolymers. The addition of a few percent of block copolymers is one of the practical methods,[2−6] in which one block is miscible with A, while the other block is miscible with B. It has been experimentally[7−14] and theoretically[15−19] demonstrated that the copolymer chains as compatibilizers are located at the interface between A and B. As stated by Paul,[20] “This type of surface activity should 1) reduce the interfacial energy between the two phases; 2) permit a finer dispersion during mixing; 3) provide a measure of stability against gross segregation; and 4) improve interfacial adhesion.” We still do not know how to experimentally answer some of these questions, when mixing one diblock or triblock copolymer with two homopolymers, such as how much is dissolved in the two homopolymer phases; how much exists in the form of micelles; and how much stays at the interface. Also, we do not know how to choose an efficient copolymer for a given system. Noolandi et al.[15−18] proposed a statistical thermodynamic model to describe the copolymer emulsification in an A/B/A−B ternary melting blend. Laradji et al.[19] investigated the phase separation of binary mixtures in the presence of surfactant by means of a time-dependent Ginzburg−Landau model. To our knowledge, there is no emulsification theory for a triblock copolymer in an A/B/(triblock copolymer) ternary blend.

On the other hand, computer simulation methods, especially the Monte Carlo simulation, have been proved to be a valuable tool in the study of polymer chain dynamics,[21−28] glass transition,[29,30] and solution dynamics near the Θ temperature.[31−35] Jo et al.[36−38] did a careful investigation of the phase separation dynamics of polymer blends in the presence of diblock copolymers. They concluded that the rate of the phase separation is significantly suppressed by the addition of block copolymers due to the reduction of the interfacial tension. This retardation effect is much dependent on block length and on the interaction energies between the copolymer blocks and their corresponding homopolymers. Our previous simulation showed that, in an A/B/A−B ternary blend, diblock copolymer chains are concentrated at the interface.[39] Below a critical copolymer concentration, the domain size of the dispersed phase decreases linearly as the copolymer concentration increases. Kawakatsu et al.[40] investigated the phase separation in binary mixtures containing surfactant by using a hybrid model and reported that the coarsening rate of the domain structures is much decreased. Takenaka et al.[41] also simulated the time dependence of the domain structures after quenching a homopolymer/homopolymer/random-copolymer ternary mixture to a temperature below its tricritical point. Nowadays, not only can microscopes observe molecules but also a computer as

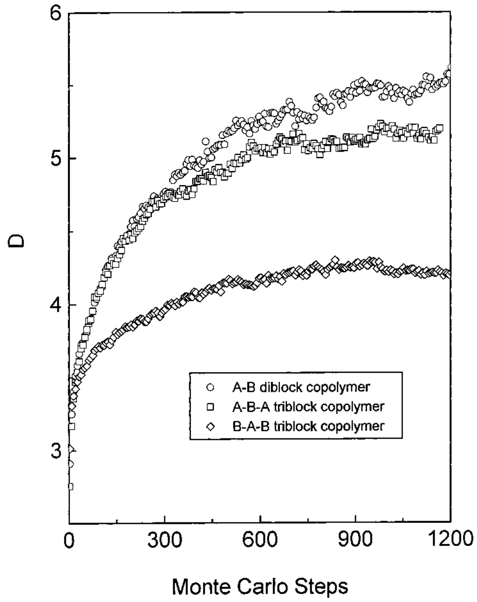

Figure 1. Monte Carlo step dependence of the domain size (D) of dispersed phase for three kinds of copolymers, where the dispersed phase concentration (ϕ_A) and the block copolymer concentrations ($\phi_{\text{copolymer}}$) were kept at 0.19 and 0.50, respectively.

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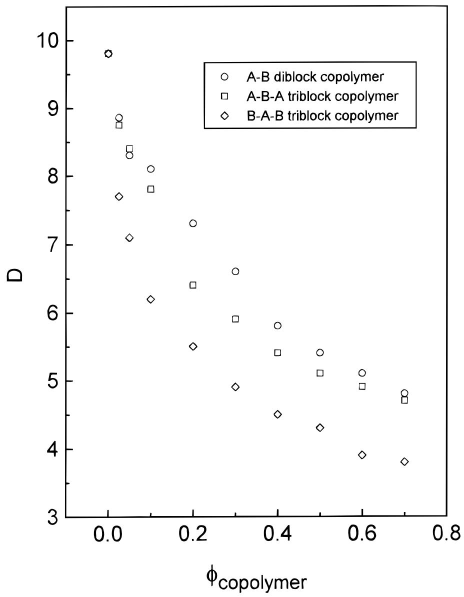

Figure 2. Block copolymer volume fractions dependence of domain size of dispersed phase after 900 Monte Carlo steps.

a powerful tool can "see" molecules. In this study, the Monte Carlo simulation was used to quantitatively investigate the morphologies of an A/B/triblock copolymer ternary mixture and the chain conformation of triblock copolymer at the interface.

Simulation

A two-dimensional simulation was used to provide a direct inspection of polymer configuration and the coarsening of the phase-separated structure. Cifra et al.[42,43] showed that there is no essential difference in the phase behavior between a two- and three-dimensional simulation.

Multiple-chain configurations were generated on a planar square 420 × 420 lattice. The system contained 8400 linear chains, and each chain had 20 segments, resulting in a polymer concentration as high as 0.95, so that it could be regarded as a bulk. The vacancy of 0.05 is handled as free volume. A standard periodic boundary condition was imposed on the lattice to mimic an infinite-size system.[44] Considering such a high polymer concentration, we adopted the "single-site bond fluctuation" model proposed by Larson et al.[45,46] and

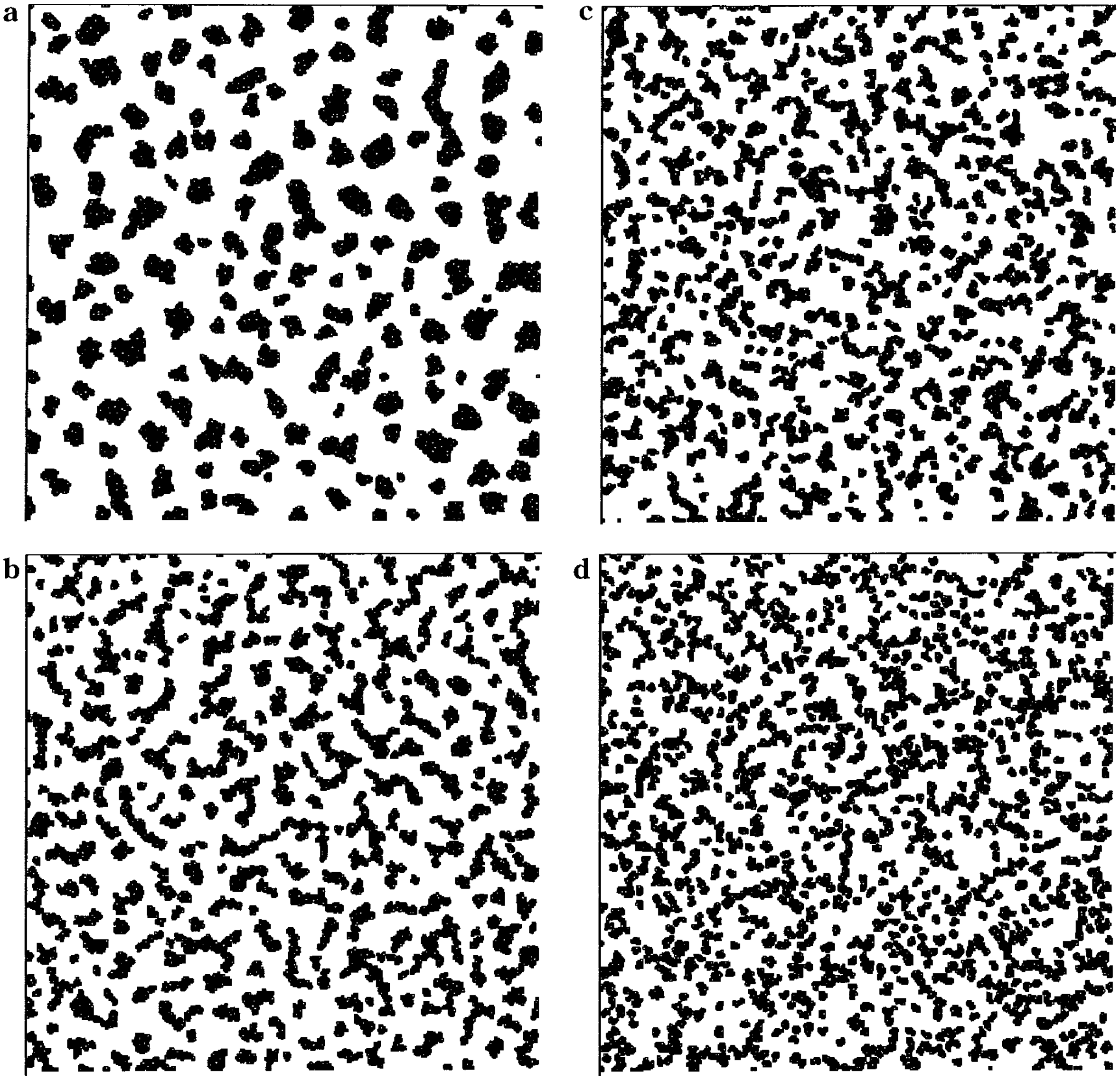

Figure 3. Domain pattern after 900 Monte Carlo Steps: (a) no copolymer; (b) $\phi_{A-B} = 0.50$; (c) $\phi_{A-B-A} = 0.50$; and (d) $\phi_{B-A-B} = 0.50$, where the system has a size of 420 × 420. The white color indicates a continuous phase made of B and copolymer, and the black color shows the dispersed phase made of A.

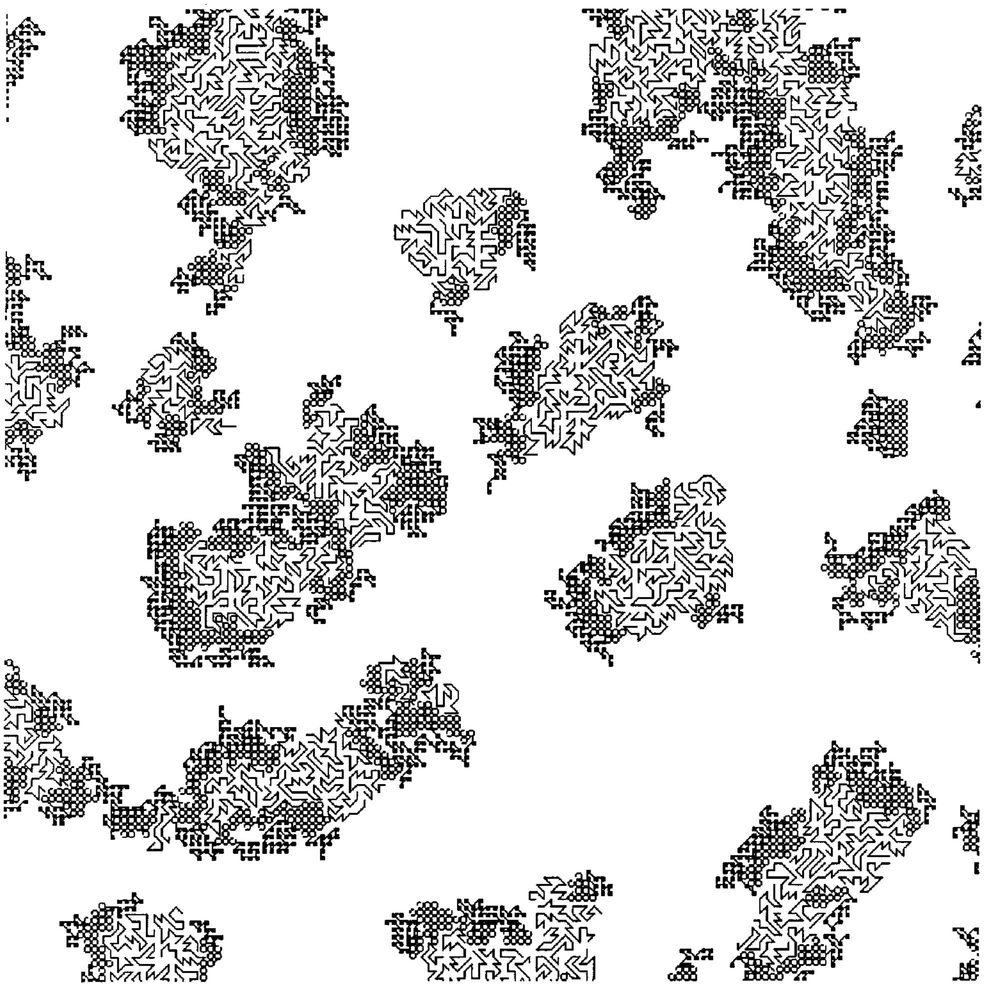

Figure 4. Typical configuration pattern of a A/B/A−B ternary polymer blends after 900 Monte Carlo steps, where $\phi_{A-B} = 0.20$. —, ○, and ■ represent homopolymer A, A-block, and B-block of the copolymer, respectively, and the white color represents homopolymer B.

Carmesin et al.[47] and the "vacancy diffusion" algorithm suggested by Lu et al.[48] to improve the Monte Carlo simulation efficiency. The schematic of the model and the corresponding microrelaxation modes can be found elsewhere.[49] The evolution of the chain configuration in simulation was achieved by random displacing of a single vacancy site to its eight nearest-neighboring sites on the lattice. Each attempted move changes the bond length, but the chain connectivity restricts the bond length to 1 and $\sqrt{2}$. The excluded-volume interaction ensures no more than one bead per lattice site. The bond crossing was checked. If one attempted move violates either the excluded volume or the bond length restriction or the bond crossing, it will be rejected. The acceptance or rejection of one attempted move is further governed by the Metropolis rule:[50] namely, it is accepted if the energy change, $\Delta E = (N^{\mathrm{n}}_{\mathrm{AB}} - N^{\mathrm{o}}_{\mathrm{AB}})\epsilon$, is negative; otherwise, it is accepted with a probability of $p = \exp(-\Delta E/kT)$, where $N^{\mathrm{n}}_{\mathrm{AB}}$ and $N^{\mathrm{o}}_{\mathrm{AB}}$ respectively are the numbers of the nearest-neighboring pair of sites taken by the pair of beads (or segments) after and before the attempted move and ϵ is the interaction energy gained when two different kinds of monomers occupy two neighboring lattice sites. The negative and positive values of $\bar{\epsilon}$ ($=\epsilon/kT$) correspond to a homogeneous and a heterogeneous state, respectively.

In the simulation, we first set $\bar{\epsilon} = -1$. After the system reaches a completely compatible state, we set $\bar{\epsilon} = 1$ to observe the change of domain structure in the phase separation.

Results and Discussion

In the simulation, the volume fraction ϕ_{a} of the dispersed phase made of homopolymer A was fixed to be 0.19. The sum of the volume fractions of homopolymer B and block copolymer $\phi_{\mathrm{b}} + \phi_{\mathrm{copolymer}}$ was 0.76. All the homopolymer and block copolymer chains have the same length (20 segments). For comparison, we also studied an A−B diblock copolymer. The structures of the block copolymers are 10A-b-10B, 5A-b-10B-b-5A, and 5B-b-10A-b-5B. To investigate the concentration influence of diblock and triblock polymers on morphologies of the A/B/copolymer ternary mixtures during phase separation, we varied the volume fraction of block polymer $\phi_{\mathrm{copolymer}}$ from 0 to 0.665. Figure 1 shows that the domain size of the dispersed phase increases as the Monte Carlo step increases and approaches a plateau after 900 Monte Carlo steps. The domain size (D) is defined as N/N_{d}, where N and N_{d} are the lattice numbers and the dispersed phase numbers on the line drawn parallel to the borderline. It is clearly shows that using triblock copolymers, especially B−A−B copolymers, as compatibilizers can result in smaller domains. Figure 2 shows that for a fixed 900 Monte Carlo steps the domain size of the dispersed phase decreases as $\phi_{\mathrm{copolymer}}$ increases. Once again, triblock copolymers as

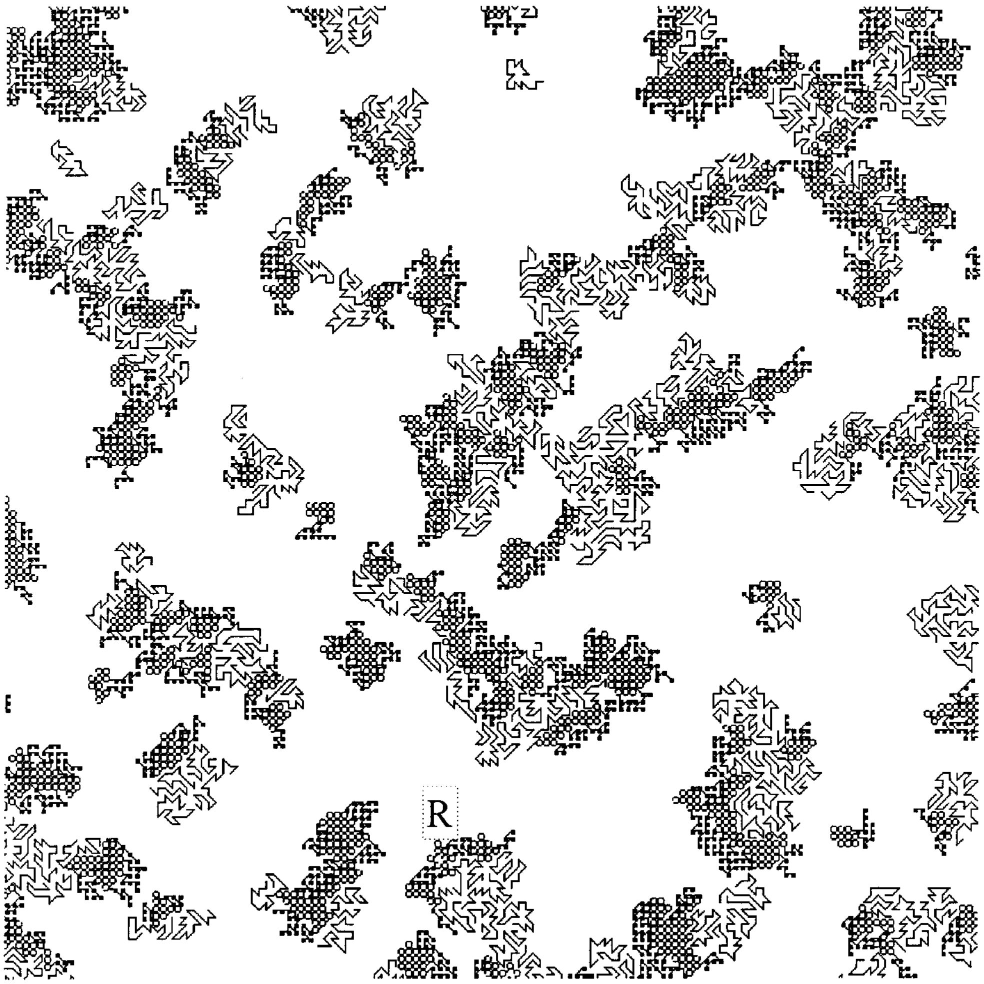

Figure 5. Typical configuration pattern of a A/B/B−A−B ternary polymer blends after 900 Monte Carlo steps, where $\phi_{\mathrm{B-A-B}} = 0.20$. −, ○, and ■ represent homopolymer A, A-block, and B-block of the copolymer, respectively, and the white color represents homopolymer B.

compatibilizers are more efficient than diblock copolymers although they have the same amounts of A and B. Figure 3 directly shows the domain size of the dispersed phase A. Using the B−A−B triblock copolymer as a compatibilizer leads to the smallest domain size of the dispersed phase A, while using the A−B diblock copolymer as a compatiblizer results in the largest domain size of the dispersed phase A.

Figure 4 shows that when the A−B diblock copolymer is used as a compatibilizer, the A block (○) stays at the surface of the dispersed phase, while the B block (■) is absorbed in the matrix phase made of B. The formation of such a diblock copolymer layer prevents the aggregation of two dispersed phases. In Figure 4, there was nearly no contact between the B block of the copolymer and the surface of the dispersed phase A. Figure 5 shows that some B−A−B triblock copolymer chains tend to lay on the surface of the dispersed phase made of A; namely, the whole triblock copolymer chain instead of only the A-block is adsorbed on the surface. In comparison with the A−B diblock copolymer, each B−A−B triblock copolymer chain can cover a larger surface area, or in the other words, the B−A−B triblock copolymer as a compatibilizer is more efficient. On the other hand, due to its special structure, some of the B−A−B triblock copolymer chains tend to form the interchain association on the interface, indicated by the letter "R" in Figure 5. The mobility of these linked long chains is so low that the aggregation of the dispersed phases is slowed down.

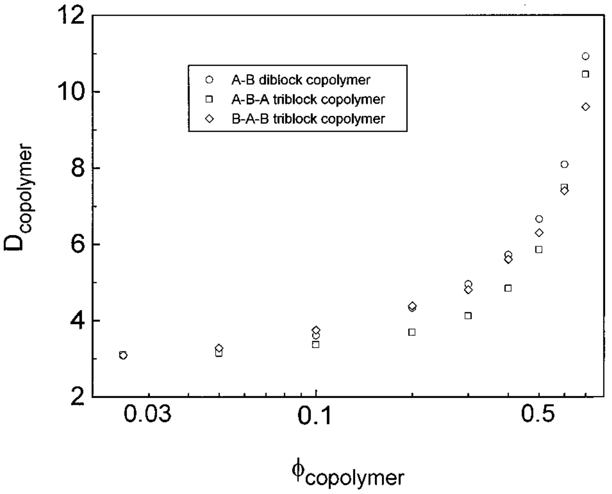

Figure 6. Copolymer volume fraction dependence of the domain size of the copolymer phases after 900 Monte Carlo steps.

Figures 4 and 5 also reveal that copolymers can form a layer at the surface of the dispersed phase. Figure 6 shows the copolymer volume fraction ($\phi_{\mathrm{copolymer}}$) dependence of the domain size ($D_{\mathrm{copolymer}}$) of the block copolymer phase, where $D_{\mathrm{copolymer}} = N/N_{\mathrm{co}}$, with N_{co} being the number of the copolymer phase on the line drawn parallel to the borderline. There are no big differences

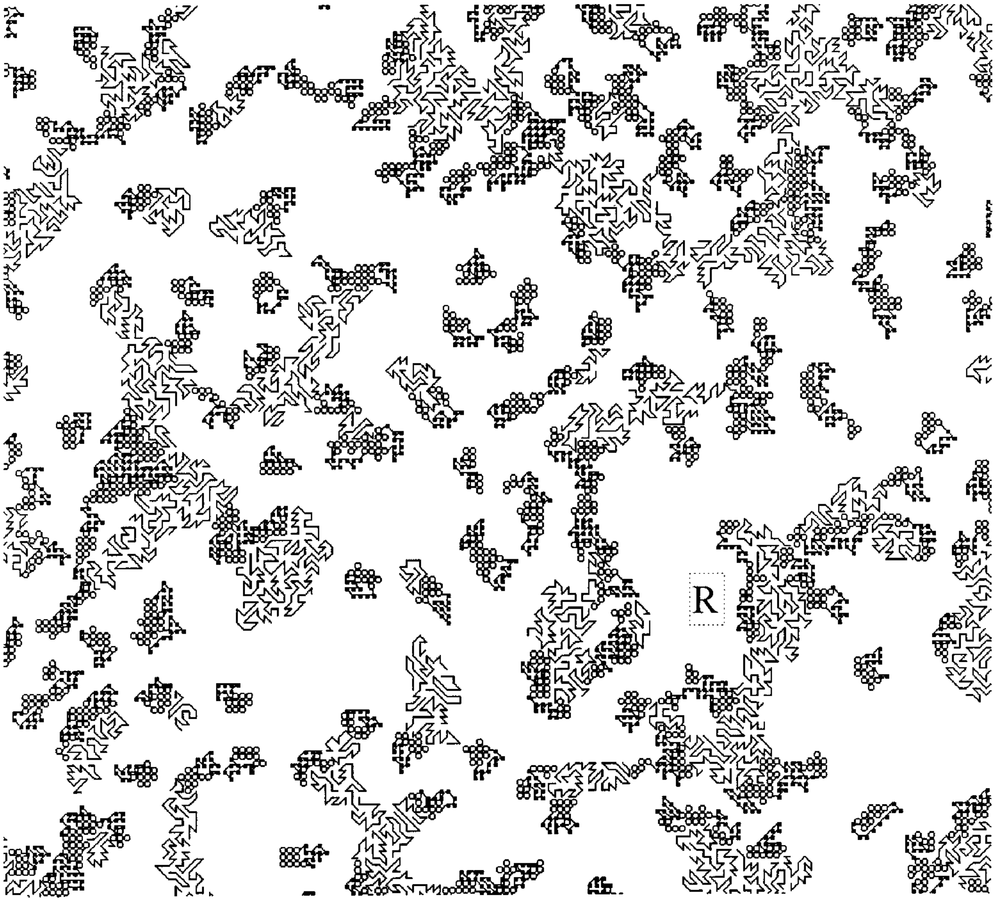

Figure 7. Typical configuration pattern of a A/B/A−B−A ternary polymer blends after 900 Monte Carlo steps, where $\phi_{A-B-A} = 0.20$. −, ○, and ■ represent homopolymer A, A-block, and B-block of the copolymer, respectively, and the white color represents homopolymer B.

among three curves despite that the B−A−B triblock copolymer is a more efficient compatibilizer. A combination of Figures 4 and 5 shows that most of the B−A−B triblock copolymer chains aggregate in a way similar to that of A−B diblock copolymer chains. However, a small number of the interchain association B−A−B triblock chains can prevent further aggregation of two dispersed phases.

Next, let us examine why B−A−B as a compatibilzer is more efficient than A−B−A. Figure 6 shows that the B−A−B triblock copolymer chains can form larger micelles than the A−B−A triblock copolymer chains. On the other hand, a comparison of Figures 5 and 7 shows that most of B−A−B chains are at the interface; even the micelles are formed at the interface. In contrast, some of the A−B−A micelles are in the matrix phase, which have no contribution in the stabilization of the dispersed phase. This is why B−A−B as a compatibilizer is more efficient than A−B−A in the A/B/copolymer ternary blends.

Conclusion

Our simulations lead to an insight of the compatibilization of A−B−A and B−A−B triblock copolymers in the A/B/copolymer ternary blends. Direct observation of the configuration of the block copolymer chains, morphologies of the dispersed phase, and the matrix phase reveals that the copolymer chains have a tendency to stay on the surface of the dispersed phase, and some of the copolymer chains can form an interchain association at the interface. This is why triblock copolymers as a compatibilizer are more efficient than diblock copolymers. If the dispersed phase is made of A, more A−B−A triblock copolymer chains tend to form micelles in the matrix phase because of the intrachain association of the two A blocks which have no contribution in the stabilization of the dispersed phase. This is why B−A−B triblock copolymers are better compatibilizers. Certainly, if the dispersed phase is made of B, A−B−A triblock copolymers will become better compatibilizers.

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