Monte Carlo Simulation of the Phase Separation Dynamics of Polymer Blends in the Presence of Block Copolymers. 1. Effect of the Interaction Energy and Chain Length of the Block Copolymers

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ABSTRACT: The effects of the addition of a small amount of C−D diblock copolymer on the phase separation kinetics of an A/B polymer blend are investigated by computer simulation. The rate of the phase separation process is significantly suppressed by the addition of block copolymers due to the reduction of the interfacial tension. This retardation effect is considerably dependent on the interaction energies (ϵ_{AC} and ϵ_{BD}) between the copolymer blocks and their respective homopolymers and the chain length of block copolymers. In the late stage of phase separation, the growth of the phase-separated domains obeys a dynamical scaling law in the cases of polymer blends both with and without a block copolymer. By a scaling analysis, we obtain universal scaling functions in the late stage which are nearly independent of the interaction energies and chain lengths of the block copolymer. This behavior indicates that the domain grows with dynamical self-similarity irrespective of the types of block copolymer used, although the block copolymer added to the immiscible polymer blend reduces the growth rate of the phase-separated domains.

Introduction

The mechanism and dynamics of ordering processes occurring during phase transitions have been the subjects of many theoretical and experimental investigations in the field of polymer physics,[1,2] as well as in the cases of small molecules such as simple fluid mixtures, metallic alloys, and inorganic glasses.[3] Polymer−polymer mixtures offer especially attractive model systems for probing the behavior of phase separation due to the large spatial and temporal scales and the large cooperative effect which is unique in polymers,[4] and which make structure formation easy to follow experimentally. Such studies involve challenging problems in the statistical physics of nonequilibrium and nonlinear systems and also require a generalization of statistical methods developed for small-molecule systems to take into account the connectivity of monomers.

A number of experimental and theoretical studies have been reported on the phase separation of polymer blends. Most of them are concerned with the effects of the basic molecular parameters and thermodynamic variables of blend systems on the mechanism and kinetics of phase separation.[1,3,5−10] However, there are few studies of the effects of the addition of a small amount of block copolymer as a compatibilizer on the phase separation behavior of polymer blends. On the other hand, the role of a block copolymer as a compatibilizer in immiscible polymer blends is well accepted on the basis of equilibrium statistical mechanics.[11,12] In this case, the copolymer chains migrate to the interface, where the blocks penetrate into their respective homopolymer phases. Interpenetration of the copolymer block into its respective matrix phase may result in a decrease of conformational entropy, which is compensated by the reduction of the unfavorable enthalpy between the two immiscible phases. The net effect is a decrease of interfacial free energy, leading to a decrease in the average size of the dispersed phase. Also, the block copolymer molecules that accumulate at the interface act as binders of the two polymer phases and thus mechanically enhance adhesion between the two phases. Although the basic principles of the role of block copolymers in immiscible polymer blends appear to be well established, the precise mechanisms and factors optimizing the role of block copolymer have not yet been understood clearly. Moreover, in real polymer processing, thermodynamic equilibrium is not usually achieved, and therefore kinetic and equilibrium aspects should be considered simultaneously. In this regard, it is meaningful to investigate the effects of block copolymers on the dynamics of phase separation of a polymer blend.

The effects of a block copolymer on phase separation kinetics in the late stage were reported by Roe et al.[13,14] for off-critical mixtures of low molecular weight polybutadiene (PB) and polystyrene (PS), and it was found that the growth rate of the average particle size of the dispersed phase is reduced upon adding a small amount of the styrene−butadiene diblock copolymer due to the reduction of the interfacial tension between the demixed phases, resulting from the accumulation of block copolymer at the interface. Recently, Hashimoto and Izumitani[15,16] experimentally studied the dynamics of the phase separation process for near-critical mixtures composed of PB and poly(styrene-*rac*-butadiene)(SBR) to which a small amount of SBR-*b*-PB is added. They observed that the growth rate decreases when block copolymer is added to the binary blend, and they also found by scaling analysis that the structure evolved is independent of the presence of the block copolymer in the blends. On the other hand, Laradji et al.[17] and Kawakatsu et al.[18] investigated the phase separation of binary mixtures containing surfactants by theory and computer experiments. The former investigated the dynamics of phase separation by means of a time-dependent Ginzburg−Landau model, solving the Langevin equations for two scalar fields, and the latter studied the same problem using a hybrid model. Both reported that, in the late stage, the coarsening rate of

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the domain structures is considerably decreased due to the reduced interfacial tension of the surfactant-adsorbed interfaces.

In this work, we investigate the effects of C−D diblock copolymer on the phase separation of A/B immiscible polymer blend by a Monte Carlo simulation technique, where the block copolymer used may consist of blocks chemically different from the A and B homopolymers. Vilgis and Noolandi[19] extensively studied the compatibility effects of block copolymers in A/B/C-*b*-D systems in the presence of solvent by means of a statistical theory. They calculated the interfacial properties such as interfacial tension, interfacial thickness, and concentration profiles and found that, under some circumstances, a C−D block copolymer can act as a compatibilizer in an immiscible blend. However, experimental results on the phase separation dynamics of such a system as an A/B/C-*b*-D have not been reported yet. Thus, we examine the effects of the pairwise interaction parameters between a copolymer block and the homopolymers and the chain length of the block copolymer on the phase separation dynamics of an A/B/C-*b*-D system using a Monte Carlo simulation.

Model and Simulation Method

The simulations are performed on a simple cubic lattice of 50 × 50 × 50 sites with periodic boundary conditions. We simulate an A/B binary blend system and then A/B/C-*b*-D ternary blend systems containing various types of block copolymers, where all polymer chains are represented as self-avoiding and mutually avoiding near-neighbor walks on the lattice. The composition of homopolymers A and B is fixed at 75/25 v/v in all cases, and the homopolymer chains have the same chain length, i.e., $N_A = N_B = 10$. The phase separation of homopolymer chains A and B is induced by introducing a positive pairwise interaction energy ϵ_{AB} ($=\epsilon'_{AB}/k_BT$, where k_B is the Boltzmann constant and T is temperature). In all cases, as ϵ_{AB} has a constant positive value (+0.5), homopolymers A and B are phase-separated. The amount of block copolymer added to the immiscible binary blend is about 5.7% of the total sites occupied by all the polymer chains. The chain length of the block copolymer (N_{block}) is varied from 12 to 30, although the content of the added block copolymer is kept constant, and all the block copolymers used in this work have a symmetric structure ($N_{block} = N_C + N_D$, where $N_C = N_D$). The total volume fraction of polymers is set at 0.61. Because the linear dimension of the lattice is much larger than the chain dimension of all the polymer chains, finite size effects are not considered here. In particular, even after the phase separation has proceeded sufficiently, the size of the phase-separated domains does not reach the system size for any blend systems in this work, which enables us to neglect size effects. Since the symmetric diblock copolymer is composed of chemically different blocks from the homopolymers, there exist six interactions including ϵ_{AB}. If the interaction energies between the homopolymer A and the block C (ϵ_{AC}) and between the homopolymer B and the block D (ϵ_{BD}) are negative, then the added block copolymers can play the role of a compatibilizing agent in the immiscible blend. In particular, in this work, we change the magnitude of the negative values of ϵ_{AC} and ϵ_{BD} systematically and examine the effects of their relative magnitude. A positive value of 0.5 is given to all other interaction energies such as ϵ_{AD}, ϵ_{BC}, and ϵ_{CD}, and thus there is no miscibility between their corresponding segments. The interaction energies between identical segments and between each segment and empty sites are set to zero.

We use the bond fluctuation model[20] to simulate the motion of the polymer chains on the lattice. In this model, each segment occupies eight lattice sites of a unit cell, and each site can be a part of only one segment (self-avoiding walk condition). This condition is necessary to account for the excluded volume of the polymer chains. For a given chain, the bond length between two successive segments can have all possible lengths from 2 to $10^{1/2}$, restricted to a particular set of vectors.[21] For a cubic lattice, the possible vectors can be derived from the basic set {(2,0,0), (2,1,0), (2,1,1), (2,2,1), (3,0,0), and (3,1,0)}. This set of bonds guarantees the self-avoiding condition and recognizes the nonintersection rule in the course of their motion. The polymer chains move by random diffusion jumps of their segments to nearest-neighbor lattice sites, simultaneously obeying the excluded volume and bond length constraints. The specific scheme for moving a polymer chain is as follows. First, a chain is chosen at random, and then a segment on that chain is also picked randomly. An attempt is made to move the chosen segment in one of six possible directions. If no other segment is present in the new location, and if the bond length of the new bonds satisfies the bond length constraints, then the move is accepted, and the simulation proceeds by choosing another chain and segment randomly. However, if the excluded volume conditions and bond length constraints are not met, then the move is rejected, and the segment is restored to its original position. The interaction energies given above exert an effect through the Metropolis algorithm.[22] Here, moves that decrease the energy of the system are accepted with a unit probability, and ones that increase the energy of the system are accepted with a probability $\exp(-\Delta E/k_BT)$. The parameter ΔE is the energy change before and after each move.

In all cases, the initial configurations are generated randomly as follows. First, from a randomly chosen but strictly self-avoiding site on the lattice, the chains grow by adding bonds to each chain end in a random direction. To more effectively add bonds to chains in the lattice, only the bond vector {2,0,0} is used, which results in chain structures similar to those from the normal lattice model. The system is then run with all interaction energies set to zero using the bond fluctuation algorithm for enough time to reach equilibrium.

To investigate the time evolution of the long-range ordering, we compute the collective structure factor of the system.[23] The starting point of the description is a Flory−Huggins lattice model of the polymer mixture, where a local concentration variable $\phi_A{}^j = 1$ if the lattice site j is occupied by an A segment and otherwise zero, and $\phi_B{}^j = 1$ if the lattice site is occupied by a B segment and otherwise zero. Here, we do not include the contribution from the block copolymer chains in calculating the structure factors, since the added block copolymer is very small in quantity compared with the homopolymers and since we are mainly concerned with the phase separation of homopolymers A and B. The time-dependent collective structure factor is then given by

$$S(\mathbf{q},t) = \langle [\sum_{r_j} \exp(i\mathbf{q}\cdot\mathbf{r}_j)(\phi_B{}^j - \phi_A{}^j - \langle \phi_B{}^j - \phi_A{}^j \rangle)]^2 \rangle / L^3 \quad (1)$$

where $L = 50$ and $\langle\ \rangle$ denotes a thermal statistical average. This quantity represents the Fourier transform of the pair correlation function and is spherically averaged as follows:

$$S(q,t) = \sum_{|\mathbf{q}|} S(\mathbf{q},t) / \sum_{|\mathbf{q}|} 1 \quad (2)$$

with $q = (2\pi/L)n$, where $n = 1, 2, ...$ denotes that, for a given n, a spherical shell is taken as $n - {}^1\!/_2 \leq qL/2\pi \leq n + {}^1\!/_2$.

Results and Discussion

In our model, time is measured in a Monte Carlo step (MCS). One MCS means that, on average, every monomer has attempted to move once. All the simulations are run up to 10^5 MCS, and five independent runs are averaged together to improve the statistics for each case.

Figure 1 shows the time evolution of structure factor plotted against the scattering vector during phase separation for an A/B binary blend. As the phase separation proceeds, the maximum structure factor becomes larger at constant wavenumber q in the early stage, but after a certain period of time the wavenumber

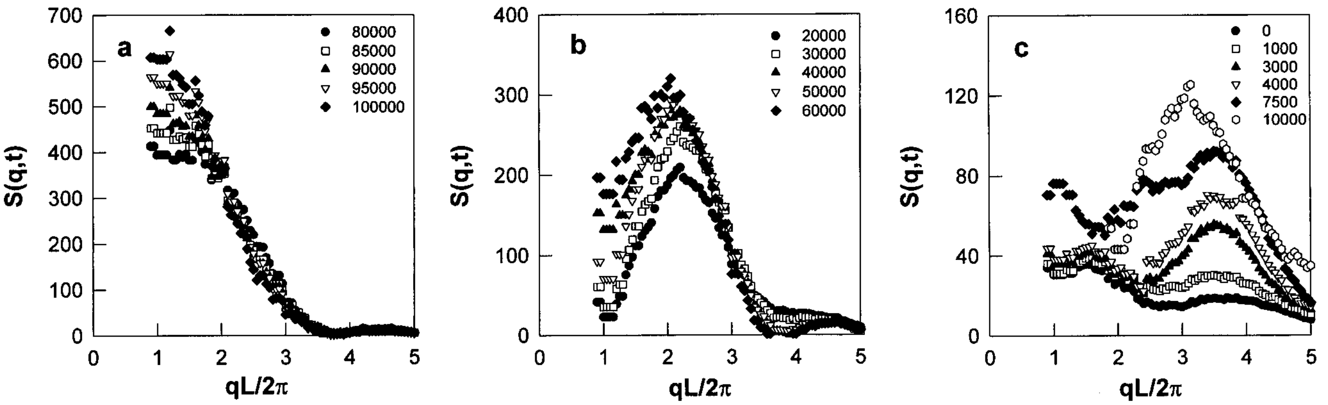

Figure 1. Time evolution of structure factor during the phase separation for A/B binary blend. Time elapses in order of c to a. The numbers next to the symbols correspond to the numbers of MC time steps which have taken place.

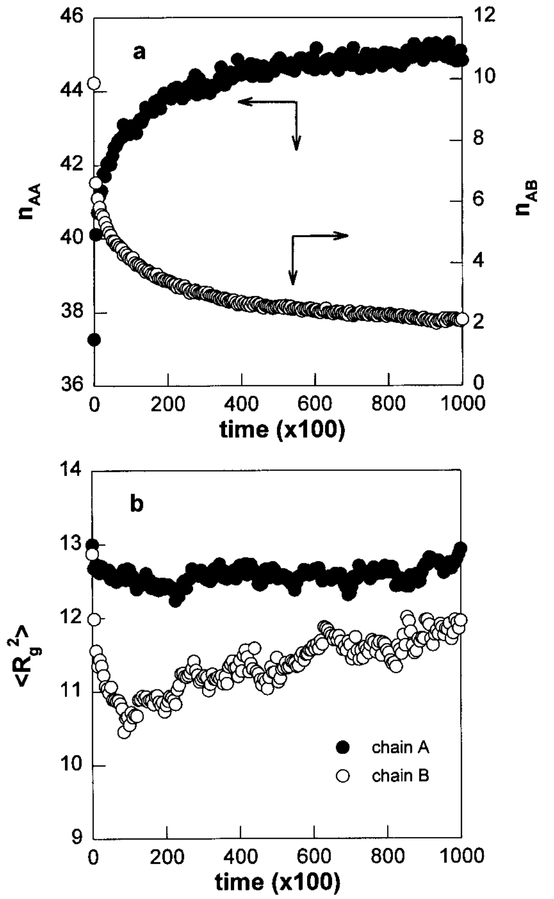

Figure 2. Change of (a) the number of nearest-neighbor contacts and (b) the linear dimension of chain A and B with time for A/B binary blend.

at the maximum shifts toward smaller q with further increase of structure factor, indicating the onset of coarsening. The features shown in Figure 1 are typically observed in real systems by light scattering or small-angle X-ray scattering, and thus it is believed that our model adequately describes the behavior in real systems.

The process of phase separation is also accompanied by a change in the number of nearest-neighbor contacts and the linear dimensions of the chains, as shown in Figure 2. Figure 2a shows the variation of the number of contacts per chain between the same kind of segments (A−A) on different chains and between the different kind of segments (A−B) with the phase separation time. The number of contacts between the same kind of segments, n_{AA}, increases fast and then levels off, while the number of contacts between the different kind of segments, n_{AB}, decreases quickly in the early stage of phase separation and then levels off as the phase separation proceeds further. Figure 2b shows the variation of the radius of gyration of chains with time. In both cases of chains A and B, the contraction of coils occurs at the early stage of phase separation, the extent of which is larger for chain B, corresponding to the minor phase, than for chain A, corresponding to the major phase.

Figure 3 shows the time evolution of the structure factor during phase separation for an A/B/C-*b*-D ternary blend systems, with ϵ_{AC} ($=\epsilon_{BD}$) being equal to −0.1, −0.2, and −0.5, respectively, where $N_{block} = 12$ for all blend systems. The time evolution of the structure factors for blend systems containing block copolymers shows a behavior similar to that of a blend system without a block copolymer. However, a closer examination reveals that the block copolymer added to an immiscible binary blend retards the rate of coarsening, and this tendency is more clearly recognizable in the later stages of phase separation. These results obtained in computer simulations are consistent with the recent works observed in real polymer systems.[13−16] In the phase separation process, the interfacial tension between the two phases plays an essential role. According to the Lifshitz−Slyozov theory of Ostwald ripening by the evaporation−condensation mechanism, the rate of growth of the particle volume is, in fact, expected to be directly proportional to the interfacial tension. When a block copolymer is added to the binary blend, the copolymer chains tend to preferentially accumulate at the interface between the two phases and thereby lower the interfacial tension. Therefore, the added block copolymer considerably reduces the phase separation rate. However, in the very early stage of phase separation, the average domain size is quite small, and thus the proportion of interface is very large. This implies that the average concentration of block copolymers at the interface is relatively small, and consequently, the interfacial tension is large, leading to a strong driving force for the phase separation process. In the later stage, the concentration of the block copolymer at the interface increases with the increase of the domain size, resulting in a considerable reduction in the interfacial tension and thus in the driving force of phase separation. Accordingly, the retardation effect of a block copolymer is expected to become more pronounced in the later stage. When one compares the parts of Figure 3, one may realize that the retardation of phase separation by the addition of block copolymer becomes more

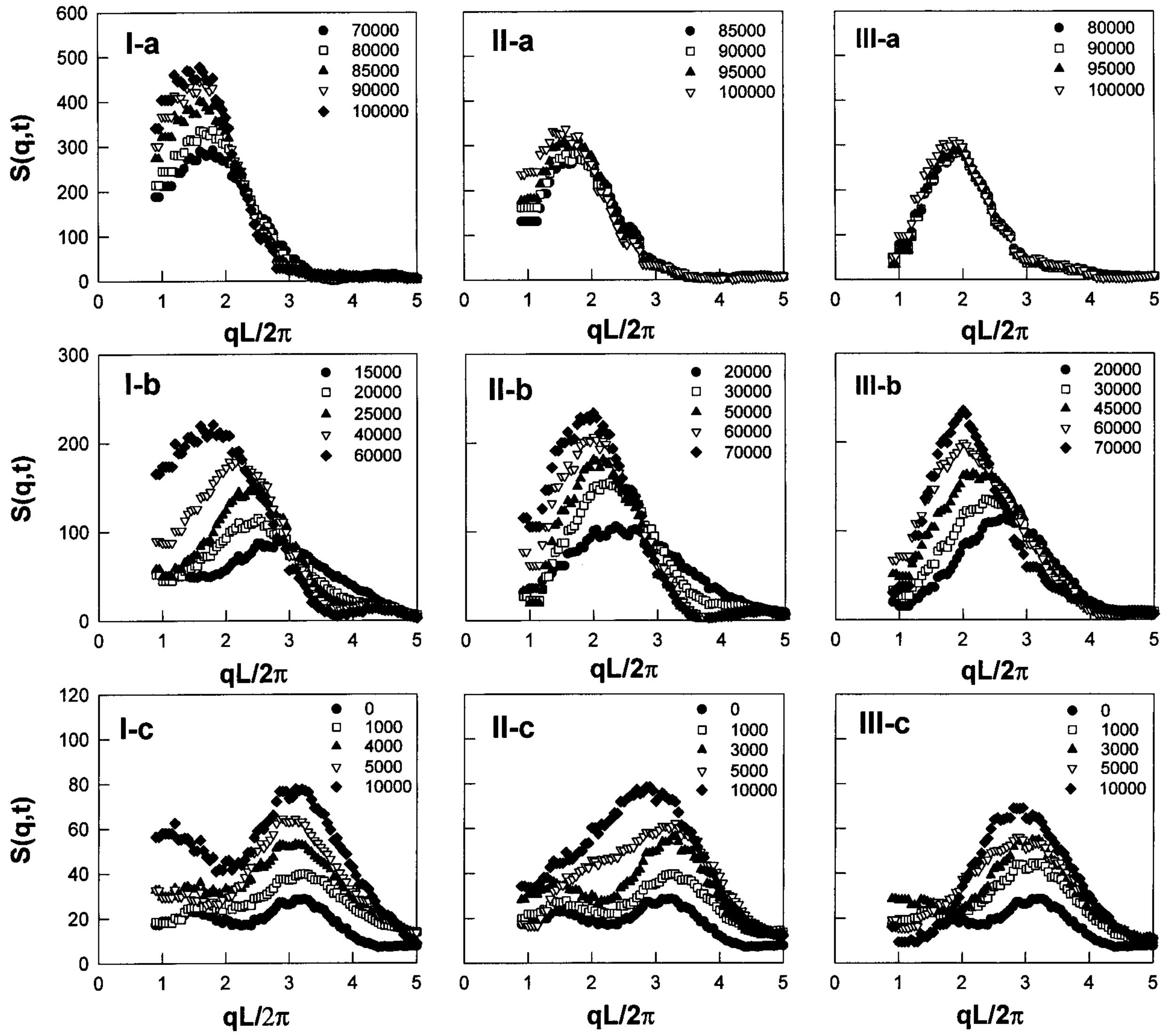

Figure 3. Time evolution of structure factor during phase separation for A/B/C-*b*-D ternary blends with ϵ_{AC} $(=\epsilon_{BD}) =$ (I) −0.1, (II) −0.2, and (III) −0.5, where $N_{block} = 12$ for all blends. Time elapses in order of c to a.

pronounced as the interaction energies (ϵ_{AC} and ϵ_{BD}) become more negative. This phenomenon seems to be closely related to the variation of the radius of gyration of block copolymers with the magnitude of interaction energy, as shown in Figure 4. The block copolymers migrate to the interface between the two phases, where the blocks penetrate into their respective homopolymer phases, leading to an increase in the linear dimension of block copolymer chains. The larger the interaction between the block and corresponding homopolymer, the larger the extension of block copolymer chains becomes. Consequently, the block copolymers with more negative interactions can accumulate more at the interface, causing a larger reduction in the interfacial tension.

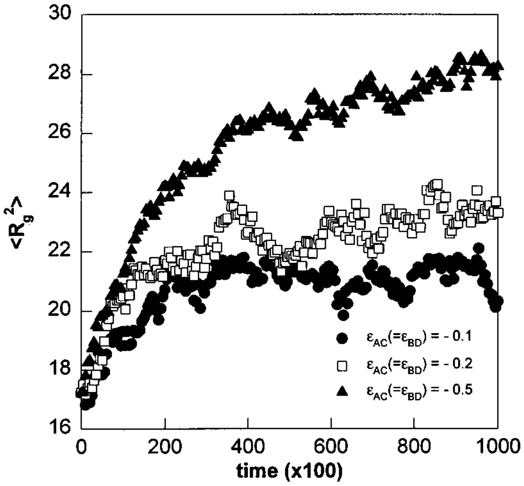

Figure 4. Change of mean-squared radii of gyration of block copolymer ($N_{block} = 12$) with different ϵ_{AC} $(=\epsilon_{BD})$ during the phase separation.

To compare the phase separation processes quantitatively, and in particular to observe the behavior of the structure factor in the later stage of phase separation, we analyzed the time dependence of the first moment, $q_1(t)$, of the structure factor as given in eq 3. It is well

$$q_1(t) = \sum_q qS(q,t) / \sum_q S(q,t) \qquad (3)$$

known that $q_1(t)$ is independent of time in the early stage and at somewhat later stage decreases with increasing time, signifying the onset of coarsening. In this time regime, the behavior of $q_1(t)$ may follow the scaling rule as given in eq 4, where the scaling exponent

$$q_1(t) \approx t^{-n} \qquad (4)$$

n is not a constant but is dependent on the phase

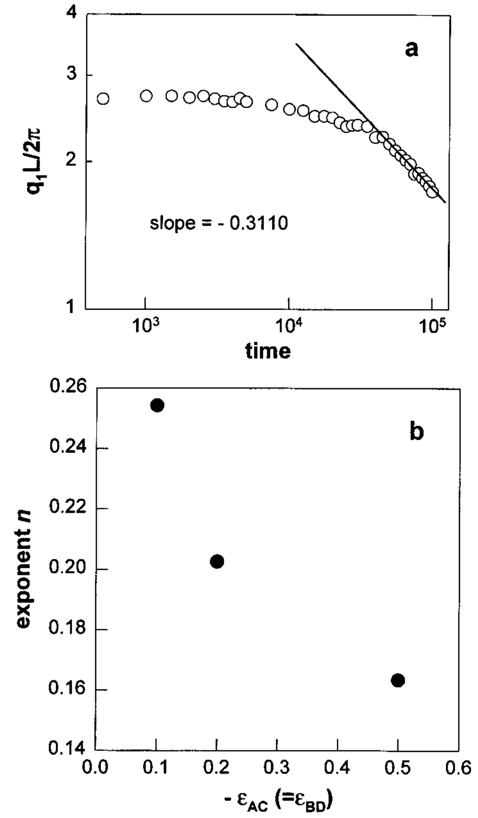

Figure 5. Change of (a) the first moment of structure factor with time for A/B binary blend and (b) exponent *n* at the late stage of phase separation with interaction energy $-\epsilon_{AC}$ ($=-\epsilon_{BD}$) for A/B/C-*b*-D ternary blends with $N_{block} = 12$.

separation time and temperature. It has been accepted, however, that the asymptotic scaling law for $t \rightarrow \infty$ gives $n = {}^1/_3$ when hydrodynamic effects are not considered, as in our simulation case, assuming that the Lifshitz–Slyozov mechanism of coarsening holds.[24] Figure 5a is a log–log plot of the first moment $q_1(t)$ as a function of time for an A/B binary blend. In the early stage, q_1 is nearly time-independent, but as the phase separation further proceeds, it decreases with time. From the slope in the time regime where q_1 decreases, we can obtain the scaling exponent *n*, which is very close to the accepted limiting value of ${}^1/_3$. Figure 5b shows the exponent *n* for A/B/C-*b*-D blend systems with various interaction energies. Because the exponent *n* is time-dependent in the later stage, as mentioned above, it is calculated in almost the same time interval for each system in order to compare the phase separation processes for all blend systems. As the interaction energies between the blocks and their respective homopolymers become more negative, the exponent *n* of the first moment of structure factor decreases, indicating that the block copolymer with more negative interaction energy retards the phase separation more effectively. This result is exactly consistent with that observed in the time evolution of structure factor.

Figure 6 shows the effect of chain length of the block copolymer on the phase separation for A/B/C-*b*-D systems. As the chain length of block copolymer increases from 12 to 18, the growth rate of phase-separated domains becomes slower, i.e., the peak intensity of structure factor decreases. But, when the chain length of block copolymer increases further to $N_{block} = 30$, the retardation effect of block copolymer rather becomes less, i.e., the peak height of structure factor increases, even compared with the case of $N_{block} = 12$. This result may also reflect the change of the linear chain dimension of the block copolymers. Figure 7 shows the change of the chain expansion ratio (α) defined as eq 5, where

$$\alpha = \langle R_g^{\ 2}\rangle_t / \langle R_g^{\ 2}\rangle_0 \tag{5}$$

$\langle R_g^2\rangle_t$ and $\langle R_g^2\rangle_0$ are the radii of gyration of block copolymer chains at time *t* and at the initial state, respectively. It can be seen in this figure that the block copolymer exhibiting the greatest retardation effect ($N_{block} = 18$) also has the largest chain extension ratio. According to the recent work by Vilgis and Noolandi[19] based on a statistical theory, in an A/B/C-*b*-D blend system, longer blocks lead to a larger reduction in the interfacial tension. In other words, the compatibilizing effect becomes better as the chain length of block copolymer increases. Most recently, Israels et al.[25] examined the interfacial behavior of symmetric A–B diblock copolymers in a blend of immiscible homopolymers A and B by means of numerical self-consistent field calculations, taking into account the formation of micellar or multilamellar phases. They found that short block copolymers form a multilamellar structure in the blend, while relatively long copolymers form microemulsions in a fully equilibrated system, indicating that longer blocks are more effective in reducing the interfacial tension between the homopolymers. These theoretical predictions are not entirely consistent with our results, because in our simulation the effect of the block copolymer increases as the chain length of the block copolymer increases up to $N_{block} = 18$, and then decreases as the chain length increases further. Although we do not have a clear explanation of this discrepancy

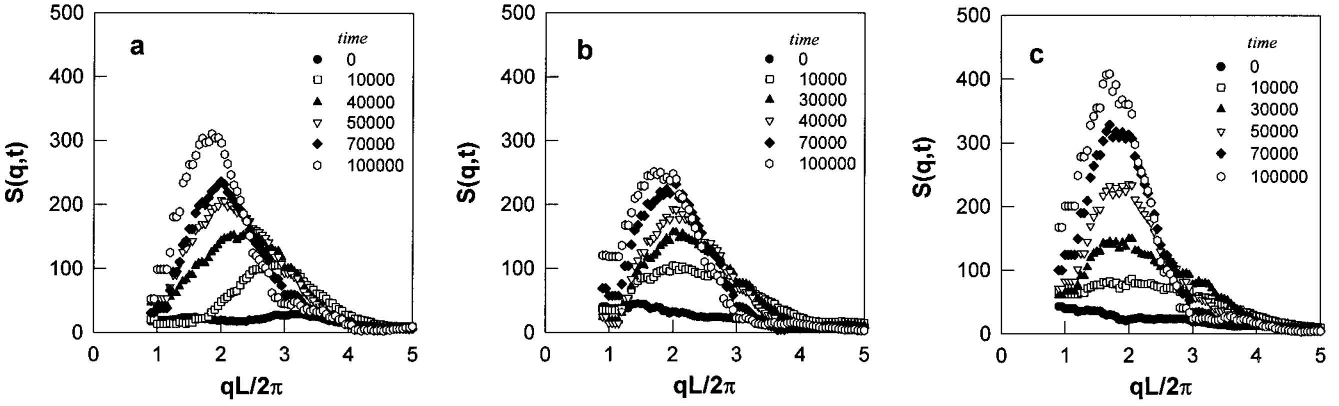

Figure 6. Dependence of chain length of block copolymer on the time evolution of structure factor during phase separation for A/B/C-*b*-D ternary blends with ϵ_{AC} ($=\epsilon_{BD}$) $= -0.5$: (a) $N_{block} = 12$, (b) $N_{block} = 18$, and (c) $N_{block} = 30$.

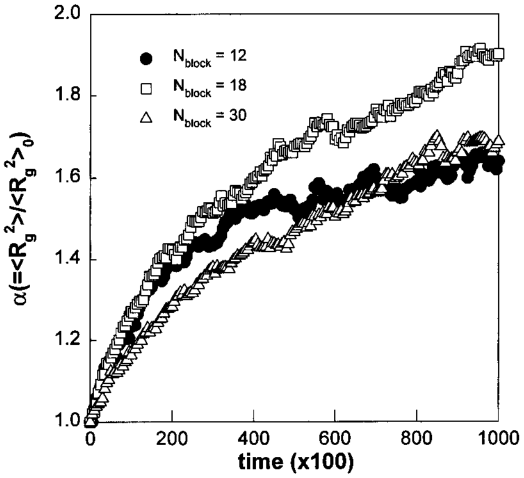

Figure 7. Change of chain expansion ratio α of block copolymers with different chain lengths during phase separation blend with ϵ_{AC} ($=\epsilon_{BD}$) = −0.5.

at present, we speculate as follows. As Vilgis and Noolandi pointed out in their paper,[19] there is a practical limit for a useful window of lengths, beyond which the block copolymer prefers to associate into micelles in the bulk of the blend. Israels et al.[25] also predicted that, although all finite-size micelles are unstable in ternary systems in thermodynamical equilibrium, nonequilibrium micelles may very well be stable in real systems, since the equilibration may be extremely slow. For this case, a limited emulsifying effect will be expected, and the effect of retarding the phase separation will not effectively be shown. On the other hand, Kawakatsu[26] investigated the phase separation dynamics of A/B/A-*b*-B ternary mixture using the time-dependent Ginzburg−Landau model combined with the density functional description of block copolymer melts. He showed that, when the block copolymer is sufficiently long, phase separation is dominated by the microphase separation of the block copolymer. Under this circumstance, as the chain length of block copolymer increases, the larger macrophase-separated domains are also obtained at the same time, which is a similar behavior to that in our simulation. However, in that system, the content of added block copolymer is 20% by volume fraction, enough to be microphase-separated, whereas in our simulation, it is at most about 6%, and thus there is little possibility that microphase separation dominates the phase separation in the ternary mixture, as also predicted by RPA calculations.[27] The kinetic processes which interfere with the system reaching equilibrium may also result in a decrease in the retardation effect of a symmetric diblock copolymer with relatively long chain lengths, especially when the interaction energies between the blocks and their respective homopolymers are attractive. This may be inferred in Figure 7, where the chain extension ratio α of the block copolymer with $N = 30$ increases at the slowest rate.

To compare our results with the phenomenological theory and to investigate the phase separation mechanism for the blend system containing the block copolymer, we considered the phase separation process to take place in separate stages. Generally, the early stage of phase separation can be described by Cahn's linearized theory,[28] and it is reported that the early-stage phase separation of a real polymer mixture with added block copolymer is also well approximated by Cahn's linearized theory.[15] This theory predicts an exponential variation of $S(q,t)$ with time during phase separation as follows:

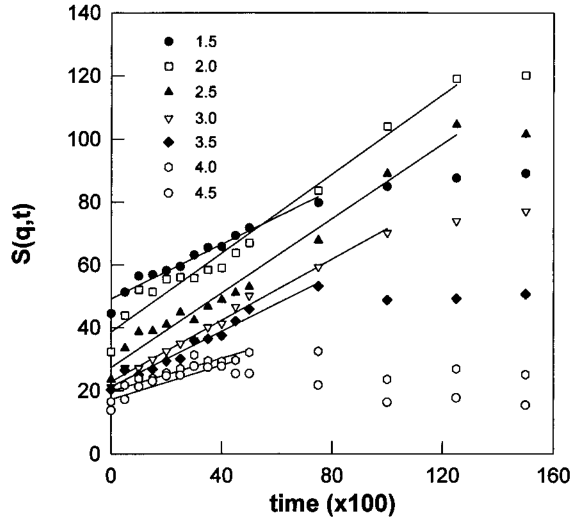

Figure 8. Structure factor $S(q,t)$ as a function of time at various values of q for A/B/C-*b*-D blend with N_{block} = 18 and ϵ_{AC} = −0.5.

$$S(q,t) - S(q,t{=}0) = [S_T^{coll}(q) - S(q,t{=}0)][1 - \exp\{2R(q)t\}] \quad (6)$$

where $S_T^{coll}(q)$ is the collective structure function and, according to the random phase approximation, is given by

$$\frac{1}{S_T^{coll}(q)} = \frac{1}{\phi_A S_A(q)} + \frac{1}{(1-\phi_A)S_B(q)} - 2\chi(T) \quad (7)$$

and $R(q)$ is the growth rate and is given by

$$R(q) = -q^2\Lambda(q)/S_T^{coll}(q) \quad (8)$$

In eq 7, ϕ_A and χ denote the volume fraction of homopolymer A and Flory−Huggins interaction energy parameter, respectively, and in eq 8, $\Lambda(q)$ is a generalized Onsager coefficient related to the chain mobility. In a homogeneous state, we would have $S_T^{coll}(q) > 0$ and hence $R(q) < 0$ for all q. Then eq 6 simply describes an exponential decay of the correlation, and the system smoothly relaxes toward its new equilibrium. On the other hand, in the unstable regime where unmixing occurs, we have $S_T^{coll}(q) < 0$ for $0 < q < q_c$, where q_c is given by the condition $1/S_T^{coll}(q) = 0$. Consequently, Cahn's linearized theory predicts an exponential increase of structure factor $S(q,t)$ with phase separation time. Figure 8 shows the structure factor $S(q,t)$ as a function of time at different q values for the A/B/C-*b*-D system with N_{block} = 18 and ϵ_{AC} ($=\epsilon_{BD}$) = −0.5.

According to eq 6, the structure factor $S(q,t)$ increases exponentially with time for $q < q_c$. However, in Figure 8, there is no time regime in which $S(q,t)$ can be said to grow exponentially with time. The curves show a linear increase with time and then bend down, reflecting the immediate onset of strong nonlinear effects. This behavior is observed in all the other blends and is the same as the behavior observed in the simulations of phase separation in metallic alloys.[29] One of reasons that the linearized theory may not be consistent with the simulation results is the fact that the theory is only valid for $\langle R_g^2\rangle q^2 < 1$, but most of the computer simulation results are in a regime where this inequality does not hold due to the finite simulation size.

It is well known that the unmixing in the late stage of phase separation of binary polymer blends obeys universal scaling laws.[10] These scaling laws are generally applied to physical systems such as simple liquid mixtures, metallic alloys, and inorganic glasses, and they imply that there exists a self-similarity between the phase-separated structures developed at different time scales. Here, the dynamical scaling law has been tested to investigate whether a universal scaling function exists for a polymer blend system containing a block copolymer. If the growth of the pattern at a given temperature T obeys a dynamical scaling law and the pattern evolved is independent of T, then the structure factor $S(q,t)$ of the unmixing systems at time t can be scaled with a single, time-dependent length parameter in terms of the universal scaling function $F(x)$:

$$S(q,t) \approx [1/q_1(t)]^d F(x) \qquad (9)$$

where the length parameter used in the work is the first moment of structure factor and d is the dimensionality of the system. The quantity x is defined as

$$x = q/q_1(t) \qquad (10)$$

To test this scaling hypothesis from our simulation results, we define the following scaled structure factor $F(x)$ via the proper normalization,[29]

$$F(x) \equiv \frac{L}{\pi} q_1^{\,3} S(q,t) / \sum_q q^2 S(q,t) \qquad (11)$$

where the scaling factor $\sum q^2 S(q,t)$ corrects for the temperature dependence of structure factor $S(q,t)$ because the data obtained at different T's have different mean-square concentration fluctuations $\langle \eta(t,T)^2 \rangle$, given by

$$\langle \eta(t,T)^2 \rangle \approx \sum_q q^2 S(q,t) \qquad (12)$$

In our model systems, this scaling factor must be considered because there is the possibility that the system can experience different temperatures due to different quench depths caused by the addition of various types of block copolymers. Figure 9 shows the scaled structure factors at different times for A/B/C-*b*-D blend system with $N_{\mathrm{block}} = 12$ and ϵ_{AC} ($=\epsilon_{\mathrm{BD}}$) $= -0.5$. In Figure 9a, corresponding to the intermediate stage of phase separation, the scaled structure factor is not universal, yet it still increases with time, mainly because $\langle \eta(t,T)^2 \rangle$ has not reached the equilibrium value, $\langle \eta(t,T)^2 \rangle_{\mathrm{e}}$. The scaled structure factors in Figure 9b, corresponding to the late stage, fall on one curve, i.e., the scaled structure factors have become universal with time since $\langle \eta(t,T)^2 \rangle$ has reached $\langle \eta(t,T)^2 \rangle_{\mathrm{e}}$. In this time regime, the growth of the phase-separated domains satisfies the dynamical scaling hypothesis with a single length parameter $1/q_1(t)$, indicating that the domains grow with dynamical self-similarity. This behavior is also observed in the other polymer blend systems (not shown here). From these results, the dynamical scaling law is also seen to apply to blend systems containing block copolymers.

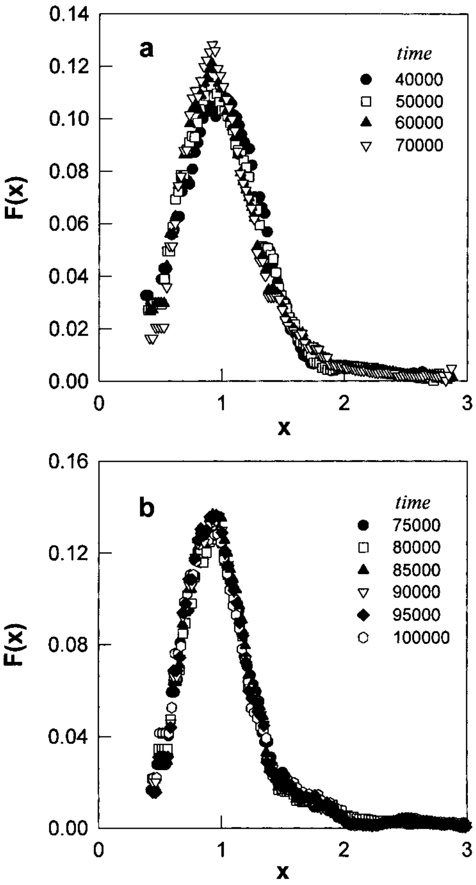

Figure 9. Scaled structure factor $F(x,t)$ of A/B/C-*b*-D blend with $N_{\mathrm{block}} = 12$ and $\epsilon_{\mathrm{AC}} = -0.5$ in (a) the intermediate stage and (b) the late stage.

Figure 10 shows the scaled structure factors which are obtained in the late stage for A/B binary and A/B/C-*b*-D blend systems with various block copolymers. In Figure 10a, it is found that the scaled structure factors are almost universal and independent of ϵ_{AC} and ϵ_{BD} at all x regions examined by the simulation, implying the self-similar growth in spite of the difference in the growth rate of domains due to the difference of the interaction energies of block copolymers. This tendency is also found in Figure 10b, where the scaled structure factors have universality independent of the chain length of the added block copolymer, although a slightly nonuniversal feature is observed at higher x regions that may reflect the characteristics of the local domain structure, i.e., possibly the interfacial structure. This behavior suggests that local structures such as the interfacial structure would obey the different scaling laws. Takenaka and Hashimoto[10] found that, before the system has reached the so-called "late stage II", the local structure cannot be scaled with the length parameter characterizing the global structure, and instead a relevant parameter such as the interfacial area density should be used to characterize the growth of the local structure. The dynamical scaling of the local structure requires further study.

It is interesting to note that the scaling function exhibits a weak maximum or shoulder around $x = 2$, which has also been observed in the most recent experimental systems and predicted in some theoretical calculations as well,[30] indicating the existence of the domains with a fairly precise spatial periodicity.

Conclusions

The effects of adding small amounts of block copolymers on phase separation dynamics of immiscible polymer blends were investigated by means of a com-

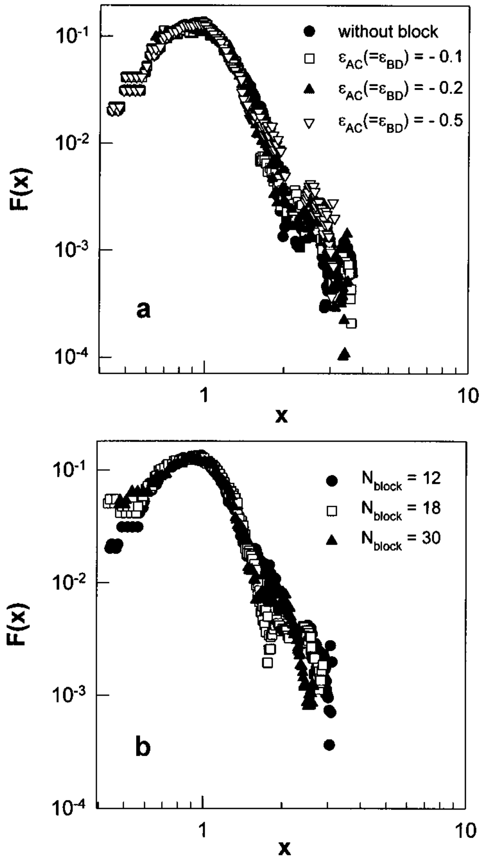

Figure 10. Scaled structure factor $F(x)$ for A/B/C-*b*-D blends (a) with different ϵ_{AC} ($=\epsilon_{BD}$) and $N_{block} = 12$ and (b) with different chain lengths of block copolymer and ϵ_{AC} ($=\epsilon_{BD}$) $= -0.5$.

puter simulation method. Here, we used a symmetric diblock copolymer composed of chemically different blocks (C and D) from a binary homopolymer pair (A and B) and investigated the effects of the interaction energies between the copolymer blocks and their respective homopolymers as well as the chain length of block copolymer on the phase separation behavior. It was found that the rate of the phase separation process is considerably suppressed by the addition of the block copolymer, resulting from the reduction of interfacial tension due to the accumulation of block copolymer at the interface between the two immiscible phases. This effect becomes more pronounced as the attractive energy between the blocks and their corresponding homopolymers increases. It is also observed that there exists an optimum chain length to give the greatest effect of suppressing the phase separation.

As with the case of binary mixtures, the growth of the phase-separated domains of a ternary blend containing a block copolymer also obeys a dynamical scaling law in the late stage of phase separation. From the scaling law, we obtained the universal scaling function $F(x)$ for blend systems with and without block copolymers. The scaling functions are independent of the interaction energies ϵ_{AC} (and ϵ_{BD}) and the chain length of block copolymer, indicating that the domains grow with dynamical self-similarity irrespective of the types of block copolymer used, although the block copolymer added to the immiscible blend reduces the growth rate of phase-separated domains.

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