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Monte Carlo Simulation of Phase Separation Dynamics of a Polymer Blend in the Presence of Block Copolymer. 2. Effect of Block Copolymer Composition

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ABSTRACT: The effects of the composition f of added C-*b*-D diblock copolymer ($f = N_C/N$, where N is the total chain length of block copolymer and N_C that of block C) on the dynamics of phase separation of an immiscible binary blend A/B were investigated by Monte Carlo simulation. The composition of the block copolymers has an important effect on the phase separation, which is also strongly dependent upon the chain lengths of the homopolymers and block copolymer. For block copolymers with chain lengths shorter than the homopolymers, a symmetric composition ($f = 0.5$) is most effective in slowing the growth rate of phase-separated domains. However, for block copolymers with chain lengths longer than the homopolymers, an asymmetric composition almost identical with the composition of the homopolymer blend (A/B = 75/25) has the best retardation effect because of the curvature properties of the interface, i.e., the elasticity and spontaneous radius of curvature of the interface. The scaled structure factors were calculated and analyzed for A/B/C-*b*-D blend systems containing asymmetric block copolymers. The universality of the scaled structure function at reduced wave number $x < 2$, where $x = q/q_1(t)$ and $q_1(t)$ is the first moment of structure factor, indicates that the global structure of the phase-separated domains has a dynamical self-similarity independent of the composition of the block copolymers.

Introduction

The mechanism and dynamics of phase separation in binary polymer blends have long been the subject for many researchers in an attempt to obtain high-performance materials by controlling morphology.[1−7] Recently, phase-separation behavior in ternary blends containing a small amount of block copolymer has been investigated,[8−11] since a block copolymer is quite often used as a compatibilizer in many polymer blends for miscibility enhancement between immiscible polymer pairs, leading to improved mechanical properties.[12−14]

In our previous work,[15] we investigated by using a Monte Carlo simulation the effects of adding C-*b*-D diblock copolymer to A/B binary blend on the phase-separation behavior in terms of the interaction energies between polymer pairs involved and the chain length of block copolymer. It was found that the rate of phase separation is significantly suppressed by the addition of a small amount of block copolymer, which is mainly caused by the reduction in interfacial tension due to the localization of block copolymer at the interface, and that this retardation effect is dependent upon both the interaction energies (ϵ_{AC} and ϵ_{BD}) between the copolymer blocks and homopolymers and the chain lengths of block copolymers. We also applied a scaling law to the ternary blend system and obtained a universal scaling function independent of the presence of block copolymer.

In this paper, we investigate further the effects of the composition f ($f = N_C/N$, where N is the total chain length of block copolymer and N_C the chain length of block C) of added block copolymer on the dynamics of phase separation of an immiscible binary blend A/B. It is not simple to determine which composition of block copolymer has the maximum compatibilizing effect on an immiscible polymer blend, since both the kinetic as well as equilibrium aspects must be considered together. Recently, Wang et al.[16,17] presented a Monte Carlo study of adsorption of symmetric and asymmetric diblock copolymers at the sharp and narrow interface between the two monomeric homopolymer fields. They reported that, in the equilibrium situation, the amount of chains absorbed at the interface becomes maximum with the symmetric copolymer when the total chain length of block copolymer is constant. However, in the nonequilibrium situation, an asymmetric diblock copolymer is found to be absorbed more at the interface than a symmetric one, although there exists an optimum composition of block copolymer which maximizes the amount of copolymer chains absorbed at the interface. On the other hand, Leibler[18] theoretically predicted in the quantitative manner the interfacial and emulsifying activity of block copolymers A-*b*-B in immiscible blends of homopolymers A and B. In particular, it was reported that, at equilibrium, the distribution of the droplet sizes of dispersed phase depends on the elasticity and the spontaneous radius of curvature of the interfacial film which can be controlled by molecular parameters of block copolymers such as the molecular weight and the composition. On the basis of the random phase approximation (RPA) presented by Leibler,[19] Tanaka and Hashimoto[20] calculated stability limits for the phase transitions of binary and ternary mixtures of A-*b*-B diblock copolymer with corresponding homopolymers A and/or B. They claimed that, in the case of a ternary mixture A/B/A-*b*-B, the compatibilizing effect of block copolymers in immiscible blends depends not only on the ratio of molecular weight of block copolymer to that of homopolymers but also on the composition f of the block copolymer. Indeed, if the stability limits of ternary mixtures are calculated according to their

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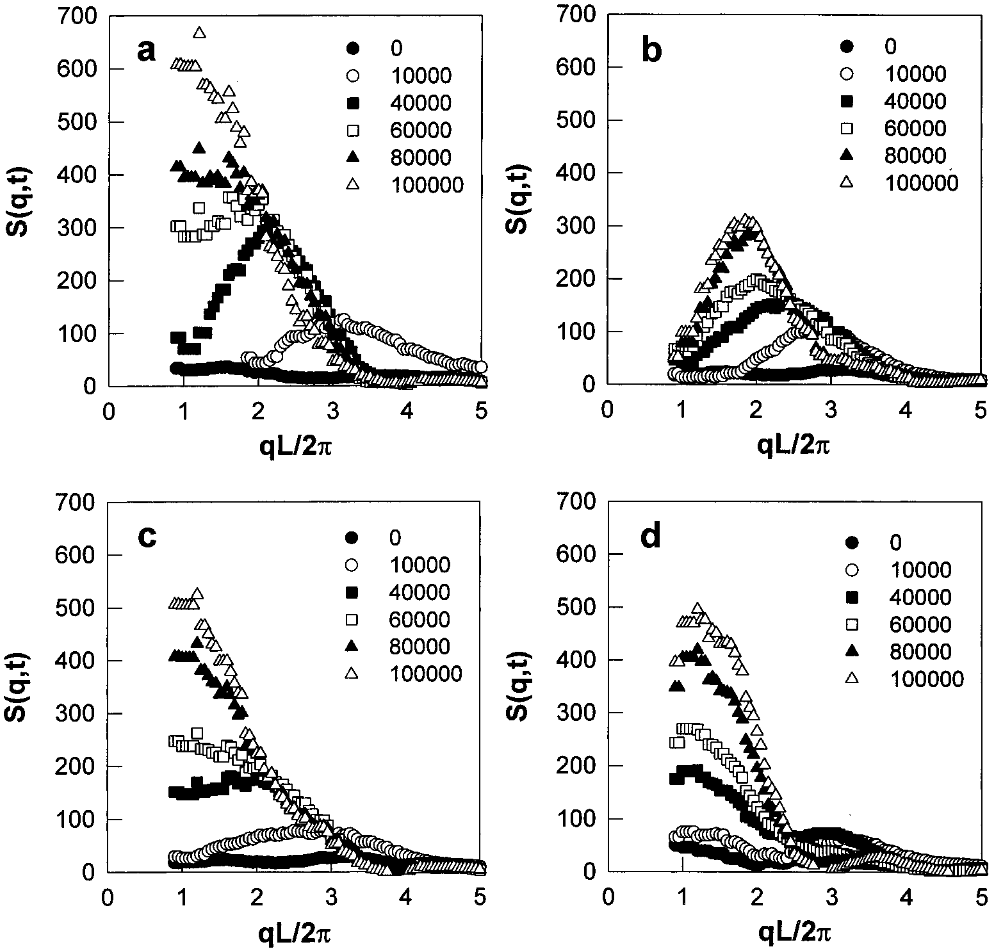

Figure 1. Time evolution of structure factor during the phase separation for a blend without block copolymer (a), and blends with block copolymers of (b) $f = 0.5$, (c) $f = 0.7$, and (d) $f = 0.9$. The total chain length of block copolymers is 12.

scheme, it can be found that the maximum compatibilizing effect can be observed when the block copolymer having the same composition as that of homopolymer blend is used.

However, most studies so far have dealt only with the A/B/A-*b*-B cases. No theoretical and experimental results for A/B/C-*b*-D mixtures have yet been reported. Here we investigate the A/B/C-*b*-D case focusing on the effects of the composition of the C-*b*-D diblock copolymer on the dynamics of phase separation. For this purpose, our results will be compared with our earlier results.[15]

Model and Simulation Method

A detailed description of our model and simulation methods will be found in our previous paper.[15] Here we consider A/B/C-*b*-D ternary blends on a simple cubic lattice of 50 × 50 × 50 sites. The composition of an A/B binary mixture is set at 75/25 (v/v) in all blends, and the homopolymer chains have a constant chain length of $N_A = N_B = 10$. The total chain length N of block copolymers added to A/B blends is varied from 12 to 54, and the amount of added block copolymer is fixed at 5.7% of the total sites occupied by all chain segments. Three different block copolymers with $f = 0.5$, 0.7, and 0.9 are used. The total volume fraction of polymers is set at 0.61. Since the lattice model is used in this simulation, the compositions of block copolymers may not correspond to the virtual block length. For example, the composition $f = 0.7$ of a block copolymer with $N = 18$ actually corresponds to $N_C = 12.6$, for which $N_C = 13$ is used in the simulation. We set the interaction energies between homopolymer A and block C (ϵ_{AC}) and between homopolymer B and block D (ϵ_{BD}) to be attractive ($\epsilon_{AC} = \epsilon_{BD} = -0.5$) and thus the added block copolymer can play a role of a compatibilizer in immiscible blends. All other interaction energies ($\epsilon_{AB} = \epsilon_{AD} = \epsilon_{BC} = \epsilon_{CD}$) are set at +0.5.

The initial conformations of all blend models are generated randomly with all interaction energies being zero. The random conformations are then run 10^5 iterations with a given set of interaction energies, and each conformation is sampled by means of bond fluctuation algorithm.[21,22] Trial moves are accepted or rejected according to the Metropolis rule. Five independent runs are performed for each case, and all the results are reported by averaging over the data from five independent runs.

To monitor the phase separation process of the polymer blend, the time-dependent collective structure factors are calculated at the constant time interval of phase separation and spherically averaged in the same way as described in the previous paper.[15]

Results and Discussion

Figure 1 shows the time evolution of structure factor $S(q,t)$ plotted against the scattering vector q during the phase separation for an A/B binary and three different A/B/C-*b*-D ternary blends containing block copolymers with $N = 12$ but different compositions. As the phase separation proceeds, a distinct maximum of structure factor appears and its value S_{max} increases, and the peak position q_{max} at which the structure factor has the

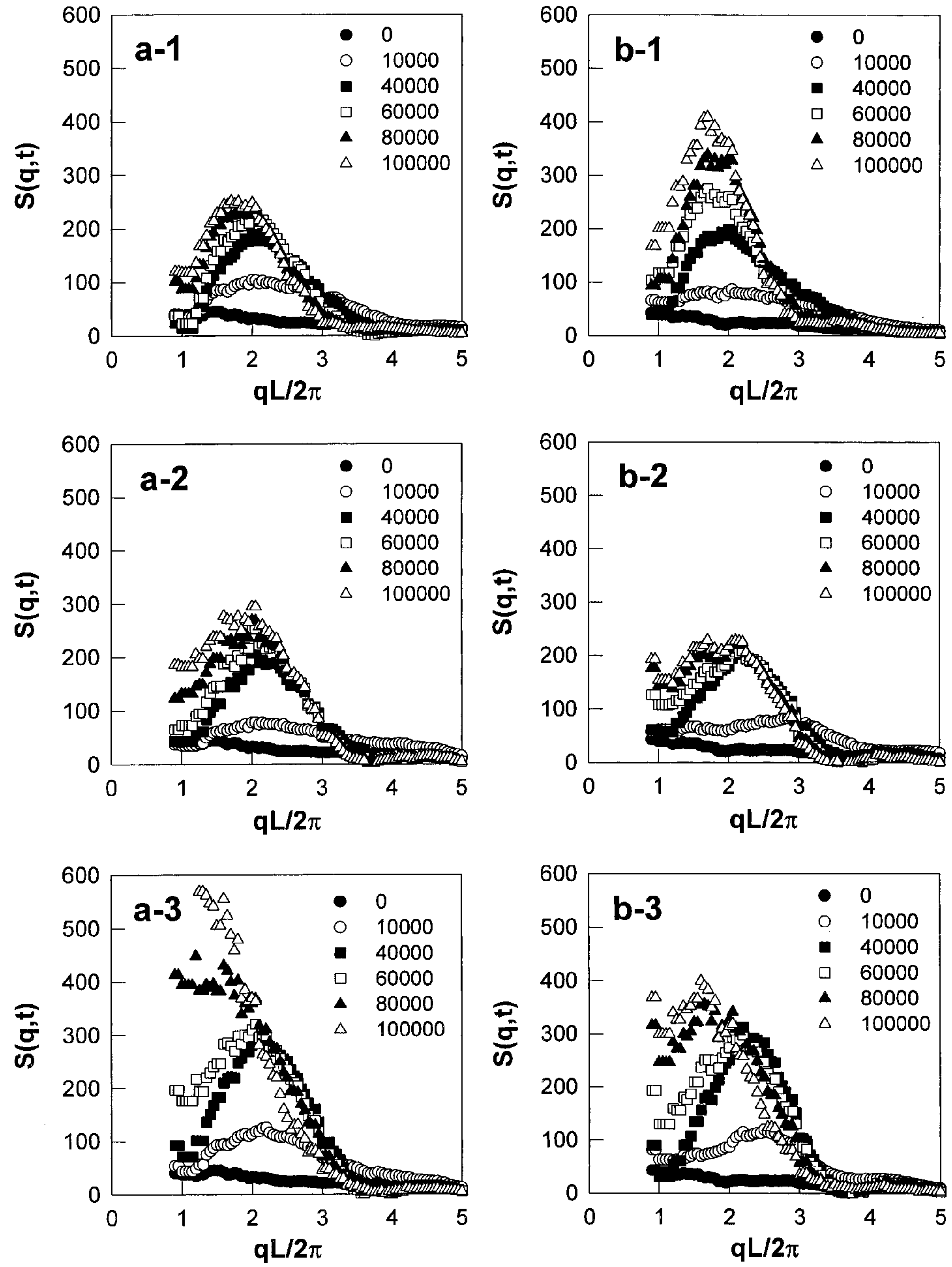

Figure 2. Time evolution of structure factor during the phase separation for A/B/C-*b*-D blends with (a) $N = 18$ and (b) $N = 30$. The numerals 1, 2, and 3 denote $f = 0.5$, $f = 0.7$, and $f = 0.9$, respectively.

maximum shifts toward a smaller q in all blends. This general trend indicates that the periodic concentration fluctuation grows and the coarsening processes occur in the later stage of phase separation. However, as shown in Figure 1, the phase separation proceeds in a different manner on the temporal and spatial scales, depending on the copolymer composition. Figure 1b shows that the rate of phase separation process is significantly suppressed by the addition of a symmetric diblock copolymer ($f = 0.5$), as compared to Figure 1a corresponding to the A/B binary blend without block copolymer. On the other hand, the asymmetric block copolymers do not reduce the growth rate of the phase-separated domains as effectively as the symmetric one, as shown in Figures 1c and 1d, although the structure factor maxima are slightly lowered compared to the binary blend without block copolymer. Therefore, it is concluded that, for block copolymers whose chain lengths are comparable to those of homopolymers, a symmetric structure is more effective in the retardation of phase separation of immiscible polymer blends than asymmetric ones.

Figure 2 shows the scattering profiles for the blends in the presence of block copolymers with longer chain lengths, and the trends associated with the copolymer composition are quite different from that observed in Figure 1, although the addition of a block copolymer always reduces the rate of phase separation. The asymmetric block copolymer with $N = 18$ and $f = 0.7$ (Figure 2a-2) shows the retardation effect to almost the same extent as the symmetric one (Figure 2a-1), but the $q_{\max}$ of $f = 0.7$ is slightly larger than that for $f = 0.5$, indicating that the average size of phase-separated domains is slightly smaller for $f = 0.7$. However, as the asymmetry is increased further from $f = 0.7-0.9$ as shown in Figure 2a-3, the phase separation proceeds

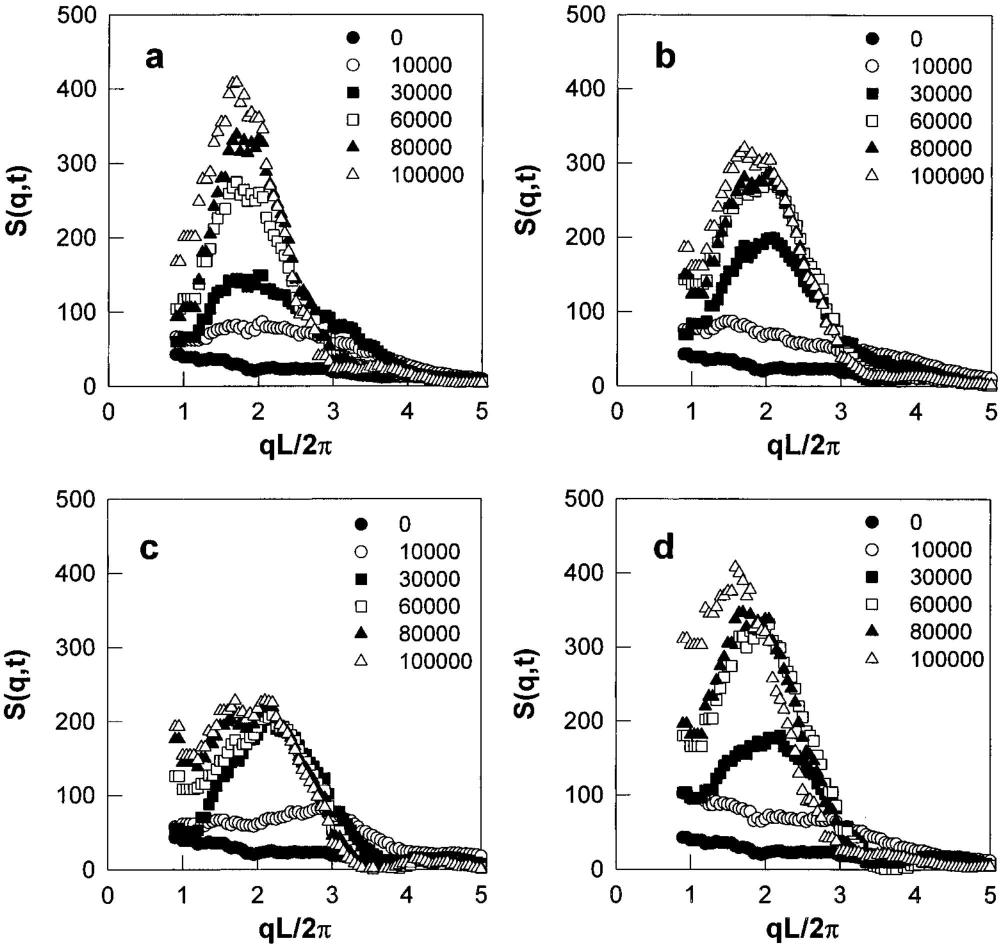

Figure 3. Time evolution of structure factor during the phase separation for A/B/C-*b*-D blends with (a) $f = 0.5$, (b) $f = 0.6$, (c) $f = 0.7$, and (d) $f = 0.8$. The total chain length of block copolymers is 30.

faster, indicating that the retardation effect is diminished. On the other hand, as the chain length of block copolymer is increased further from $N = 18$ to 30, the polymer blend with an asymmetric block copolymer of $N = 30$ and $f = 0.7$ (Figure 2b-2) exhibits slower process of phase separation than that with the symmetric one (Figure 2b-1), indicating that an asymmetric block copolymer is more effective in slowing the phase separation and thus can be used as a better compatibilizer than a symmetric one. For the blend with a block copolymer of $N = 30$ and $f = 0.9$ (Figure 2b-3), however, the phase separation becomes faster compared to the blend with a block copolymer of $f = 0.7$, but one can still observe a retardation effect as compared with the results observed for the blends with block copolymers of shorter chain lengths, i.e., $N = 12$ and $N = 18$ (Figures 1c and 2a-3). Therefore, in block copolymers with longer chain lengths than the homopolymers, an asymmetric structure is more effective in the retardation of phase separation and thus better in the compatibilization of the immiscible polymer blends than a symmetric one.

To observe these features more clearly, we also simulated the blends in the presence of the block copolymers of $N = 30$ with $f = 0.6$ and $f = 0.8$ to obtain more continuous spectrum of the copolymer composition effect. As the composition of block copolymer is changed from 0.5, to 0.6, to 0.7, the phase separation becomes slower as shown in Figure 3. However, as the asymmetry increases further to $f = 0.8$, the phase separation becomes faster, giving higher $S_{\max}$ and lower $q_{\max}$ on the same time scale. In summary, an asymmetric block copolymer with the chain length of $N = 30$ and the composition of $f = 0.7$ is most effective in slowing the growth rate of the phase-separated domains. This behavior is qualitatively consistent with the theoretical prediction by the calculation of stability limits through the RPA-based theory originally proposed by Leibler.[19] Tanaka and Hashimoto[20] calculated the stability limit by the RPA-based theory and reported that the compatibilizing effect of block copolymer in incompatible blends depends not only on the molecular weight ratios of homopolymer to block copolymer N_A/N and N_B/N but also on the volume fractions of the homopolymers relative to the volume fraction f in the block copolymer. We followed their scheme and found that the block copolymer with the composition of $f = 0.75$ showed most effective in slowing the phase separation for our system where the blend ratio was fixed at A/B = 75/25 (v/v). Our simulation result that the block copolymer with $f = 0.7$, which is nearest to $f = 0.75$, is most effective in the retardation of phase separation agrees with their theoretical prediction qualitatively. This observation may arise from the so-called curvature effect. Recently, Kawakatsu et al.[23] investigated by means of the hybrid model the dynamics of phase separation of the binary mixtures in the presence of added surfactant molecules with an asymmetric shape. Although they considered only the case where the volume fractions of the components of the binary mixture are equal, they reported that, as the phase separation proceeds, the morphology changes from a bicontinuous structure to a globular domain structure, the latter having a slower growth rate than the former, and that such a morphological change

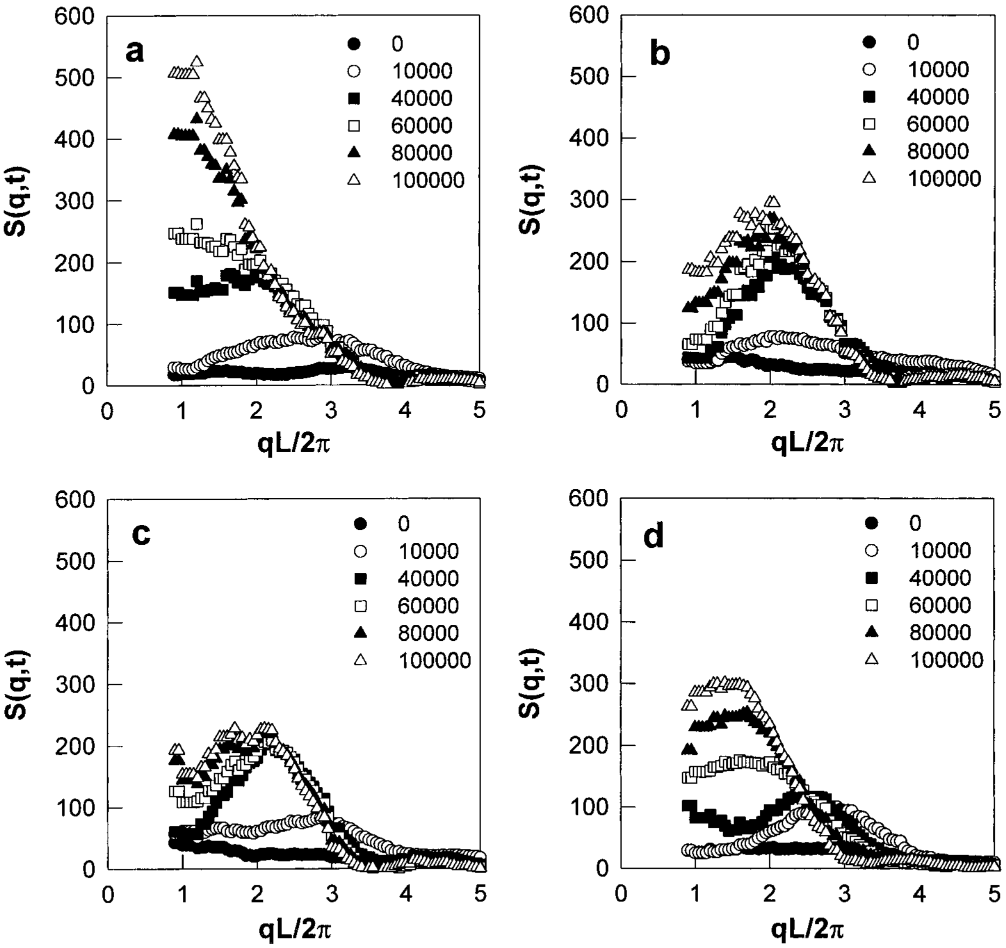

Figure 4. Change of mean-squared radii of gyration of block copolymer of chain length of (a) $N = 12$, (b) $N = 18$, and (c) $N = 30$ in A/B/C-*b*-D blends with different compositions.

is caused by the spontaneous curvature of the interface where the asymmetric surfactants are absorbed. Leibler[18] also investigated the effects of the curvature properties of the interface on the formation of droplets through the theoretical approach. He showed that the size of droplets is essentially determined by the spontaneous radius of curvature and that the size becomes smaller as the asymmetry of copolymers increases. Therefore, the curvature properties of the interface obtained during the phase separation are the main factor controlling the efficiency of a block copolymer, and the effect of the block copolymer composition becomes more clearly in the late stage of the phase separation, because the well-defined interface is formed in the late stage and thus the concentration of block copolymers at the interface becomes somewhat high in this time regime. This characteristic feature is exactly the same as that observed in our simulations.

Figure 4 shows variations of the radius-of-gyration of the block copolymers in the ternary blends during the phase separation. As the phase separation has proceeded, the block copolymers migrate into the interface between two phases and each block copolymer penetrates into its respective homopolymer phase having favorable interaction, leading to the extension in the chain conformation of the block copolymer and thus to the reduction of the interfacial tension. A closer examination of Figure 4 indicates that the longer the block copolymer chains, the more extended the chain conformation. Especially, the extension level of block copolymer chains with five different compositions shown in Figure 4c exactly matches to the degree of the phase separation observed in Figures 2 and 3. Above results clearly demonstrate that the chain extension of block copolymer absorbed at the interface reduces the interfacial tension and consequently retards the phase separation.

Figure 5 shows the effects of the total chain length on the dynamics of the phase separation of the immiscible polymer blend when the asymmetry of block copolymer is fixed at 0.7. As the chain length of block copolymer increases from 12 to 30, the growth rate of the phase-separated domains becomes slower. However, upon a further increase of the chain length to $N = 54$ from $N = 30$, the trend is reversed and the retardation effect of the block copolymer becomes rather worse. There exists an optimum chain length to exhibit the best retardation effect, as observed for a symmetric diblock copolymer in the previous work.[15] But the optimum length becomes longer for the asymmetric block copolymer than for the symmetric one. The difference in optimum chain length may come from the difference in the potential of micelle formation between asymmetric and symmetric block copolymer. Vilgis and Noolandi[24] theoretically calculated the interfacial tension of immiscible homopolymers in the presence of block copolymer and reported that the longer blocks lead to a larger reduction in the interfacial tension, but there is a practical limit for the chain length of block copolymer, beyond which the diblock copolymer prefers to associate into micelles in the bulk of the blend. However, it should not be excluded that an optimum chain length may arise from the kinetic effect.

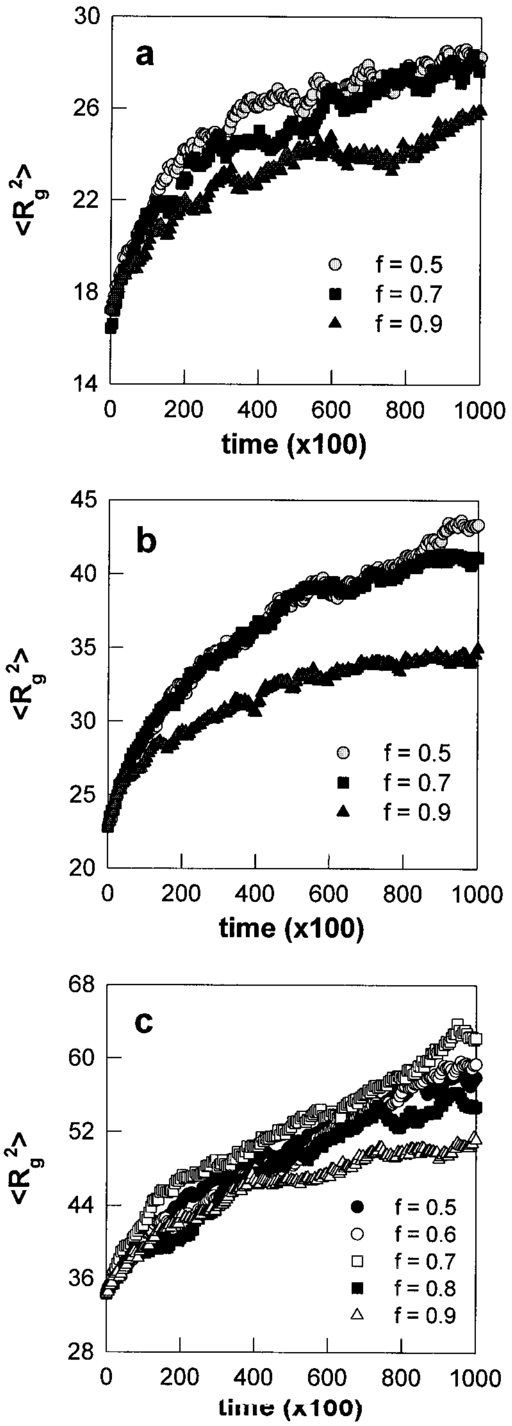

Figure 5. Time evolution of structure factor during the phase separation for A/B/C-*b*-D blends with (a) $N = 12$, (b) $N = 18$, (c) $N = 30$, and (d) $N = 54$. The composition of block copolymers is 0.7.

To more clearly examine the phase-separation process in the late stage, we calculated the characteristic wavenumber. The characteristic wave number q_1, which is the inverse of a domain correlation length, is defined as the first moment of the structure factor and given by eq 1:

$$q_1(t) = \sum_q qS(q,t) / \sum_q S(q,t) \qquad (1)$$

Figure 6a shows the variation of q_1 with time in the double-logarithmic plots for the ternary blend containing a block copolymer of $N = 12$ and $f = 0.7$. It can be seen that there are two different time regimes. The first is the so-called linear regime. In this regime, the characteristic wave number does not change and only the peak height of $S(q,t)$ grows. Such behavior is shown in Figure 6a as a plateau at $t < 7500$. After this linear regime, $q_1(t)$ decreases with time due to the nonlinear effects. In this regime, the behavior $q_1(t)$ can be described in terms of a power law[25] as given by eq 2:

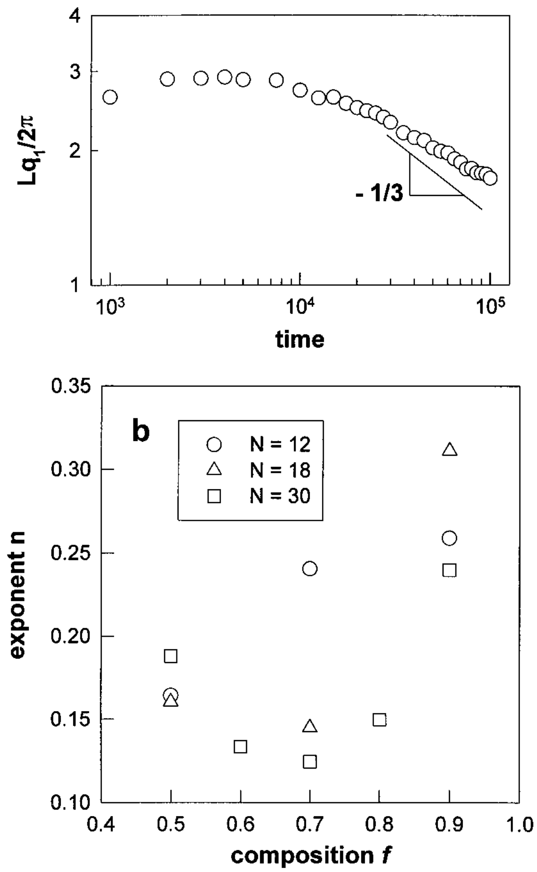

Figure 6. Change of the characteristic wave number q_1 with time for A/B/C-*b*-D blends with $N = 12$ and $f = 0.7$, and (b) the change of exponent n at the late stage of phase separation with different chain lengths and compositions of block copolymer.

$$q_1(t) \sim t^{-n} \qquad (2)$$

where the exponent n is known to be dependent upon the phase-separation mechanism and the composition of blend. However, it is generally accepted that n has an asymptotic value of $^1/_3$ for $t \rightarrow \infty$ for the mixtures separated without the hydrodynamic interaction, assuming that the Lifshitz–Slyozov's mechanism of coarsening holds.[26] Thus, the behavior ($n < {}^1/_3$) shown in Figure 6a indicates that the system still approaches to the asymptotic value in the time regime examined. Figure 6b shows the exponent for the A/B/C-*b*-D blend as a function of the composition of block copolymer. Here a lower value of exponent n means that the phase separation proceeds to a lesser extent, i.e., the growth rate of the phase-separated domains becomes slower on the same time scale. As shown in Figure 6b, the value of exponent n depends on the chain length and the composition of block copolymers. For shorter chain length, a symmetric block copolymer has the lowest value, but for longer chain length, an asymmetric block copolymer of $f = 0.7$ has the lowest. This behavior is exactly consistent with that observed in the structure factor profiles.

The characteristic features of the phase-separated structure can well be extracted by calculating the scaled structure factor, $F(x)$, as done in the previous work,[15] which is defined through the following relationship:

$$S(q,t) = Mq_1(t)^{-d}F[q/q_1(t)] \qquad (3)$$

where $q_1(t)$ is the first moment of structure factor and M is an arbitrary normalization constant. If the growth of the phase-separated domains obeys a dynamical scaling law, the $S(q,t)$ of the unmixing systems can be scaled with a single length parameter $q_1(t)$, i.e., there exists self-similarity among the phase-separated structures developed at different time scales in the late stage. This scaling law can also be applied to the polymer blend systems containing a small amount of the symmetric block copolymer.[11] Actually we have proved in a previous paper that this is quite true.[15] Here, we investigate whether the dynamical scaling law can be applied to the A/B/C-*b*-D blend system containing an asymmetric block copolymer and whether a universal scaling function can be obtained. We define the scaled structure factor $F(x)$ as follows:

$$F(x)\ (L/\pi)q_1^{\,3}S(q,t)/\sum_q q^2 S(q,t) \qquad (4)$$

where $x = q/q_1(t)$ and L is the size of simulation box. In order to test the dynamic scaling law for A/B/C-*b*-D ternary systems, the scaled structure factor $F(x)$ is plotted against x. Figure 7 shows that the scaled structure factors calculated by eq 4 fall on a single curve and become universal with time. This indicates that the amplitude of concentration fluctuation reaches an equilibrium value and that the phase-separated domains grow with a dynamical self-similarity in this time regime.

The scaled structure factors are plotted against x on the double logarithmic scale for A/B/C-*b*-D blends of $N = 30$ with different copolymer composition. As shown in Figure 8, the scaled structure factors are universal at $x < 2$, independent of the composition of block copolymer, but at higher x deviate from the universality. This behavior indicates that the mechanism of growth of the global structure is independent of the composition of block copolymer used, but the growth of local structure such as the interfacial structure is dependent upon the composition of block copolymer, indicating that the growth of local structure cannot be scaled with the length parameter $q_1(t)$ which is relevant to the global structure. This result agrees well with the experimental observations of Izumitani and Hashimoto[11] made for A/B/A-*b*-B blend system. Another interesting feature observed in Figure 8 is that one can also observe the higher-order maximum of the scaled structure factors, implying the existence of spatially periodic domains.[27] However, the noisiness of the data makes it difficult to draw a definite conclusion.

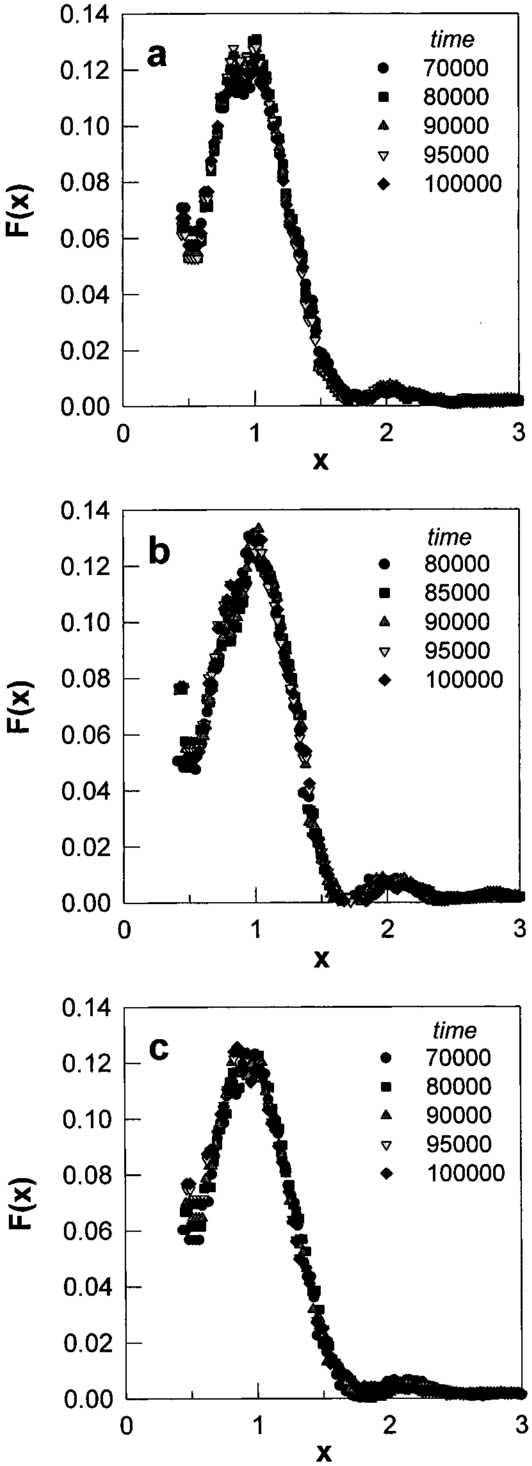

Figure 7. Scaled structure factor $F(x)$ for A/B/C-*b*-D blends with (a) $f = 0.6$, (b) $f = 0.7$, and (c) $f = 0.9$. The total chain length of block copolymers is 30.

Conclusions

In this paper, we investigated by means of a Monte Carlo simulation the effects of the composition of block copolymer, when added to the immiscible binary polymer blend, on the dynamics of phase separation, which is the extension of our previous work.[15] We found that the retardation of the phase separation observed in A/B/C-*b*-D blends due to the addition of the block copolymer is significantly affected by the composition of block copolymers, depending on the chain length of block copolymer. For shorter chain length than the homopolymers, a symmetric block copolymer has better effect in retarding the phase separation. However, for longer chain length than the homopolymer, an asymmetric one becomes more effective in slowing the growth rate of phase-separated domains. The composition of block copolymer exhibiting the best effect is determined mainly by the composition of homopolymer blend. The reason for this observation can be explained by considering the curvature properties of the interface, i.e., the bend elasticity and the spontaneous radius of curvature of the interface formed during the phase separation. We also observed that there exists an optimum chain length

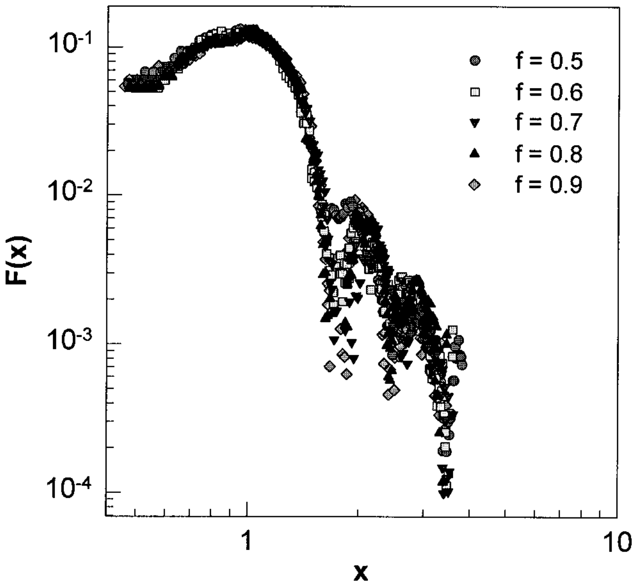

Figure 8. Scaled structure factor $F(x)$ for A/B/C-*b*-D blends with different compositions of block copolymers at the constant chain length $N = 30$.

which shows the best retardation of phase separation for the asymmetric block copolymer, but this optimum length increases as the composition of block copolymers becomes asymmetric. In any case, the retardation effect of block copolymer arises from the reduction in the interfacial tension due to the accumulation of block copolymers at the interface. The phase separation process in the late stage was analyzed on the basis of the scaled structure factor $F(x)$. We found that the scaled structure factor at $x < 2$ is independent of the structure of block copolymers added to the immiscible blend, implying the self-similar growth of the global structure. However, $F(x)$ is not universal at $x > 2$ but dependent on the composition of block copolymer, indicating that the interfacial structure of the phase-separated domains cannot be scaled with the characteristic wavenumber $q_1(t)$ which is relevant to the global structure. To draw some definite conclusions on this matter, further study is needed.

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