A Monte Carlo Simulation of Phase Separation Dynamics of Polymer Blends in the Presence of a Block Copolymer. 3. Effect of Interaction Energies among Constituent Segments

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ABSTRACT: A Monte Carlo simulation has been performed on the dynamics of phase separation of A/B immiscible polymer blends to which various C-*b*-D diblock copolymers with repulsive interactions between the blocks and homopolymers were added. For comparison, the results for a blend containing a block copolymer with attractive interactions are also presented. It is found that even the block copolymer with repulsive interactions between the blocks and the homopolymers still has a retardation effect on the phase separation. This effect may arise from strong interfacial activity that is due to the competitive interactions of the blocks with the different homopolymers. The phase separation proceeds by following the usual spinodal decomposition process, and thus the scaling law between the first moment of the structure factor and the time, $q_1(t) \propto t^{-1/3}$, can be applied in the later stage of separation. By analyzing the changes in the linear dimensions and the contact numbers of the block copolymers with the phase separation time, we investigate the effects of the type of block copolymer interaction and its relative strength on the interfacial activity and the consequent retardation of separation.

Introduction

In our previous studies,[1,2] we investigated by Monte Carlo simulations the factors affecting the dynamics of phase separation of an A/B immiscible polymer blend to which various C-*b*-D diblock copolymers were added as compatibilizers. It was found that, when a small amount of C-*b*-D block copolymer was added to an A/B binary blend, the growth rate of phase-separated domains was significantly retarded, especially in the later stage of phase separation. It is generally known that such a retardation effect, which has been observed experimentally for various A/B/A-*b*-B blends,[3−6] results from the localization of the block copolymer at the interface between the two phases and the consequent reduction of interfacial tension. It was also found that this retardation effect was strongly dependent upon the molecular parameters and the thermodynamic variables of the added block copolymers. As the interactions between the copolymer blocks and the respective homopolymers become more attractive, stronger localization of the block copolymer at the interface and higher extension of its chain dimensions were observed, which are in turn responsible for the slower growth rate of phase separation. The total chain length and composition of a block copolymer also had a strong effect in retarding the phase separation. The longer chains showed a larger retardation effect. When the composition of A/B is not 50/50, an asymmetric block copolymer was found to be more effective in retarding the growth of phase separation, which was related to the curvature properties of the interface such as the elastic rigidity and the spontaneous radius of curvature of the interfacial film.[7]

Our previous studies have dealt with the case in which the interactions between each block of block copolymer and its respective homopolymer were attractive; that is, the values of the interaction energies were negative ($\epsilon_{CA} < 0$ and $\epsilon_{DB} < 0$). In this work, we focus our attention on the effect of repulsive interaction energies on the phase separation behavior of immiscible blends. For this purpose, the blocks of the added copolymers are assumed to be chemically different from both homopolymers and the interactions between blocks and homopolymers are repulsive ($\epsilon_{CA} > 0$ and $\epsilon_{DB} > 0$). Vilgis and Noolandi[8] investigated the thermodynamical behavior of an A/B/X-*b*-Y blend using a statistical theory. They reported that, under proper conditions, for example, if block X (or Y) is very immiscible with homopolymer B (or A) but is less immiscible with homopolymer A (or B), there exists a thermodynamic driving force that will orient the block copolymers at the interface and lead to compatibilization. However, in order to understand more clearly the compatibilizing effect of block copolymers of this type, information on the kinetic properties of such systems is also needed. Therefore, in this paper, we examine the effects of interaction energies between blocks and homopolymers on the dynamics of phase separation in an A/B/C-*b*-D blend. A Monte Carlo simulation will be used here since it has been shown from our previous studies to be a very powerful tool in understanding the dynamics of phase separation of polymer blends.

Model and Simulation Method

The blend model and simulation method employed in this work are detailed in the previous papers,[1,2] and hence, only the main points are summarized here. The simulation is performed on a cubic lattice of dimension 50 × 50 × 50 with periodic boundary conditions in all three directions. The composition of homopolymers A and B is set at 75/25 (v/v) in all blends, and the homopolymer chains have a constant length of $N_A = N_B = 10$. All the block copolymers have a constant total chain length N of 12 and a constant composition f $(=N_C/N$, where N_C is the chain length of block C) of 0.5. The

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Table 1. Interaction Energies and Composition of Block Copolymers Added to Immiscible Blends in This Work

block copolymer code	ϵ_{AB}	ϵ_{CA}	ϵ_{CB}	ϵ_{DA}	ϵ_{DB}	ϵ_{CD}	composition f
E11f5	0.5	0.1	1.0	1.0	0.1	1.0	0.5
E21f5	0.5	0.1	2.0	2.0	0.1	1.0	0.5
E22f5	0.5	0.1	2.0	2.0	0.1	2.0	0.5
attractive	0.5	−0.5	0.5	0.5	−0.5	0.5	0.5

content of added block copolymer is fixed at 5.7% of the total sites occupied by all polymer chain segments. Since the chemical structure of the added block copolymer is totally different from that of the homopolymers, six different interaction parameters should be considered. In this work, all interactions are set to be repulsive, and hence there exists no attractive interaction between any of the polymer pairs involved. In principle, we can vary all these values in the simulations, but it would be a formidable task to examine the effect of each interaction energy on the phase separation individually. Hence, we choose three sets of interaction energies, as shown in Table 1. Here the values of ϵ_{AB}, ϵ_{CA}, and ϵ_{DB} remain unchanged for all blend systems investigated and ϵ_{DA}, ϵ_{CB}, and ϵ_{CD} are varied for three sets. The essential feature of the interaction energies given in Table 1 is that blocks C and D have repulsive interactions with both homopolymers A and B but one of the blocks is less repulsive with a homopolymer than the other, i.e., $\epsilon_{CB} > \epsilon_{CA}$ and $\epsilon_{DA} > \epsilon_{DB}$ so that the C-*b*-D diblock copolymer can act as the compatibilizer for the A/B immiscible blends.

The initial conformations of all blend models are generated randomly by setting all interaction energies to zero. The bond fluctuation algorithm is used to convert one conformation into another.[9] Acceptance or rejection of a new conformation is decided according to the Metropolis rule. The time-dependent collective structure factors are calculated at constant time intervals of phase separation and spherically averaged in the same way as described in previous papers.[1,2]

Results and Discussion

Figure 1 shows the time evolution of the structure factors $S(q,t)$ during phase separation for an A/B binary and two A/B/C-*b*-D ternary blends. For the ternary blends, the content of C-*b*-D is set at the same level but the interaction energies between the blocks and the homopolymers are different. One represents the case with attractive interactions (Figure 1b) and the other with repulsive interactions (Figure 1c). In general, the phase separation of a polymer mixture proceeds by spinodal mechanism, when the mixture is quenched from a single-phase state to a two-phase state. Immediately after quench, periodic concentration fluctuations are built up throughout the whole sample space and small domains spontaneously form. The phase-separated domains grow with an increase in the amplitude of concentration fluctuation and finally result in complete phase separation. All three blends exhibit typical behavior of phase separation; that is, a structure factor maximum S_{max} appears and its value increases while the scattering vector q_{max} at S_{max} shifts toward smaller q. First of all, it can be seen from Figure 1 that the rate of phase separation is faster for the binary blend than for two ternary blends containing a block copolymer. This observation clearly indicates that the added block copolymer plays the role of compatibilizer. Another interesting feature from Figure 1 is that even the block copolymer having the repulsive interactions with homopolymers can suppress the growth rate of phase-separated domains, as shown in Figure 1c, although the suppression is not so effective as the case where the block copolymer having the attractive interactions is added. This indicates that the block copolymer having repulsive interactions with the homopolymers can also act as a compatibilizer as long as block C is less compatible with homopolymer B than with homopolymer A, i.e., $\epsilon_{CB} > \epsilon_{CA}$ and block D is less compatible with homopolymer A than with homopolymer B, i.e., $\epsilon_{DA} > \epsilon_{DB}$. This behavior does not simply result from a dilution effect of the block copolymers. As will be shown later, block C preferentially penetrates into the homopolymer A phase, and block D into the

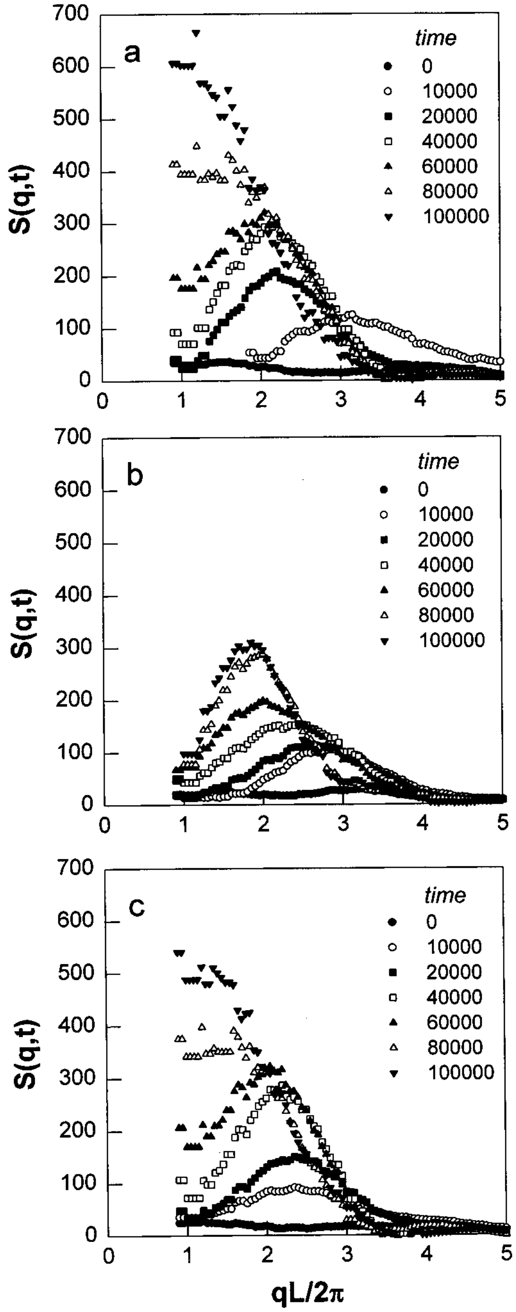

Figure 1. Time evolution of the structure factor during phase separation for a blend without block copolymer (a) and blends with block copolymers of (b) attractive interaction ($\epsilon_{CA} = \epsilon_{DB} = -0.5$) and (c) repulsive interaction (E11f5: $\epsilon_{CA} = \epsilon_{DB} = 0.1$) between the blocks and the homopolymers. The total chain length and the composition of the block copolymers are $N = 12$ and $f = 0.5$, respectively.

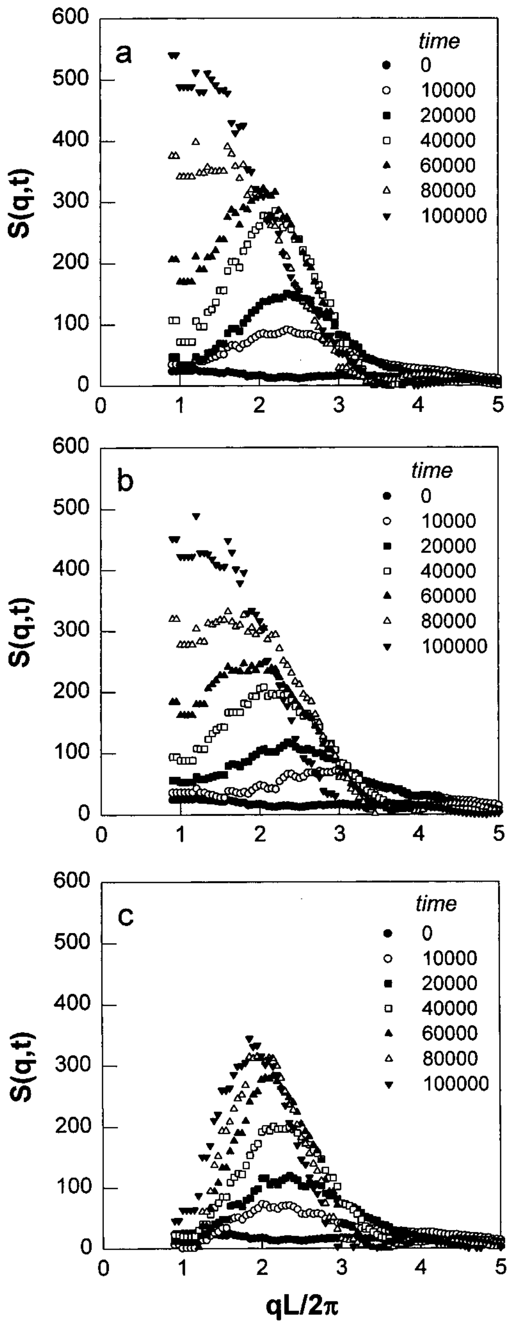

Figure 2. Time evolution of the structure factor during the phase separation for A/B/C-*b*-D blends with block copolymers: (a) E11f5; (b) E21f5; (c) E22f5.

homopolymer B phase under such a situation. In this case, as reported by Vilgis and Noolandi,[8] the competitive interactions of the blocks with the homopolymers force the block copolymers to preferentially localize at the interface between the two phases and consequently result in the reduction of interfacial tension. This is responsible for the retardation effect observed in Figure 1c where the block copolymers have repulsive interactions with the homopolymers.

To investigate the compatibilizing effects of the block copolymer addition on the phase separation in terms of interaction energies between the block copolymer and homopolymers, the interaction energies are systematically varied, as given in Table 1. All the block copolymers have repulsive interactions with homopolymers, that is, $\epsilon_{CA} > 0$ and $\epsilon_{DB} > 0$, but also have such a feature that $\epsilon_{CA} > \epsilon_{CB}$ and $\epsilon_{DB} > \epsilon_{DA}$. Figure 2 shows that the best retardation effect is obtained with E22f5. The block copolymer E22f5 has the largest values of ϵ_{CB}, ϵ_{DA}, and ϵ_{CD} among the block copolymers investigated in this work. Thus, the competitive interactions of the blocks with the different homopolymers are shown to promote the retardation. In other words, as the relative repulsions between block C and homopolymer B and between block D and homopolymer A increase, i.e., if the interaction of block C (D) with homopolymer B (A) is more repulsive than that of block C (D) with homopolymer A (B), the rate of phase separation is retarded more effectively. One can expect an intermediate retardation with E21f5, since the repulsions between block C and homopolymer B and between block D and homopolymer A are greater than in the E11f5 case and the repulsion between blocks C and D is the same as in the E11f5 case. Vilgis and Noolandi also predicted strong interfacial activity of block copolymers with such interactions.[8] However, contrary to the initial expectation, the E21f5 system does not exhibit an effective retardation of domain growth and rather retards the separation to almost the same degree as E11f5. As the chain length of E21f5 increases, the retardation effect of E21f5 becomes intermediate between E11f5 and E22f5.[10] This behavior may be related to the extent to which the copolymer chains migrate into the interface and penetrate into the homopolymer phases, which will be later explained in detail. Therefore, it can be concluded that the interaction energy between the blocks also has an important effect on the phase separation of immiscible blends.

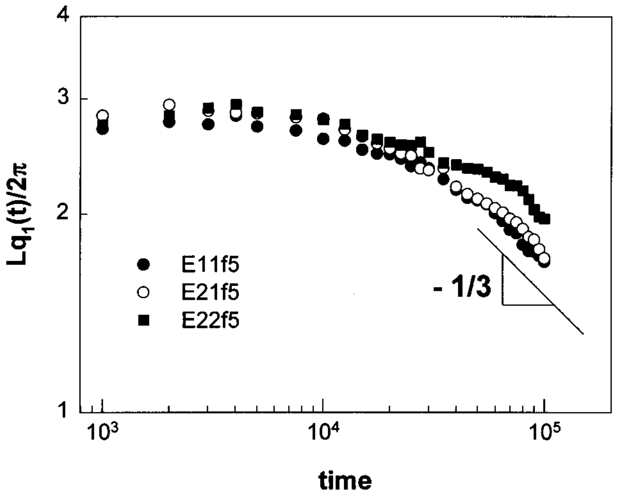

Figure 3. Temporal changes of the first moment $q_1(t)$ of the structure factor for the blends containing block copolymers with repulsive interactions.

In order to compare in a quantitative manner the effect of block copolymer addition on the rate of phase separation in terms of repulsive forces between the components, we calculate the first moment $q_1(t)$ of the structure factor given by eq 1, and double-logarithmic

$$q_1(t) = \frac{\sum_q qS(q,t)}{\sum_q S(q,t)} \tag{1}$$

plots of $q_1(t)$ with time are given in Figure 3. It is known that, in the early stage of phase separation where Cahn's linearized theory[11,12] can be applied, $q_1(t)$ is independent of time and remains constant. Indeed, this behavior can be seen in Figure 3 for all ternary blends.

A difference between the added block copolymers can hardly be observed in this stage. After the early stage, $q_1(t)$ decreases with time due to nonlinear effects, signifying the gradual onset of the coarsening process. In this stage, one can definitely observe that the retardation effect is different among block copolymers having different interaction energies. The blend containing E22f5 exhibits the highest q_1 at the same separation time, meaning that the phase separation is slowest. Thus the addition of E22f5 leads to a finer structure and is more effective in compatibilization than the other two block copolymers. In the later stage of phase separation, the time dependence of $q_1(t)$ has been characterized by a power law[13]

$$q_1(t) \sim t^{-\alpha} \tag{2}$$

where the exponent α itself is time-dependent, reflecting a crossover between various coarsening mechanisms.[14] In the asymptotic universal power law, the polymer mixtures without hydrodynamic interaction exhibit $\alpha = 1/3$[15] while the polymer mixtures with hydrodynamic interaction show $\alpha = 1$, as proposed by Siggia.[16] Hydrodynamic effects are not included in our model system. Therefore, it is expected that the exponents will approach 1/3 in the later stage for all three blends. This is exactly what we observe in Figure 3. Good agreement between the theoretical prediction and our simulation results indicates that the Lifshitz–Slyozov's coarsening mechanism[15] holds for all the blends investigated here irrespective of block copolymer addition and the interaction energies of the added block copolymers.

Figure 4 shows the change of the contact number n_{AB} between segments A and B with the phase separation time for the ternary blends containing the block copolymers. The contact number $\langle n_{AB}\rangle_t$ at time t is normalized with respect to its initial value $\langle n_{AB}\rangle_0$. This reduced contact number $\tilde{n}_{AB}$ is a useful measure of the extent of phase separation. As shown in Figure 4a, $\tilde{n}_{AB}$ decreases drastically with time for all ternary blends, indicating that phase separation proceeds and domains grow with time. In order to more clearly compare the degree of phase separation for each block copolymer added to an immiscible blend, $\tilde{n}_{AB}$ in the late stage is more closely shown in Figure 4b, where the data for the blend containing the block copolymer with attractive interactions are also included for comparison. As expected, the blend containing the block copolymer with attractive interactions has the highest value of $\tilde{n}_{AB}$ over the entire time examined. This means that the block copolymer with attractive interactions is more effective in retarding the phase separation of an immiscible blend than the block copolymers with repulsive interactions. Among the block copolymers with repulsive interactions, the blend with E22f5 has the highest value of $\tilde{n}_{AB}$. These results are also consistent with our discussion on the results shown in Figure 3. It is worthy to note here that the contact number n_{AB} can be used as a powerful tool for judging the extent of phase separation quantitatively.

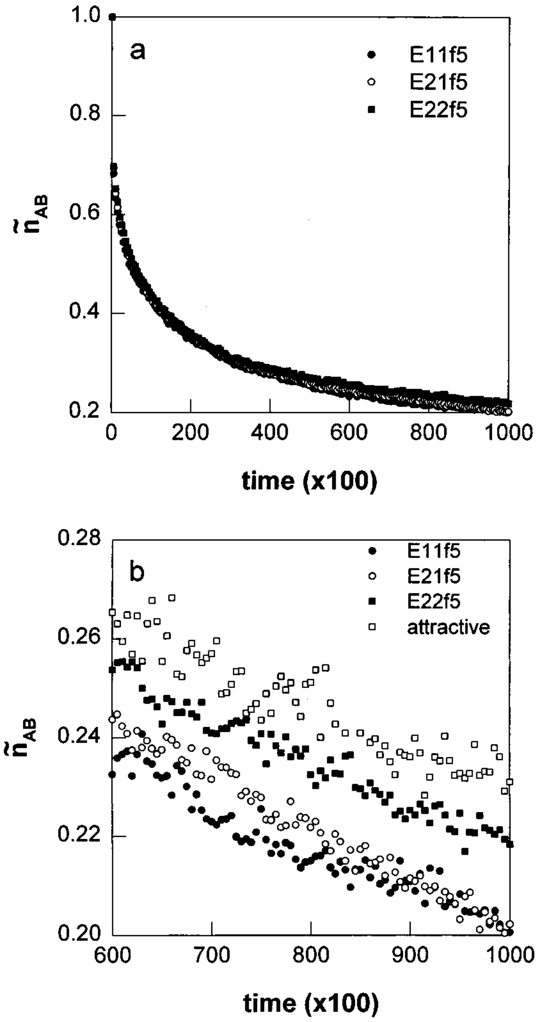

Figure 4. Change of normalized number, $\tilde{n}_{AB}$, of contacts between the homopolymer chains A and B during the phase separation for the ternary blends containing block copolymers with different interactions (a). For closer examination, the scales in the later stage are expanded in (b).

The progress of phase separation may be accompanied by a large change in linear dimensions of all polymer chains in the blends. In our previous papers,[1,2] we showed that the chains of homopolymers A and B have a tendency to contract as the phase separation proceeds and this tendency is more pronounced for the minority component (corresponding to homopolymer B here) than for the majority component (corresponding to homopolymer A here). On the other hand, it was also found that the linear chain dimensions of block copolymers increase as they migrate to the interface between the two separated phases and each block penetrates into its respective homopolymer phase. Particularly, it was observed that the change of chain dimension of block copolymers has a significant effect on the phase separation of an immiscible blend. Such effects for the blends in this work are shown in Figure 5, where the variation of the radius-of-gyration of block copolymers with time is given. As the separation proceeds, all block copolymer chains become extended. This behavior results from the preferential localization of the block copolymer at the interface and the penetration of each block into its respective homopolymer phase. However, there is a large difference in the degree of extension of block copolymer chains, depending on the block copolymer type used. As shown in Figure 5, the block copolymer with attractive interaction exhibits the largest extension. Among the block copolymers with repulsive interactions, E22f5 is extended more than the other two block copolymers. There is little difference between E11f5 and E21f5. When the results of Figure 4 are related to those of Figure 5, it reveals that phase separation proceeds more slowly concomitantly with chain extension of the block copolymer. Therefore, this

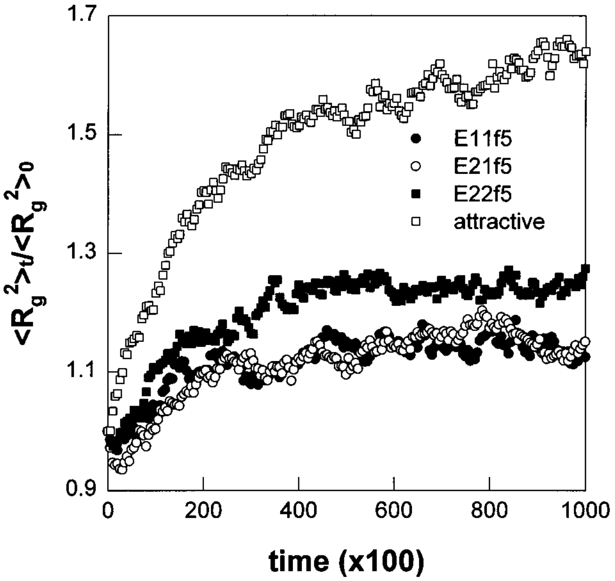

Figure 5. Change of mean-square radii of gyration of block copolymers during the phase separation.

result is another evidence that E22f5 is a more effective compatibilizer than E11f5 or E21f5.

When the linear dimension of the block copolymer is changed, the contact number of segments comprising the block copolymer may also be varied accordingly. The results are presented in Figures 6 and 7, where the contact numbers of each block with each segment in the blend divided by the total contact numbers of the block are plotted against the phase separation time. As the phase separation proceeds and a large portion of block copolymers are absorbed onto the interface between the two phases, the fractions of contact number n_{CA} between block C and homopolymer A and the fractions of contact number n_{DB} between block D and homopolymer B increase very fast in the early stage of phase separation, as shown in Figures 6a and 7a. At the same time, the fractions of contact numbers n_{CB} between block C and homopolymer B and the fractions of contact number n_{DA} between block D and homopolymer A decrease abruptly, regardless of the block copolymer type (Figures 6c and 7c). These results indicate that, in the very early stage of phase separation, the majority of block copolymers are segregated to the interface and each block penetrates into its respective phase. Therefore, it is conceivable that even the block copolymers with repulsive interactions are localized at the interface strongly enough to play the role of compatibilizer. However, there is a difference between the block copolymers depending on the type of interaction. The fractions of contact numbers n_{CA} and n_{DB} increase monotonically for the block copolymer with attractive interaction, whereas for block copolymers with repulsive interaction they reach a maximum in the early stage and then slightly decrease. For block copolymers with repulsive interaction, a decrease in the fraction of contact numbers n_{CA} (or n_{DB}) gives rise to an increase in the fractions of contact number n_{CC} and n_{DD} between the same kind of segments on different chains (Figures 6b and 7b). On the other hand, the fractions of n_{CC} and n_{DD} decrease monotonically for the block copolymer with attractive interaction. These changes of contact numbers of block copolymers are interpreted as follows: when the interactions between the blocks and the respective homopolymers are attractive, each block is well mixed with homopolymer chains and, accordingly, the fractions of n_{CA} and n_{DB} increase and the fractions of n_{CC} and n_{DD} decrease. On the contrary, when the interactions between the blocks and the respective homopolymers are repulsive, each block that is localized at the interface is not well mixed with homopolymer chains and rather forms relatively favorable CC and DD self-contacts. Nevertheless, the block copolymers may still reduce the total free energy of the system by reducing the number of the most unfavorable contacts, n_{CB} and n_{DA}.

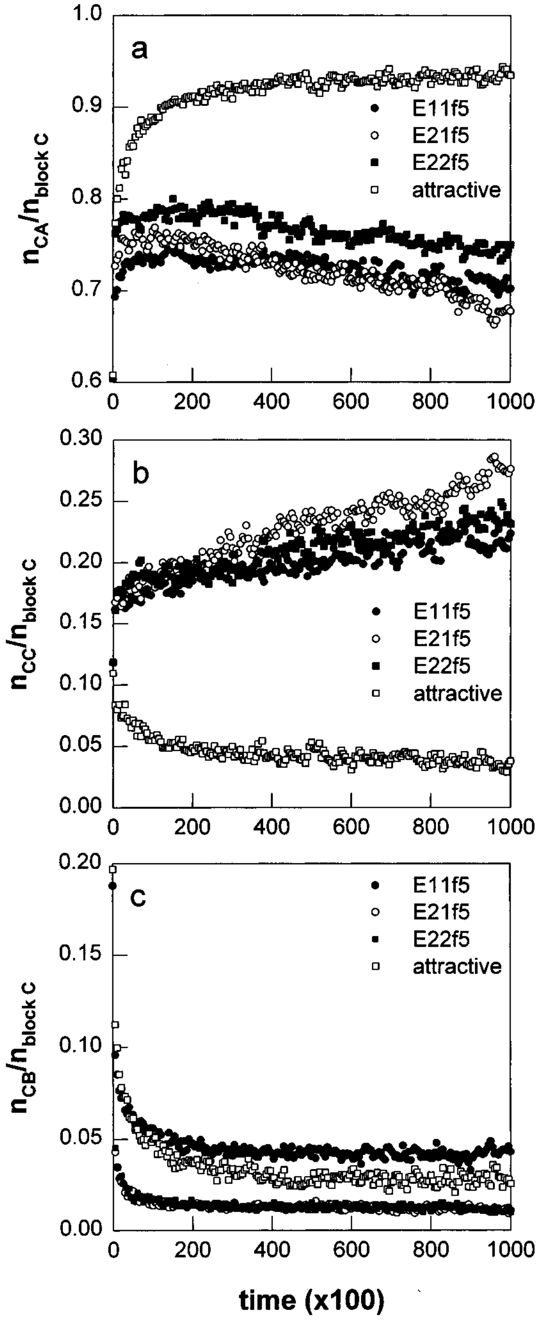

Figure 6. Change of the fraction of the contact number of block C with (a) homopolymer A, (b) block C, and (c) homopolymer B during the phase separation for A/B/C-*b*-D blends.

A closer observation on the change of fractions of contact numbers for the block copolymers with repulsive interactions reveals that there exists a difference between them. E22f5 has the largest fractions of n_{CA} and n_{DB} compared to the other two, which explains the reason for the best retardation effect of this block copolymer. The reason that E11f5 has the worst retardation effect can be explained by the largest fractions of contact numbers n_{CB} and n_{DA} (Figures 6c and 7c)

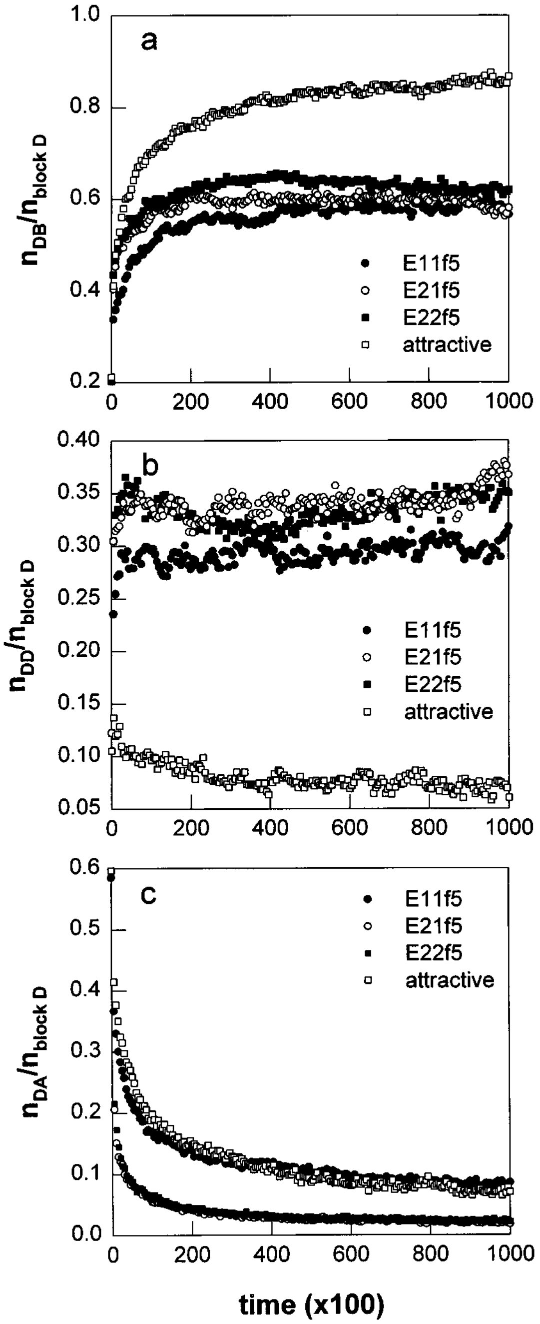

Figure 7. Change of the fraction of the contact number of block D with (a) homopolymer B, (b) block D, and (c) homopolymer A during the phase separation for A/B/C-*b*-D blends.

compared to the other two block copolymers. This indicates that the block copolymers are not effectively located at the interface between the two immiscible phases. Surprisingly, the block copolymer with attractive interactions also has a large fraction of n_{CB} and n_{DA}. This may be the reason why the retardation is not as good as expected from the change of linear dimension of this block copolymer. Therefore, it can be concluded that, depending on the type of interaction and its relative magnitude, the retardation effect associated with various conformations and interfacial activity changes.

Conclusions

In this paper, we examine by Monte Carlo simulation the effects of the interaction energies between block copolymers and homopolymers on the dynamics of phase separation, when block copolymers are added to an immiscible polymer blend as a compatibilizer. It was found that even block copolymers having repulsive interactions with homopolymers can reduce the rate of phase separation of the immiscible blend under a proper condition, although the retardation effect is not so effective as the block copolymer having the attractive interactions with homopolymers. The proper condition means that a C-*b*-D block copolymer has interactions such that block C is less compatible with homopolymer B than with homopolymer A and that block D is less compatible with homopolymer A than with homopolymer B. Under this condition, the competitive interactions of the blocks with the different homopolymers force the block copolymer to localize at the interface between two phases, thus leading to the reduction in the interfacial tension. This is responsible for the retardation effect of block copolymers with repulsive interaction. However, the phase separation of the blends containing block copolymers with repulsive interaction follows the usual spinodal decomposition process, as observed in the case of A/B binary blends.

The retardation effect of the block copolymer depends on the degree of immiscibility between the blocks and the homopolymers. The stronger is the repulsion between block C and homopolymer B and between block D and homopolymer A, the slower becomes the growth rate of phase-separated domains. The relative repulsion between blocks C and D also has a significant effect on the dynamics of phase separation. However, as mentioned above, the block copolymer having repulsive interactions with the homopolymers is not as effective as the block copolymer with attractive interactions in retarding the growth rate of the domains, since each block chain penetrating into its respective homopolymer phase is not extended but rather contracted due to the repulsion between the block and homopolymer.

Finally, it should be emphasized that when the block copolymers are added to an immiscible polymer blend, one must also take the effects of the chain length and the composition of the block copolymers into account, because the retardation effect of a block copolymer on phase separation is highly dependent on its chain length and composition as with the cases of block copolymers with attractive interactions. This remains for future work.

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