Influence of block lengths and symmetries of block copolymers on phase behavior of polymer A/polymer B/block copolymer ternary blends

Bing Dai[a], Mo Song[b], Douglas J. Hourston[b], Xuehao He[a], Haojun Liang[a,*], Caiyuan Pan[a]

[a]*Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*
[b]*Institute of Polymer Technology and Material Engineering Loughborogh University, Loughborough LE11 3TU, UK*

Abstract

Monte Carlo simulations were used to investigate the compatibilizing effects of diblock copolymers in A/B/A−B diblock copolymer ternary blends and triblock copolymers in A/B/triblock copolymer ternary blends, respectively. The volume fraction of homopolymer A was 19% and was the dispersed phase. The simulation results show that diblock copolymers with longer A-blocks are more efficient as compatibilizers, and symmetric triblock copolymers with a shorter middle block length are easily able to bridge each other through the association of the end blocks. This kind of triblock copolymers have relatively high ability to retard phase separation as compatibilizers.
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1. Introduction

Incompatible polymer blends usually exhibit poor mechanical properties because of weak interactions at the interfaces between phases. Efforts to improve the compatibility of incompatible polymer blends are still widely encountered. One of the very successful methods is to add a few percent of a block copolymer, in which one block is miscible with polymer A, while the other block is miscible with polymer B. It has been demonstrated experimentally and theoretically that the copolymer chains are located at the interface and act as a compatibilizer [1–5]. Considerable effort had been devoted in recent years to understand the performance of block copolymers in such blends. Noolandi et al. [6–9] proposed a statistical thermodynamic theory to describe copolymer emulsification in an A/B/A−B ternary melt blend. Laradji et al. [10] investigated the phase separation of binary mixtures containing surfactants by means of a time-dependent Ginzburg–Landau model. Jo et al. [11–13] has recently carried out detail studies on the phase separation dynamics of polymer blends in the presence of diblock copolymers. They concluded that the rate of the phase separation process is significantly suppressed by the addition of block copolymers because of the reduction of the interfacial tension. This retardation effect is very dependent on the chain lengths of the block copolymer and on the interaction energies between the copolymer blocks and their corresponding homopolymers. Our earlier simulation [14] showed that the diblock copolymer chains concentrated at the interfaces acting as a compatibilizer in such A/B/copolymer ternary blends. Below the critical copolymer concentration, the domain size of the dispersed phase decreased linearly with increasing copolymer concentration. When homopolymer A is the dispersed phase in such blends, B−A−B type triblock copolymers are more efficient compatibilizers than A−B−A and A−B type copolymers [15]. In our previous simulation, the block copolymers were chosen to have A and B blocks of equal length. However, it is very difficult, if not impossible, to synthesis such idealized copolymers. How diblock copolymers with different block lengths influence on compatibilization performance is still unknown. In this paper, we have studied the aggregation behavior of A−B diblock copolymers with different block lengths, and their ability to act as compatibilizers. Simulation results should provide useful information for the design of more efficient diblock copolymers for compatibilization. Meanwhile, we also extend our study to the efficiency of triblock

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* Corresponding author. Tel.: +86-5513607824; fax: +86-5513601592.
 E-mail addresses: hjliang@ustc.edu.cn (H. Liang).

copolymers as compatibilizers. Both the composition and the asymmetry of triblock copolymers will be investigated.

2. 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. [16,17] showed that there is no essential difference in the phase behavior between a two- and a 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 of 0.95, so that it could be regarded as being in the bulk state. The remaining 0.05 unfilled space is handled as free volume. A standard periodic boundary condition was imposed on the lattice to mimic an infinite-size system [18]. Considering that the polymer concentration is high, we adopted the 'single-site bond fluctuation' model proposed by Larson et al. [19,20] and Carmesin et al. [21] and the 'vacancy diffusion' algorithm suggested by Lu et al. [22] to improve the Monte Carlo simulation efficiency. A schematic of the model and the corresponding micro-relaxation modes can be found elsewhere [23]. The evolution of the chain configuration in the simulation was achieved by the random displacement of single vacancy site to its one of 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. If one attempted move violates either the excluded volume or the bond length restriction, it is rejected. The acceptance or rejection of one attempted move which satisfies both the excluded volume and the bond length conditions is further governed by the Metropolis rule [24]. Namely, it is accepted if the energy change, $\Delta E = (N_{AB}^n - N_{AB}^0)\varepsilon$, is negative. Otherwise, it is accepted with a probability of $p = \exp(-\Delta E/kT)$, where N_{AB}^n and N_{AB}^0, respectively, are the numbers of the nearest-neighboring pairs of sites taken by the pair of beads (or segments) after and before the attempted move. ε is the interaction energy gained when two different kinds of repeat units occupy two neighboring lattice sites. The negative and positive $\bar{\varepsilon} = \varepsilon/kT$, respectively, correspond to a homogeneous and a heterogeneous state.

In the simulation, we first let $\bar{\varepsilon} = -1$. After a long Monte Carlo time, the system reaches a completely compatible state. Then let $\bar{\varepsilon} = 1$, so that the change of domain structures in the phase separation process can be observed.

3. Results and discussion

In all simulations, each polymer chain has 20 segments.

The volume fraction, ϕ_a, of homopolymer A, the dispersed phase, was fixed at 0.19. The sum of the volume fractions of homopolymer B and diblock copolymer or triblock copolymer was 0.76. First, for A/B/diblock copolymer ternary blends in order to investigate the influence of the block length on the behavior of a diblock copolymer in blends during the phase separation, the A-block was varied from 1 to 19 segments, namely, 19–1, 18–2,…2–18, 1–19. Fig. 1 shows that the domain size of the dispersed phase increases with the number of Monte Carlo steps during phase separation for three different A block lengths. The domain size (D_A) is defined as N/N_d, where N and N_d are the lattice numbers and the dispersed phase numbers on the lines drawn parallel to the borderline. For great clarity, the domain sizes of the dispersed phase A and the diblock copolymer phase, D_A and $D_{copolymer}$, after 1800 Monte Carlo steps as a function of A-block length at 15% volume concentration of diblock copolymer are plotted in Fig. 2. From this figure, it is clear that when the length of the A-block is 1 segment, the domain size of dispersed phase is much bigger, but the domain size of diblock copolymer phase is smaller than that for the other diblock copolymers (Fig. 2). After careful analysis of the distribution of diblock copolymer chains in the ternary blend (Fig. 3(a)), we found that a number of diblock copolymers did not concentrate at interfaces, but instead, they were dissolved into the matrix phase, so did not contribute to the compatibilization of the blend. This is most probably because the sum of the attractive interaction force on B-blocks by the matrix phase is much stronger than that on A-blocks by the dispersed phase due to the much longer B-blocks. When the A-block contains 2 segments, the attractive interaction forces on A-blocks executed by the dispersed phase is strong enough so that most of the diblock copolymers concentrate at the interface (Fig. 3(b)), which results in a sudden reduction in the domain size of the dispersed phase. The sudden increase of domain size of the diblock phase occurs because of the aggregation of the diblock copolymer at the interface. As
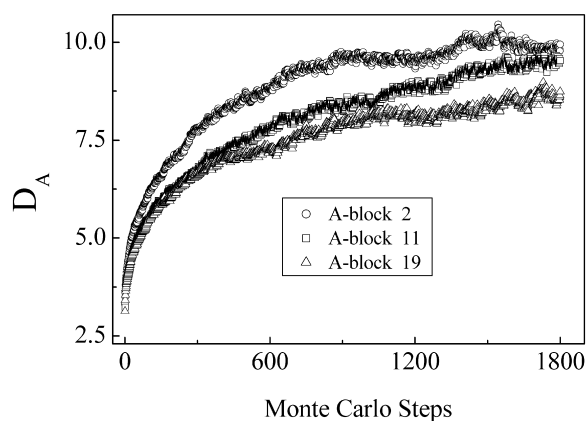

Fig. 1. Monte Carlo steps dependence of the domain size (D_A) of dispersed phase for diblock copolymers with different A-block length, where the dispersed phase concentration and the block copolymer concentration were kept at 0.19 and 0.15, respectively.
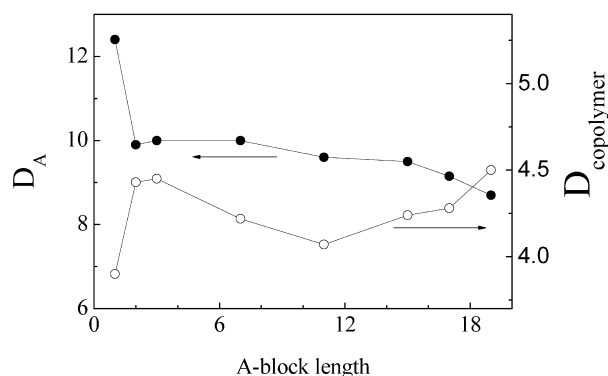
Fig. 2. A-block length of diblock copolymer dependence of domain sizes of dispersed phase and copolymer phase, D_A and $D_{copolymer}$ after 1800 Monte Carlo steps.

shown in Fig. 2, the symmetrical diblock copolymer tends to form the smallest domains ($D_{copolymer}$). However, the asymmetrical diblock copolymers prefer to aggregate into larger domains, as can be directly observed in Fig. 3(b)–(d). The symmetrical diblock copolymers distribute uniformly on the interface, resulting in a smaller domain size (Fig.

3(c)). The asymmetrical diblock copolymers tend to self-aggregate at the interfaces (Fig. 3(b) and (d)), leading to relatively large domain sizes.

As seen in Fig. 1, the longer A-block diblock copolymers lead to smaller dispersed phases. Therefore, they are more efficient in reducing phase separation rate of polymer blends. Again, the A-block length dependence of the dispersed phase domain size after 1800 Monte Carlo steps (Fig. 2) showed that the longer A-block copolymers result in somewhat smaller domain sizes. In other word, they are more efficient as compatibilizers. This can be further verified in Fig. 4. According to Noolandi's theories [1–4, 6–9], the domain size of the dispersed phase decreases linearly with the concentration of diblock copolymer below its critical micelle concentration (CMC). From the results shown in Fig. 4, it is believed that the diblock copolymers with a 19-segment A-block have low CMC value, and the diblock copolymers with 3 and 11 A block segments have higher CMCs. So, it is clear that the diblock copolymer with 19 A-block segments is the most efficient compatibilizer. This is most probably because a diblock copolymer chain with long A-blocks has a larger contact area on the dispersed
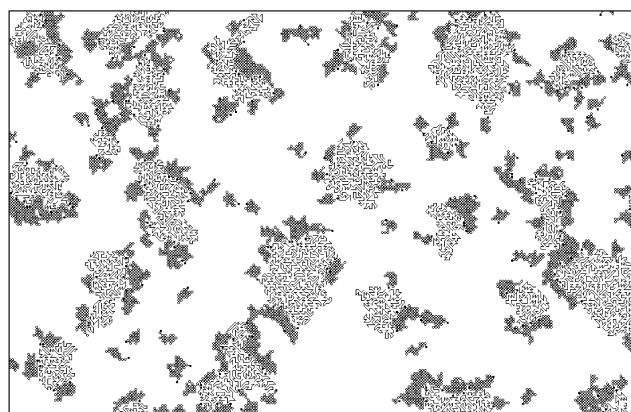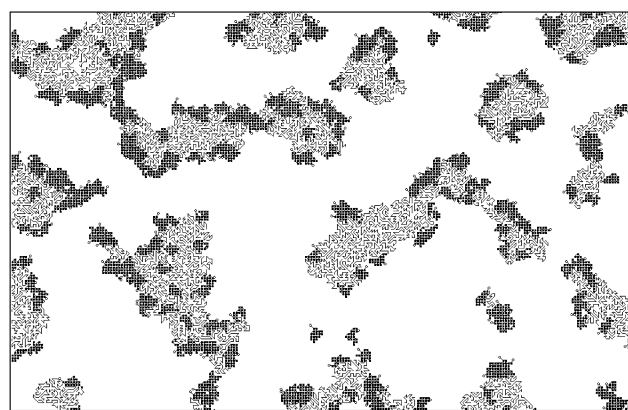

(a)
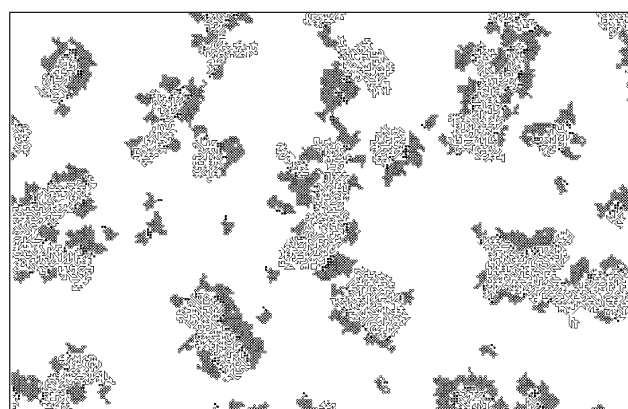
(b)
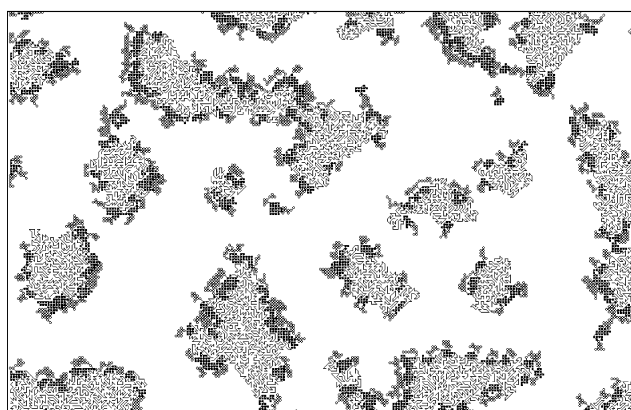
(c)

(d)

Fig. 3. Typical configuration pattern of A/B/A−B ternary polymer blends after 1800 Monte Carlo steps. Where the dispersed phase concentration and the block copolymer concentration were kept at 0.19 and 0.15, respectively. —, ■, ○ represent homopolymer A, A-block, and B-block of the copolymer, respectively, and white color represent homopolymer B. (a) A−B (1−19); (b) A−B (2−18); (c) A−B (11−9); (d) A−B (19−1).
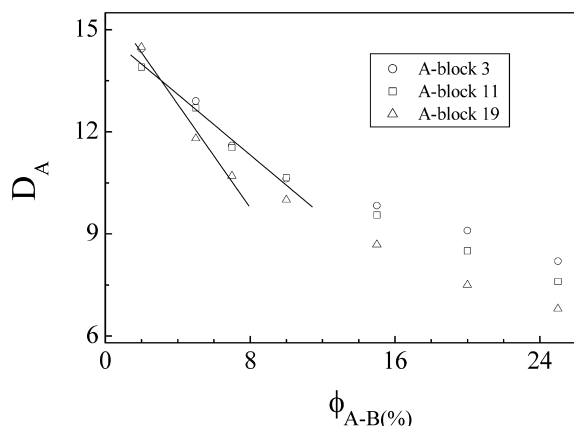
Fig. 4. Block copolymer volume fractions dependence of domain size (D_A) of dispersed phase for diblock copolymers with different A-block length after 1800 Monte Carlo steps.

phase surface, i.e. it occupies more area at the interface, which results in a relatively low CMC.

For A/B/triblock copolymer ternary melt blends, the volume fractions of homopolymer A, the dispersed phase, and triblock copolymer were fixed at 0.19 and 0.10, respectively. The influence of triblock copolymer architecture on the phase behavior of A/B/triblock copolymer ternary blend was investigated through the adjustment of the block length and the asymmetry of the triblock copolymer. The block length of the triblock copolymer was adjusted by changing the end block length (A and B block in A−B−A and B−A−B block copolymer, respectively) from 1 to 9, namely; 1−18−1, 2−16−2…9−2−9. For triblock copolymers with a fixed 10-segment middle block, the asymmetry was gained by redistributing the two end block lengths, i.e. one end block changed from 1 to 5 segments, accordingly, the other was changed from 9 to 5 segments. Namely; 1−10−9, 2−10−8,…5−10−5.

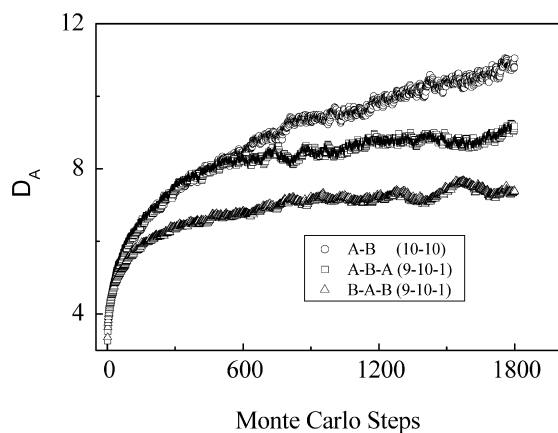First, an example of how the block copolymer architecture affects the phase behavior of blend is provided. Fig.

Fig. 5. Monte Carlo steps dependence of the domain size (D_A) of dispersed phase for different kind of block copolymers, where the dispersed phase concentration and the block copolymer concentration were kept at 0.19 and 0.10, respectively.

5 shows that the domain size (D_A) of the dispersed phase increases with the number of Monte Carlo steps during phase separation. It approaches a plateau after 900 Monte Carlo steps for different kinds of copolymers, indicating the system has reached its equilibrium state after this number of steps. The triblock copolymers A−B−A (1−10−9) and B−A−B (1−10−9) can be regarded as tiny modification of the 10−10 diblock copolymer, e.g. remove one A-segment from the A-block of diblock copolymer chain to the other end, then the A−B−A (1−10−9) triblock copolymer chain is obtained. The domain size of dispersed phase after 1800 Monte Carlo steps are 7.37, 9.17 and 11.05 with B−A−B (1−10−9), A−B−A (1−10−9) and A−B (10−10) copolymers are, respectively, used as compatibilizer (Fig. 5), indicating that these tiny modifications significantly influence their phase separation retardation ability. Still, the B−A−B is best compatibilizer as we have pointed out in our previous study [15].

Fig. 6 shows that the domain size (D_A) of the dispersed phase is very much dependent on the relative block lengths of the triblock copolymer. The domain size of the dispersed phase remains lower value when the middle block length is shorter than 8 segments for both A−B−A and B−A−B triblock copolymers, but it starts to increase after the middle block length is longer than 8 segments. This evidence shows that triblock copolymer with a somewhat shorter middle block, or longer end block, has a relatively high ability of retardation to phase separation of the blend. Further evidence can be directly obtained from Fig. 7. Again, the B−A−B (7−6−7) triblock copolymer leads to the smallest domain size of the dispersed phase (Fig. 7(b)), whereas, A−B−A (1−18−1) triblock copolymer leads to the largest domain size of dispersed phase (Fig. 7(c)). In A/B/triblock copolymer melt blends, the retardation of phase separation is realized by triblock copolymer on which different blocks melting into different phase domains are connected by covalent bonds and constrain the movement of phase interface. The longer middle block, the weaker association of joint points in a triblock copolymer chain for phase interface and the phase interface move more easily. As a result, the
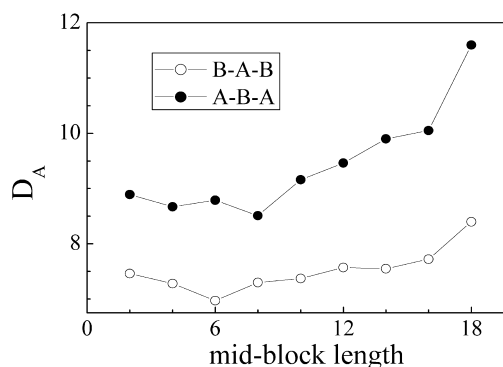

Fig. 6. Middle block length of triblock copolymer dependence of domain size (D_A) of dispersed phase after 1800 Monte Carlo steps.
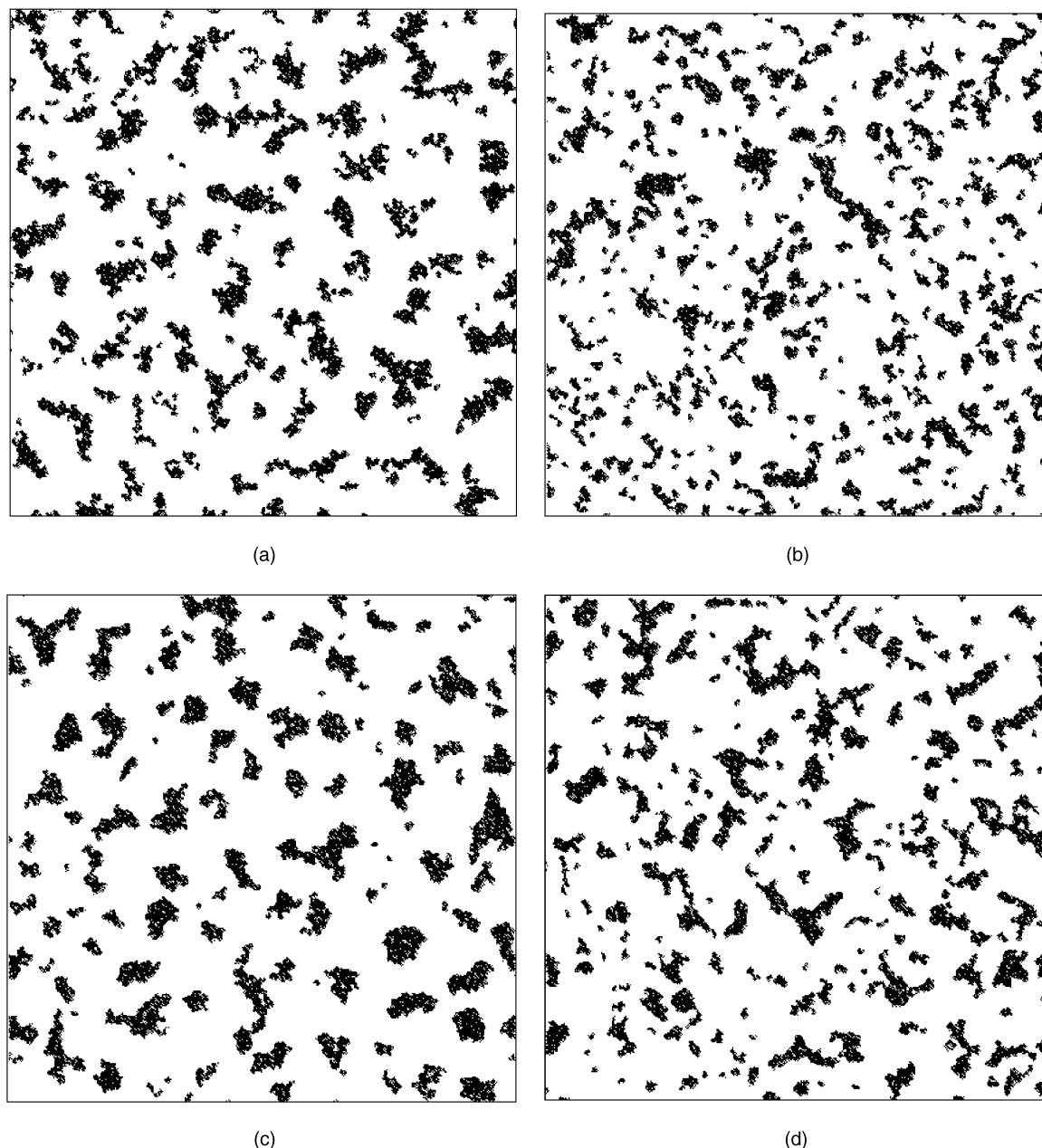
Fig. 7. Domain pattern after 1800 Monte Carlo steps for different triblock copolymer as compatibilizer. (a) B−A−B (1−18−1); (b) B−A−B (7−6−7); (c) A−B−A (1−18−1); (d) A−B−A (6−8−6).

phases separate more quickly and the disperse phase domains are more sphere-like. From Fig. 7, the dispersed phase with the longer middle block length compatibilizer has a sphere-like structure (Fig. 7(a) and (c)). However, the one with the shorter middle block length prefers to form into somewhat irregular stretched phase morphologies (Fig. 7(b) and (d)).

It is believed that the triblock copolymer architecture is related to the performance of triblock copolymer chains in blends. The fraction of triblock copolymer chain at the interface and associated behavior of triblock copolymers, themselves will directly influence its efficacy to retard phase separation. Keeping this in mind, our following analysis will

concentrate on the influence of the above points on the behavior of polymer blends.

Fig. 8 shows that not all the triblock copolymer chains will concentrate at the interface, as some of them distribute into the matrix phase. The fractions of B−A−B and A−B−A triblock copolymer at interface are 76−85 and 65−75%, respectively, depending on the special structures of triblock copolymer. In comparison the B−A−B triblock copolymers, less A−B−A triblock copolymer prefers to concentrate at the interface. Most probably, this is the main reason why A−B−A triblock copolymers are not so effective as B−A−B triblock copolymers, because copolymers not located at the interface will not contribute to the retardation of phase
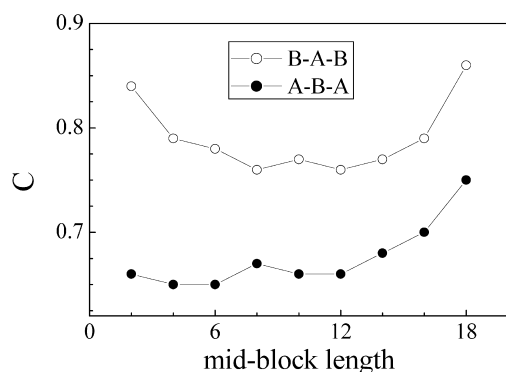
Fig. 8. Middle block length of different triblock copolymer dependence of percentage (C = number of block copolymer on interface/number of total block copolymer in the blend) of triblock copolymer on interface.

Fig. 9. Middle block length of different triblock copolymer dependence of domain size ($D_{copolymer}$) of triblock copolymer.

separation. In another word, more copolymers distributed at the interface, the stronger retardation to phase separation and this kind of block copolymer should be more effective as compatibilizer.

In general, it seems reasonable that the triblock copolymer with more A segments in the chain will prefer to concentrate at the interface because of its stronger attractive force with the dispersed phase which consists of polymer A. However, to our surprise, the A−B−A triblock copolymer chains with longer B block length, i.e. shorter A block length, prefer to concentrate at the interface. As indicated in Fig. 8, when the B-block length is shorter than 12 segments, about 65% of the block copolymer chains are at the interface. However, when longer than 12 segments, more block copolymer chains start to stay at the interface and 75% of A−B−A triblock copolymer concentrate on the interface when B block length are 18 segments, i.e. only one A segment at each end of the chain. Due to the relaxation of polymer chains, the two end blocks of triblock copolymer with longer middle block reach the boundary of phase domain more easily, i.e. stay at the interface. On the other hand, the performance of the B−A−B triblock copolymer at the interface is very different from that of A−B−A triblock copolymer. The B−A−B triblock copolymers with comparable components of A and B segment on the chain, e.g. A block lengths are 8, 10 and 12 segments, do not like to stay at the interface, but the ones with much less or more A segments, e.g. A block length with 18 and 2 segments, more strongly like to stay on the interface.

Fig. 9 shows that the domain size for block copolymers, $D_{coplymer}$, as a function of the middle block length. Both types of block copolymer with shorter middle blocks tend to aggregate into large domain sizes, i.e. these types of copolymer chain are easily self-aggregation, which can also be directly observed in Fig. 10. This is because the longer end blocks (triblock copolymer with shorter middle block length) easily entangle or associate to bridge each other to form the bigger domains. From Fig. 6, the triblock copolymer with shorter middle block length led to smaller dispersed phase domain sizes. Comparing Fig. 6 with Fig. 9,
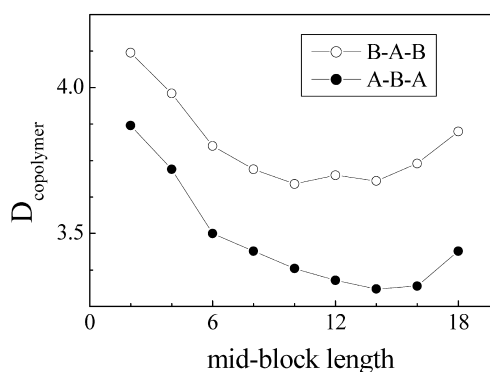
it is concluded that these associated shorter middle block length block copolymers have high contribution to stop the phase separation process. The reason is that the associated triblock copolymer chains form high-molecule-like chains, which should be difficult to move and have a high ability to prevent dispersed phase domains coagulating. Jo [11–13] also indicated that high molecular weight block copolymers have a marked ability to stop phase separation.

As seen in Fig. 10, almost all copolymer chains are either at interfaces or in matrix phase. Hence, the number of copolymer segments connected with the dispersed phase is supposed to be equal to the areas of dispersed phase covered by copolymer. Fig. 11 shows that the total number (S) of segments of triblock copolymers connected with dispersed phase (polymer A), depend on the composition of the triblock copolymer, i.e. the triblock copolymers with longer A-blocks prefer to occupy more area at the interface. This is because that the triblock copolymer chain with longer A-block has relatively stronger attractive force with the dispersed phase. Once they are on the interface (some of copolymers distribute in the matrix), more segments on the triblock copolymer chain will more easily be connected with dispersed phase. As recognized, the block copolymers occupying more interfacial areas should become effective compatibilizers. Combining Figs. 6 and 11, the A−B−A triblock copolymers with longer A-blocks can occupy more interfaces and such result in small domain size of the dispersed phase, However, for the case of B−A−B triblock copolymer, although the interfacial areas occupied by the triblock copolymer with longer A-block copolymer are larger, the domain size of dispersed phase is still larger. The detailed analysis shows that the self-association ability of A−B−A triblock copolymers is weak, i.e. as shown in Figs. 9, 10(c) and (d), seldom A−B−A triblock copolymer associate each other, which leads to smaller block copolymer domain sizes. In this case, the contribution of A−B−A triblock copolymer to the compatibility of the blends mainly depends on its capability to occupy the interfacial areas. However, B−A−B triblock copolymers are easily bridged to each other through end block association (Fig. 10(b)). So the contribution of B−A−B
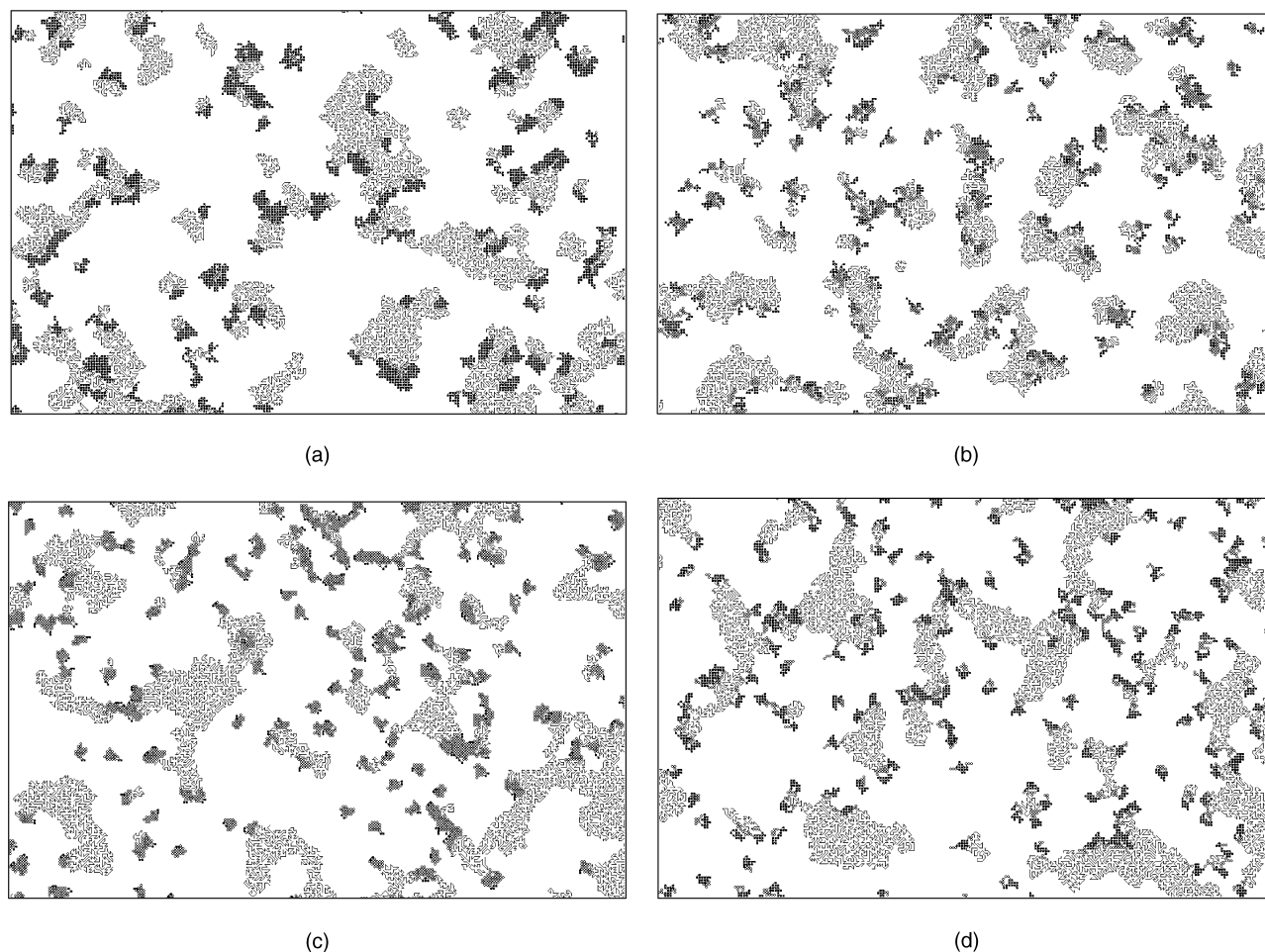
Fig. 10. Typical configuration pattern of A/B/(triblock copolymer) ternary polymer blends after 1800 Monte Carlo steps. Where —, □, ○ represent homopolymer A, B-block and A-block of the copolymer, respectively, and white color represent homopolymer B. (a) B−A−B (9−2−9); (b) B−A−B (5−10−5); (c) A−B−A (9−2−9); (d) A−B−A (3−14−3).

triblock copolymers to the compatibility of the blends depends not only on their capability to occupy the interfacial areas, but also to the ability of B−A−B triblock copolymer self-association. These bridged copolymers have a relatively high ability to stop phase separation of blends because of its hard in moving. When the A-block length (middle block) becomes longer, the end B-block become shorter, the

Fig. 11. Middle block length of different triblock copolymer dependence of number (S) of segments connected with dispersed phase.

numbers of bridged copolymers reduces. This will result in larger domain sizes of dispersed phase.

The above studies were concentrated on the cases of triblock copolymer with equal end block length. However, it is hard, if not possible, to synthesize such an idealized copolymer chain in chemistry. It is necessary to study how the asymmetry of triblock copolymer influent on its capability as compatibilizer. The composition of block copolymers here is fixed to be 50/50 segments/segments i.e. 10 A and 10 B segments on each chain. The middle block length is kept to be10 segments. The one end block length are changed from 1 to 5 segments, as a result, the other end block length will be 9 to 5 segments, namely, 1−10−9, 2−10−8…5−10−5. Fig. 12 shows that except that A−B−A and B−A−B triblock copolymer of 1−10−9 results in the bigger domain size of dispersed phase, others, such as 2−10−8 to 5−10−5, lead to the similar domain size of dispersed phase. The discussion in above section indicates that the bridge of triblock copolymer through the end block leads to the more efficient compatibilizer. The attractive force between these extremely short blocks and other block is so weak that it is not strength enough to form the steady
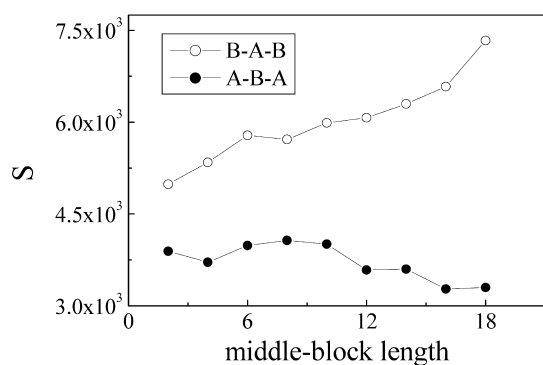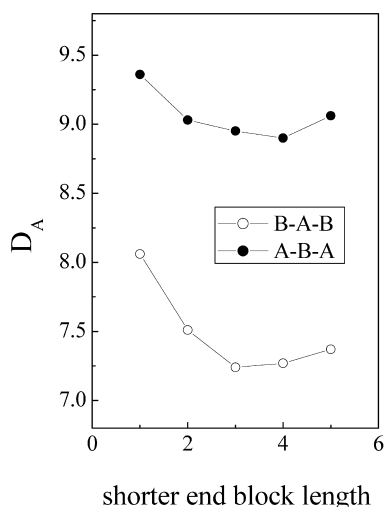
Fig. 12. Shorter end block length of different triblock copolymer dependence of domain size (D_A) of dispersed phase.

bridged copolymer. On the other hand, the architecture of $1-10-9$ triblock copolymer is more similar to that of $10-10$ diblock copolymer in comparison with the other kinds copolymer, such as $2-10-8$ to $5-10-5$ triblock copolymers. It was approved that diblock copolymer is not so effective as that of triblock copolymer when used as compatibilizer [15]. After the length of shorter end block increase to 2 segments in our simulation, the bridged copolymer are formed and the efficiency as compatibilizer is similar for $2-10-8$ to $5-10-5$ triblock copolymer.

4. Conclusions

These computer simulations have lead to an insight into the influence of the block lengths and asymmetries of diblock copolymers in A/B/A−B diblock copolymer ternary blends, and A−B−A and B−A−B triblock copolymers in A/B/triblock copolymer ternary blends. A direct observation of the morphology of the dispersed phase and the configuration of the block copolymer chains reveals that the symmetrical diblock copolymers tend to distribute uniformly at the interface. The asymmetrical diblock copolymers prefer to aggregate into somewhat larger domain sizes at the interface. The diblock copolymer with longer A-blocks results in a lower CMC because of their ability to occupy more interfacial area, which results in a relatively smaller dispersed phase. It is, therefore, concluded that diblock copolymers with longer A-blocks are more efficient as compatibilizers. For A/B/triblock copolymer ternary melt blends, The B−A−B triblock copolymer is better compatibilizer in compare with A−B−A triblock copolymer for

blend with polymer A as dispersed phase. The symmetrical triblock copolymers with shorter middle block length tend to form bridge each other with the association of the longer end block. These bridged copolymers are not easy to move in the blends. So for the blends with fixed percentage of dispersed phase, matrix phase and copolymer, the triblock copolymers with shorter middle block length are more efficient in retardation of phase separation. The asymmetrical triblock copolymer with one of very shorter block is not a good compatibilizer.

Acknowledgements

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