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The effects of copolymer architecture on phase separation dynamics of immiscible homopolymer blends in the presence of copolymer: a Monte Carlo simulation

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Abstract

The effects of copolymer architecture on phase separation dynamics of an immiscible binary blend A/B in the presence of copolymer were investigated by Monte Carlo simulation. Five types of copolymers, with each having the same composition ($f = 0.5$) but different sequence distribution, are used for simulation. The sequence distribution is varied from the symmetric diblock copolymer to the alternating copolymer. It is found that the rate of phase separation is significantly suppressed by the addition of copolymer due to the reduction of interfacial tension. This retardation effect is considerably dependent on the sequence distribution of the copolymer and such an effect is more pronounced when the block copolymer is added. It is also found that the longer the chain length of copolymer, the better such a retardation effect. When the chain extension of copolymer at the interface is examined, the block copolymer chains are extended to each corresponding homopolymer phase across the interface, whereas the alternating copolymers lie on the interface and the random copolymers weave back and forth across the interface. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Copolymer architecture; Phase separation dynamics; Monte Carlo simulation

1. Introduction

It has been known that most polymer pairs are immiscible due to the low entropy gain upon mixing [1]. For immiscible polymer blends, coarse phase dispersion and poor adhesion between the phases are limiting factors in their applications. Since it has been recognized that block copolymers could reduce the interfacial tension between homopolymers and retard the phase separation, the block copolymer has often been used as a compatibilizer for such phase-separated polymer blends. This interfacial activity of block copolymers is attributed to their preferential location at the interface and extension of each block into the homopolymer phase with which its energetic interactions are favorable [2–6]. However, block copolymers have some disadvantages in being used as an interfacial agent: they are relatively difficult to synthesize and have a tendency to form micelles, thereby drastically lowering the ability of segregation to the interfaces [7,8].

Recently, random copolymers have been suggested as a good alternative to block copolymers since they can be produced economically and provide a great extent of design flexibility [9,10]. A few theoretical studies [11–14] have been reported on the miscibility behavior of blends containing random copolymers. Roe and coworkers [11] have reported that a random copolymer lowers the cloud point temperature when the copolymer is added to an immiscible polymer blend. Balazs and Demeus [12] calculated a new phase diagram for the ternary mixtures composed of a copolymer and two homopolymers by introducing the triad–triad interaction parameter as a function of sequence distribution in copolymer. They showed that the sequence distribution of the copolymer plays an important role in the phase behavior of ternary mixture and that the block copolymers do not always act as the best thermodynamic compatibilizer for all the blend systems. They also studied the interfacial activity of a random copolymer using the self-consistent mean field method and reported that a desired reduction of interfacial tension can be achieved by adding random copolymers into homopolymer blends [14].

Brown and coworkers [10] reported that styrene–methyl methacrylate random copolymers reinforce the PS/PMMA interface effectively, although the fracture energy in the presence of the random copolymer is lower as compared to the addition of block copolymers. They proposed that

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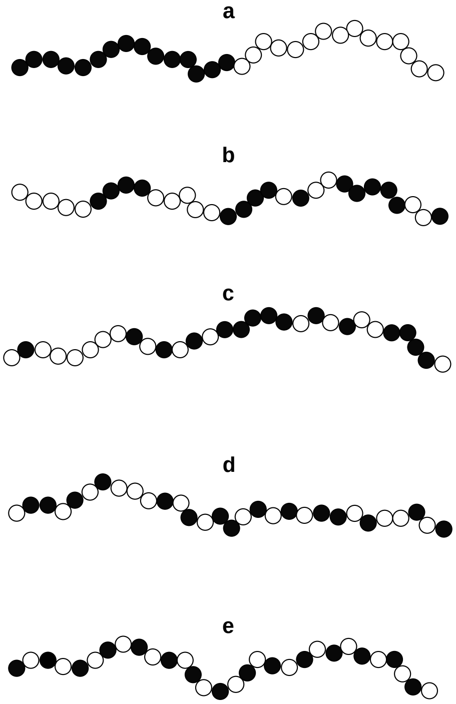

Fig. 1. Typical structures of copolymers with $N_c = 30$: (a) block copolymer ($U = 1$); (b) blocky-random copolymer ($U = 0.5$); (c) random copolymer ($U = 0$); (d) random–alternating copolymer ($U = -0.5$); and (e) alternating copolymer ($U = -1$).

the random copolymer organizes itself so as to make multiple trips across the interface. Subsequently, Kramer and coworkers [9] reported that a long random copolymer is more effective than a short symmetric block copolymer in strengthening the interface between immiscible homopolymers. In contrast to these studies, Dadmun [15] argued that the random copolymers have a relatively weak effect on interfacial strengthening, whereas both the block and the alternating copolymers are promising as interfacial modifiers. These various reports indicate that the compatibilizing activity of the random copolymers is not as clearly understood as that of the block copolymers. Hence, the important question still remains whether the random copolymers play an important role as a compatibilizer for immiscible polymer blends. Moreover, the effect of copolymer architecture on the phase separation dynamics is not systematically studied. In this paper, the copolymer architecture is systematically varied and its effect on the phase separation behavior is examined by the computer simulation method.

2. Model and simulation method

The simulations are performed on a simple cubic lattice of $L \times L \times L$ sites with $L = 50$. Periodic boundary conditions [16] are imposed in the x, y and z directions in order to overcome the finite system size. We first simulate an A/B binary blend system; then five kinds of copolymers with different architecture are added to the A/B binary blend in order to elucidate their architecture effect on the phase separation dynamics. The blend ratio of homopolymer A to B is fixed at 75/25 in all cases, by which dispersed domains can be easily developed from the matrix. The choice of other blend composition, e.g. 50/50, may change the phase separation dynamics due to the difference in the quench depth. However, the effect of copolymer architecture on phase separation dynamics may not be changed regardless of the copolymer composition. Homopolymer chains have the same length, i.e. $N_A = N_B = 10$. By introducing a repulsive interaction energy, ε_{AB}, the phase separation of homopolymers A and B is induced. A pair-wise interaction energy, $\varepsilon_{AB} = 0.5$, is given whenever the non-bonded segments of A and B are nearest neighbors. All other pair-wise interactions are assumed to be zero. The amount of copolymer added to the binary blend is 5.7% of the total sites occupied by all the chain segments. In this work, the total volume fraction of the polymers is fixed at 0.61. The chain length N_c of the copolymer is varied from 12 to 30 in which the fraction of the segments of A is set to be 0.5.

The bond fluctuation model [17] is used to simulate the motion of polymer chains since it reproduces many properties of dense polymer melts. In this model, each segment occupies eight lattice sites of a unit cell and the bond lengths between two successive segments are 2, $\sqrt{5}$, $\sqrt{6}$, 3 or $\sqrt{10}$ in units of lattice spacing. The initial configurations of all the blend models are randomly generated as follows. The first segment of each chain is placed at a randomly chosen lattice site in the cubic lattice, and the chain grows by adding bonds to each chain end in a random direction. After the chains are completely generated in the cubic lattice, the structures are equilibrated with all the interaction energies being set to zero for enough time to reach equilibrium. The simulation for phase separation is then performed by applying the pair-wise interaction energy to the system, and a new configuration space is sampled by the Metropolis sampling method.

A quantitative description of the copolymer architecture can be made by introducing a parameter that allows us to distinguish between the block, random and alternating copolymers. In this work, the uniformity factor, U_A and U_B, which are introduced by Dadmun [15], is used to specify the sequence distribution of copolymers. U_A is defined as:

$$U_A = \frac{\left[\sum_{n=1}^{N-1} s_n\right] + 1}{N_A - 1} \tag{1}$$

where $s_n = 0$ if the nth monomer is type B, $s_n = 1$ if both the nth and the $(n+1)$th monomer are of type A, and $s_n = -1$ if the nth and the $(n+1)$th monomers differ. N_A is the number of A monomers in the copolymer. For the symmetric copolymer used in this work, $U_A = U_B = U$. A block copolymer, a random copolymer and an alternating copolymer are described by $U = 1$, $U = 0$ and $U = -1$,

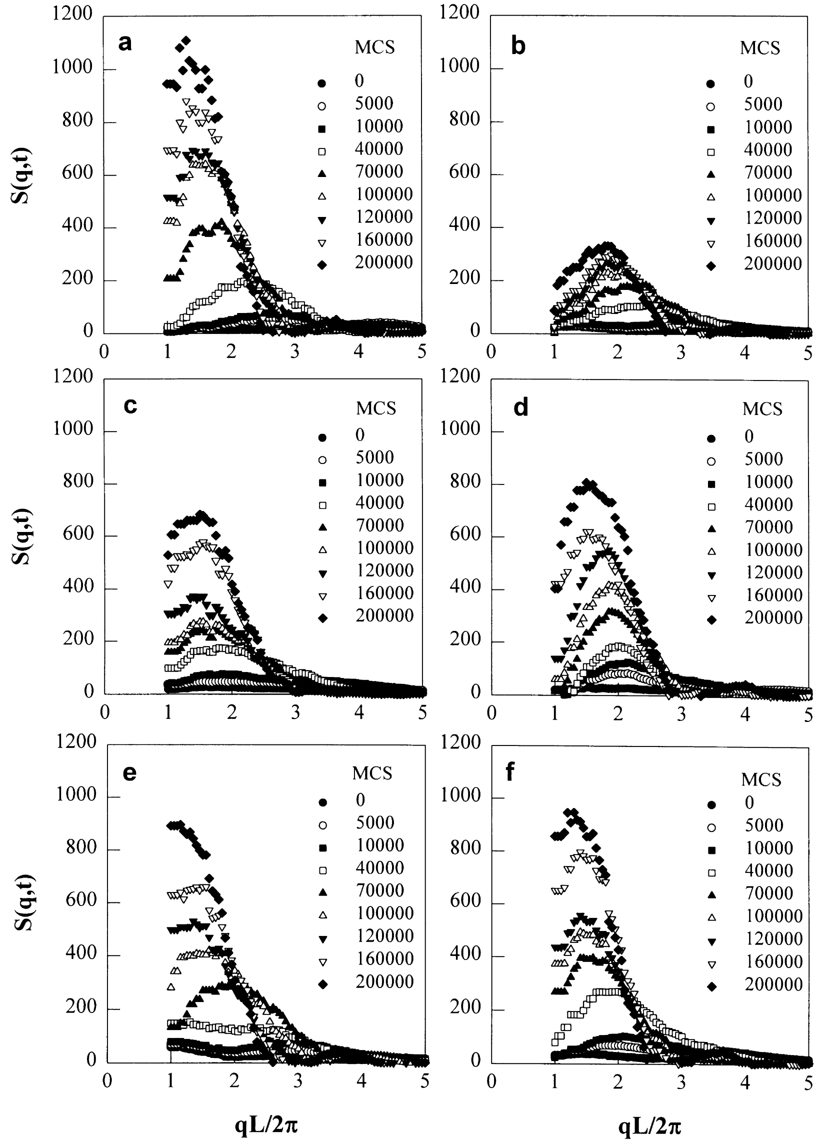

Fig. 2. Time evolution of structure factor during phase separation for: (a) an A/B binary blend and ternary blends of $N_c = 30$ with; (b) block copolymer ($U = 1$); (c) blocky-random copolymer ($U = 0.5$); (d) random copolymer ($U = 0$); (e) random–alternating copolymer ($U = -0.5$); and (f) alternating copolymer ($U = -1$).

respectively. In the same way, the copolymer with $U = 0.5$ represents the blocky-random copolymer, which has an intermediate structure between block and random copolymer, and the copolymer with $U = -0.5$ represents the random–alternating copolymer, i.e. an intermediate structure between random and alternating copolymers. Fig. 1 shows typical structures of the copolymers used in this study.

In order to investigate the time evolution of long-range ordering, the time dependent collective structure factor is calculated and averaged spherically to improve the statistics in q space as described in the previous papers [18–22]. The time dependent collective structure factor is given by:

$$\mathbf{S}(\mathbf{q},t) = \langle \sum \exp(i\mathbf{q}\cdot\mathbf{r})[\phi(\mathbf{r}+\mathbf{r}',t)\phi(\mathbf{r}',t) - \langle\phi\rangle^2]\rangle/L^3 \quad (2)$$

where L is the dimension of the system, the vector $\mathbf{q}$ is defined as $\mathbf{q} = (2\pi/L\ \Delta r)\mathbf{n}$, in which $\mathbf{n}$ represents a positive integer vector, i.e. $\mathbf{n} = (\mathrm{n_x}, \mathrm{n_y}, \mathrm{n_z})$, and $\langle\,\rangle$ denotes an average over the number of runs. This quantity represents the Fourier transform of the pair correlation functions and is spherically averaged as follows:

$$S(q,t) = \sum_{q-(\Delta q/2)\le q\le q+(\Delta q/2)} \mathbf{S}(\mathbf{q},t)/p(\mathbf{q},\Delta q) \quad (3)$$

where

$$p(\mathbf{q},\Delta q) = \sum_{q-(\Delta q/2)\le q\le q+(\Delta q/2)} 1 \quad (4)$$

The quantity defined in Eq. (4) represents the number of lattice points in a spherical shell of radius q with Δq in

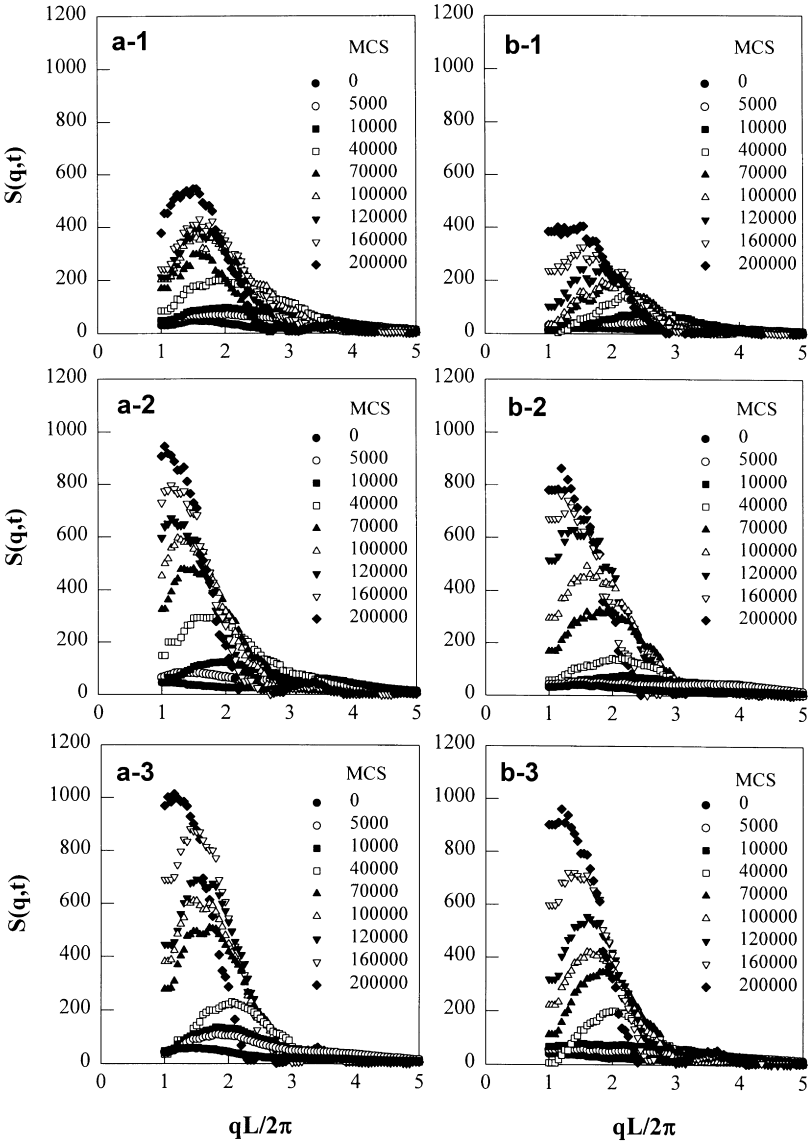

Fig. 3. Time evolution of structure factor during phase separation for ternary blends with: (a) $N_c = 12$;and (b) $N_c = 18$. The numerals 1, 2 and 3 behind (a) and (b) in figure designation denote the block copolymer ($U = 1$), the random copolymer ($U = 0$) and the alternating copolymer ($U = -1$), respectively.

shell thickness. Ideally, one must take Δq to be as small as possible. To save the computing time for $S(q,t)$, Δr is selected as 2 and hence $\Delta q = \pi/L$.

In this study, time is measured in unit of a Monte Carlo step (MCS). One MCS is defined as the time necessary for every segment to attempt to move once on average. All the simulations are run up to 2×10^5 MCS, and five independent runs are averaged to improve the statistics for each case.

3. Results and discussion

Fig. 2 shows the time evolution of structure factor $S(q,t)$ plotted against the scattering vector **q** during phase separation for an A/B binary and five different A/B/A-*co*-B ternary blends with $N_c = 30$. As the phase separation proceeds, the structure factor maximum shifts toward smaller q and the peak intensity increases with the phase separation time for all the blend systems. These features, typically observed in the scattering patterns of real experiment by light scattering, reflect that periodic concentration fluctuations are built up throughout the whole sample space and that small domains are spontaneously formed. When the phase separation of the binary blend is compared with that of the ternary blends (Fig. 2), it is revealed that the rate of phase separation is faster for the binary blend than for the ternary blends containing copolymers. This result clearly indicates that the added copolymers are segregated to the interface between the two homopolymer phases and that they then play the role of compatibilizer. Another feature realized from Fig. 2 is that such a retardation effect on phase separation becomes better as the copolymer reaches a blocky

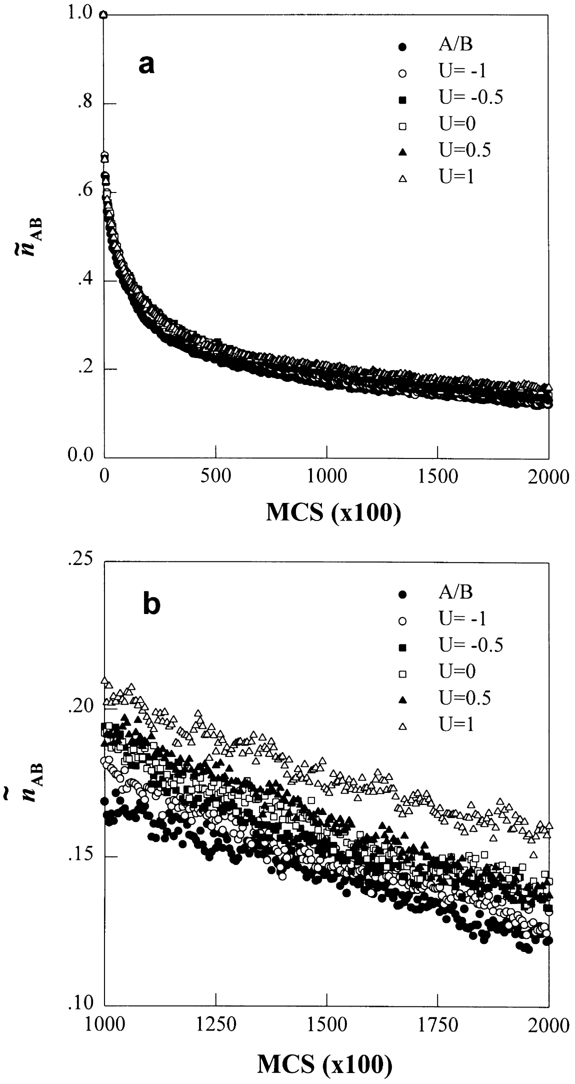

Fig. 4. (a) Change of normalized number $\tilde{n}_{AB}$ of contacts between homopolymer segments A and B during the phase separation for the ternary blends containing copolymers of $N_c = 30$ with different sequence distribution. For closer examination, the scales in the later stage are expanded in (b).

structure, i.e. the block copolymer shows the best retardation efficiency and the alternating copolymer exhibits the worst efficiency, as shown in Fig. 2b–f. In order to investigate the effect of chain length of copolymer on the phase separation dynamics, the time evolution of structure factor is also examined for A/B/A-*co*-B systems with different copolymer chain lengths. As the chain length of the copolymer with the same architecture increases from $N_c =$ 12–18, the growth rate of the phase-separated domains becomes slower, as shown in Fig. 3. From Figs. 2 and 3, it is concluded that the longer the chain length of the copolymer the better the retardation effect.

The process of phase separation is accompanied with a change in the contact number n_{AB} between segments of homopolymer A and B. Therefore, this contact number can be used as another measure of the degree of phase separation. When the contact numbers $\langle n_{AB} \rangle_t$ at time t are normalized by their initial value $\langle n_{AB} \rangle_0$, the normalized contact number, $\tilde{n}_{AB}$, decreases with time for all the blend systems of $N_c = 30$ as the phase separation proceeds, as shown in Fig. 4a. The change of the reduced contact number in the late stage is shown in Fig. 4b, in order to examine more closely the degree of phase separation for each blend. The blends containing the copolymer show higher value of $\tilde{n}_{AB}$ than does the A/B binary blend, indicating that copolymers retard the phase separation. It is also found that the blends containing the block or blocky-random copolymer have higher values of $\tilde{n}_{AB}$. These results are consistent with the results of time evolution of structure factor.

Variations of radius of gyration of the copolymer with $N_c = 30$ in the ternary blends during phase separation are shown in Fig. 5. As expected, the block copolymer chain is more extended than the other copolymers. This means that the block copolymer migrates to the biphasic interface and each block preferentially penetrates into its respective homopolymer phase, resulting in an increase in the linear dimension of the block copolymer. However, for the other copolymers, the chain extension is not so significant because the chains are confined to the interfacial regions due to the repulsive interaction between the copolymer and homopolymers.

The interfacial characteristics in the phase-separated structure can be inferred from the monomer distribution at the interface. Simulations on the interfacial properties usually assume the sharp and stationary interface; otherwise it is difficult to define the interface accurately. In reality, the interface has a curvature in the phase-separated structure of polymer blends. Thus, in this study, we examine the distribution of A and B monomer segments of homopolymers at the interface indirectly, without such assumptions, by counting the difference of the number of contacts between copolymer segments along the chain and A (or B) homopolymer segments. n_A is the contact number between a copolymer segment and segments of homopolymer A, and n_B is the contact number between the copolymer segment and segments of homopolymer B. If a segment in the copolymer stays in A-rich phase, this segment is mostly in contact with segments of homopolymer A, resulting in a positive value of $(n_A - n_B)$. If this segment stays at the interfacial region, the difference between the contact numbers of the copolymer segment with segments of homopolymer A and with segments of homopolymer B becomes small. In the case of the block copolymer with $N_c = 30$ in this study, the segments are all A types from the first to the fifteenth segment, and the remaining are all B types. In the case of the alternating copolymer, the odd segments are of type A and the even segments are type B. Fig. 6a illustrates the monomer distribution of the blend containing the block copolymer at 2×10^5 MCS. As expected, the A segments in the block copolymer contact preferentially with homopolymer A segments, resulting in larger positive value of $(n_A - n_B)$, and the B segments in the block copolymer contact

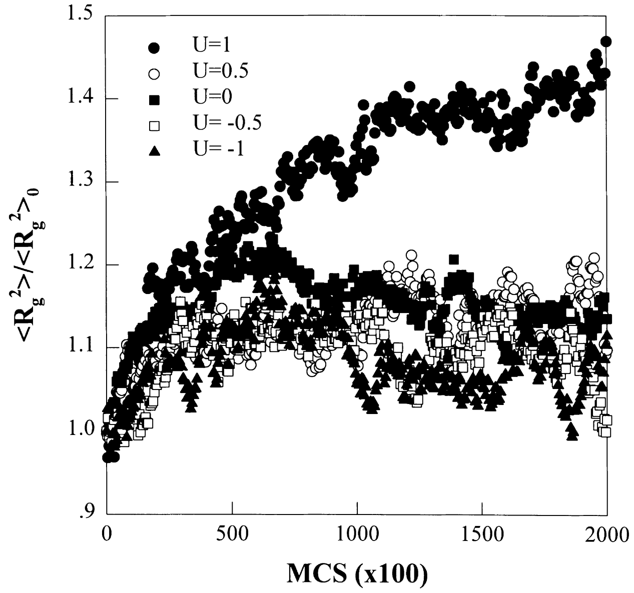

Fig. 5. Change of mean-square radii of gyration of copolymers of $N_c = 30$ during phase separation.

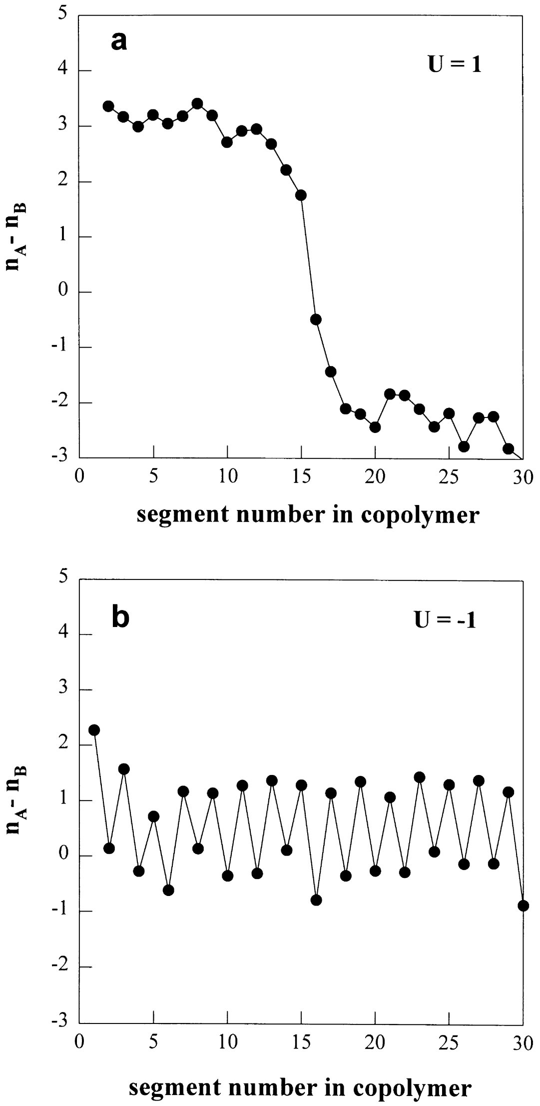

Fig. 6. The difference between contact numbers of a copolymer segment with homopolymer A segments and with homopolymer B segments in A/B/A-*co*-B blends at 2×10^5 MCS: (a) block copolymer; and (b) alternating copolymer. n_A is the contact number between a copolymer segment and the homopolymer A segment and n_B is the contact number between the copolymer segment and the homopolymer B segment. The chain length of the copolymer is set at $N_c = 30$.

dominantly with homopolymer B segments, resulting in a larger negative $(n_A - n_B)$. This indicates that each block penetrates into its respective homopolymer phase, and it can be related to the variation of radius of gyration of block copolymer, as shown in Fig. 5. This is qualitatively consistent with our previous result [23] that each block is stretched perpendicular to the interface and as a consequence the distribution of copolymer segments is broadened when the block length is longer than the homopolymer length. On the other hand, in the case of the alternating copolymer, the difference in contact number is almost zero along the chain segment, as shown in Fig. 6b. This indicates that the alternating copolymer migrates to the interface and just lies on the interface. For the other copolymers, it is not possible to define the specified structure systematically since each chain has a segment sequence different from others along the chain. Hence, we observed the respective conformations of random, blocky-random and random–alternating copolymers at the interface from snapshot (not shown here). The random–alternating copolymer has similar conformation to the alternating copolymer. On the other hand, both the blocky-random and the random copolymers are seen to weave back and forth across the penetrable interface on the average. This structure may allow these copolymers to decrease the number of A/B contacts between the homopolymers and therefore the copolymers may retard phase separation. From the above observation, the retardation efficiency can be related to the conformation of copolymer at the interfacial region and it seems that the degree of penetration of the copolymer chain into the homopolymer phase can be an important factor for evaluating the retardation efficiency. The large degree of penetration of chains leads to a decrease in the number of unfavorable A/B contact and thereby results in the reduction of the interfacial tension. Therefore, the weaving conformation of the random copolymers and the penetrating conformation of the block copolymers are expected to retard the phase separation more effectively, compared with the conformation of the alternating copolymer. This reduction of the interfacial tension can also be predicted by the self-consistent mean field calculation when the random copolymer is added to the immiscible homopolymer blends [14].

In order to examine the degree of penetration of copolymer into homopolymer phase quantitatively, the fractions of contact number of copolymer segments with homopolymer segments are monitored with the phase separation time. The number of contacts between the copolymer segments and

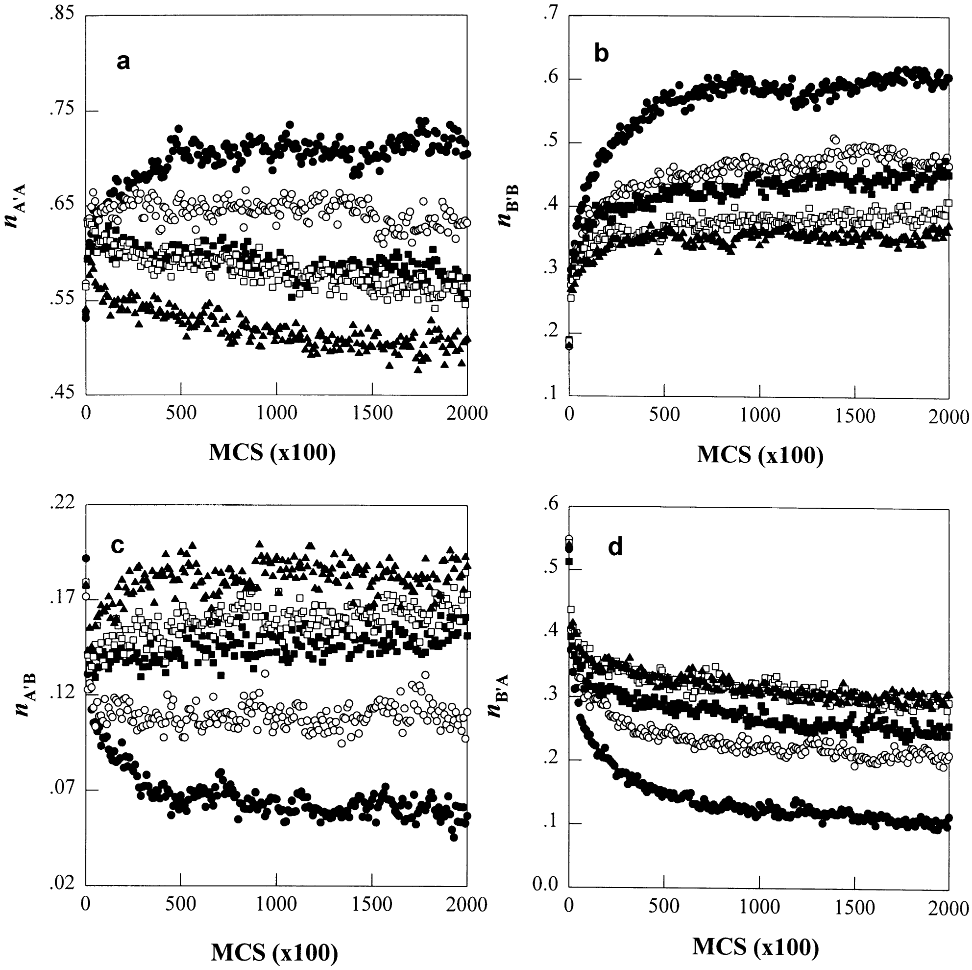

Fig. 7. Change of the fraction of the contact number of copolymer segment A or B with homopolymer A segment and homopolymer B segment during the phase separation for A/B/A-*co*-B blends. The contact number n_{ij} is normalized with respect to the total contact number of each copolymer segment. Symbols are the same as shown in Fig. 5. The chain length of the copolymer is set at $N_c = 30$.

the homopolymer segments may strongly depend upon the conformation of the copolymer chain. The results for ternary blends of $N_c = 30$ are shown in Fig. 7, where the contact numbers are normalized with respect to the total contact number of each copolymer segments. Subscripts A, B, A$'$ and B$'$ in the normalized contact number n_{ij} denote the segments belonging to homopolymer A, homopolymer B, copolymer A and copolymer B, respectively. For the blend containing block copolymers, $n_{A'A}$ and $n_{B'B}$ increase very fast in the early stage of phase separation, while $n_{A'B}$ and $n_{B'A}$ decrease rapidly as shown in Fig. 7. These results indicate that, in the early stage of phase separation, the block copolymers are absorbed onto the interface between the two phases and that each block penetrates into its respective phase. The blocky-random copolymer also exhibits a behavior similar to that of the block copolymer. However, for the random, random–alternating and alternating copolymers, the $n_{A'A}$ slightly decreases with phase separation time. Since the initial mixture of the polymer blend is prepared to be homogeneous, the copolymer segments have a better chance to contact with homopolymer A segments, because the homopolymer A is the major component in the blend system. As a result, the value of $n_{A'A}$ at 0 MCS is large. As the phase separation proceeds, these copolymers are segregated into the interfacial region, but the degree of penetration into the homopolymer phase is not as high as that of block copolymers. Consequently, $n_{A'A}$ decreases whereas $n_{A'B}$ increases with phase separation time. From this result, it is conjectured that the copolymer with block-like structure can easily penetrate into the homopolymer phase and thereby reduce the interfacial tension, resulting in the retardation of phase separation. From this Monte Carlo study and the previous self-consistent field study [14], it is concluded that random copolymers not only retard the rate of phase separation effectively at the initial stage of phase separation, but also lead to the thermodynamically equilibrated interface with a lower energy state.

4. Conclusions

In this study, we used the Monte Carlo simulation to examine the effects of copolymer architecture on the dynamics of phase separation when copolymers are added to immiscible polymer blends as a compatibilizer. Five types of copolymers with each having different architectures are used for the simulation. It is found that when a small amount of copolymer is added to an A/B binary blend the rate of phase separation is suppressed irrespective of the copolymer structure. This means that all the types of copolymers used in this study are segregated into the interface between the immiscible phases. The block copolymer is the most effective in retarding the phase separation and the random copolymer shows better retardation effect than does the alternating copolymer. Such a retardation effect is more significant when a copolymer with large N_c is added to the A/B immiscible blend. These results suggest that the random copolymers may be used as potential compatibilizers for immiscible polymer blends, although the retardation efficiency of the random copolymer is not as effective as that of the block copolymer.

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