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Effect of a Block Copolymer on the Kinetics of Spinodal Decomposition of Polymer Blends. 1. Nonuniversality in Scaled Characteristic Quantities versus Reduced Time[†]

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ABSTRACT: Effects of adding a small amount of a block copolymer to polymer blends composed of the same constituent polymers as the block copolymer on the kinetics of early-to-late-stage spinodal decomposition (SD) were investigated by a time-resolved light scattering (LS) at three different temperatures in a deep quench condition. The early-stage SD for the blends with and without the block copolymer was well described by the linearized theory of SD over the small q range covered by the LS method. At each temperature, the coarsening process of the structure self-assembled via SD, as observed by the time changes of the peak scattering intensity $I_m(t)$ and the scattering vector $q_m(t)$, was slowed with increasing block copolymer content. For each blend the scaling postulate was found to be approximately valid; i.e., the time changes I_m and q_m at different temperatures fall onto respective master curves on the reduced plots: reduced intensity $\tilde{I}_m$ and reduced scattering vector Q_m plotted against reduced time τ. However, the master curves on $\tilde{I}_m(\tau)$ and $Q_m(\tau)$ obtained for each blend depend on the amount of the block copolymer, thus showing a "branch (or nonuniversality)" on the reduced plot. The greater the amount of the block copolymer, the slower the coarsening of Q_m and $\tilde{I}_m$ in the reduced time scale τ. The branching designated "B-branching" where B stands for block copolymer is due to a reduction of interfacial tension as a consequence of localization of the block copolymer at the interfaces during the ordering process.

I. Introduction

The kinetics of spinodal decomposition of polymer mixtures have been a research topic actively investigated in recent years.[1] However, not much attention has been focused on the effects of adding a small amount of the block copolymers whose constituent polymers are the same as those of the mixtures on the kinetics. On the other hand, there is a well-accepted concept that the block copolymer which is localized at the interface of the corresponding homopolymer phases lowers the interfacial tension of the corresponding polymer mixtures in the segregation limit.[2] This concept based upon *equilibrium* statistical mechanics has been applied to the interpretation of the "*compatibilizing effect*" of block copolymers: the block copolymer reduces the size of phase-separated domains as a consequence of the reduction of interfacial tension. However, the size of the domains depends not only on the interfacial tension but also on the time spent for the phase separation, detailed coarsening (ordering) mechanism of the domains, flow and deformation imposed to the mixtures, etc. Thus, it is important to distinguish unequivocally whether the size of the domains observed for the systems some time after phase separation represents thermodynamic equilibrium or is kinetically frozen. If the phase separation is slow, as is typical for high polymers, the unequivocal distinction requires an in situ study of its phase separation process. Thus, a deeper understanding of the compatibilizing effect requires basic research on the effects of the block copolymer on the kinetics of the unmixing and ordering mechanism, especially unmixing via spinodal decomposition (SD), since the SD process is a prevailing unmixing process in polymer mixtures.

In this study we explored the effects of the block copolymer on the kinetics of the isothermal unmixing process, i.e., on the early-stage SD in which the SD process is considered to be well approximated by the linearized theory[3] and on coarsening of the domains self-assembled in the early-to-late-stage SD. In general one can consider the effects of block copolymers on the kinetics as due to two major physical factors: (i) a change of the phase diagram and therefore a change of the quench depth at a given phase separation temperature and (ii) a change of the interfacial tension between the phase-separating domains as a result of localization of block copolymers at the interfaces. The former (i) affects ordering kinetics in the early-stage SD as well in the later-stage SD, while the latter effect (ii) becomes increasingly important toward the late stage. This is because in the late stage the interfaces are developed; the interfacial area per unit volume decreases with time t, and the interface thickness decreases toward an equilibrium value with t. Therefore, the number density of block copolymer junctions at the intefaces generally increases with time, and hence the reduction of the interfacial tension also becomes increasingly large with time, causing the increasing effect of the block copolymer with time on the coarsening process driven by the interfacial tension.

The effects of a block copolymer on the phase separation kinetics in the "late stage" [4] were reported by Roe and Kuo[5] for off-critical mixtures of the polymer blends composed of low molecular weight polybutadiene (PB) and polystyrene (PS) to which a small amount of poly(styrene-*block*-butadiene) is added. They reported a small suppression of the growth rate of the domains by adding a small amount of the copolymer.

Here we focus on the same effect but report our results on near-critical mixtures of the homopolymers which contain a small amount of a copolymer. The homopolymers and the copolymer used in our work have much larger molecular weights than those used by Roe and Kuo. Moreover, our near-critical mixtures are expected to have a bicontinuous phase-separated domain structure[1,4] in the time scale covered in our experiments. We aim to study systematically the effect in the early-stage to the late-

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Table I. Characteristics of Polymers Used in This Work

specimen code	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	content (%)		microstructure[f] (%)		
			w_{PS}[d]	w_{SBR}[e]	vinyl	cis-1,4	trans-1,4
SBR1[a]	10.0	1.18	20	100	61	16	23
PB2[b]	16.5	1.16	0	0	46	19	35
SBR-*b*-PB[c]	21.1		30	50	51	20	29

[a] Poly(styrene-*ran*-butadiene). [b] Polybutadiene. [c] Poly((styrene-*ran*-butadiene)-*block*-butadiene), i.e., poly(SBR-*block*-butadiene). [d] Weight percentage of styrene in poly(styrene-*ran*-butadiene). [e] Weight percentage of poly(styrene-*ran*-butadiene) in a given polymer or block copolymer. [f] Microstructure in the butadiene unit in each polymer.

Table II. Composition of Constituent Polymers in the Blends Studied in This Work

specimen code	wt % of polymers		
	SBR1	PB2	SBR-*b*-PB
B0	58.0	42.0	0
B3	56.3	40.7	3.0
B6	54.5	39.5	6.0

stage SD. Our study is closely related also to a series of work, by Kawakatsu and Kawasaki on theory and computer experiments on the dynamics of the ordering process in immiscible binary mixtures with a surfactant.[6-8] In fact this work corresponds to a part of the polymer work cited in their series of papers.

II. Experimental Methods

Specimens used in this work were all prepared by living anionic polymerization. They were polybutadiene (PB), poly(styrene-*ran*-butadiene) (SBR), and poly((styrene-*ran*-butadiene)-*block*-butadiene) (SBR-*b*-PB), coded, respectively, as PB2, SBR1, and SBR-*b*-PB in Table I. Table I shows characteristics of those polymers. Three kinds of blends, B0, B3, and B6, having the compositions of SBR1/PB2/SBR-*b*-PB indicated in Table II were solution cast into thin films about 0.2 mm thick. For this purpose homogeneous toluene solutions containing 7 wt % polymer total were first prepared, and the solvent was slowly evaporated in a Petri dish to obtain thin films. The film specimens were further dried under vacuum for more than one week. It should be noted that the compositions of the ternary blends B3 and B6 are such that the relative fractions of PB and SBR units are roughly the same as in the binary blend B0.

The film specimens prepared were homogenized by applying "Baker's transformation" at room temperature, i.e., by the repeated folding and pressing over many times as reported earlier.[9] The homogenized specimens were quickly sandwiched between two glass plates with a spacer 0.1 mm thick and were subjected to time-resolved light scattering experiments at 50, 60, and 70 °C. The time was set at zero immediately after homogenization.

The phase separation conditions without the copolymer were fully described in our earlier paper.[10] The reduced parameter ϵ_T defined by

$$\epsilon_T \equiv [\chi_{eff}(T) - \chi_s]/\chi_s \qquad (1)$$

was estimated to characterize the thermodynamic driving force for the SD, where $\chi_{eff}(T)$ is the effective Flory interaction parameter χ between PB and SBR per monomer base at the phase separation temperature T, and χ_s is the χ parameter at the spinodal point. The value $\epsilon_T \rightarrow 0$ for a weak segregation near the spinodal point, but $\epsilon_T \gtrsim 1$ for a strong segregation far below the spinodal point. The value ϵ_T for the blend B0 at T = 50–70 °C was evaluated to be 2.6–2.8 as shown in Table III, implying that our blends B0 at T = 50–70 °C correspond to a deep quench.[10] The reduced parameters ϵ_T for B3 and B6 at T = 50–70 °C were also evaluated and summarized in Table III where χ_s for the blends containing the block copolymer (χ_{s,ϕ_b}) were estimated on the basis of the random phase approximation (RPA) as shown in the Appendix. ϵ_T for them are large so that the blends B3 and B6 at T = 50–70 °C also correspond to a deep quench. The cloud point curves measured as a function of polymer concentration ϕ_b for SBR1/PB2/dioctyl phthalate[13] may qualitatively indicate that our blends are very immiscible and they are in the strong segregation at the measuring temperatures.

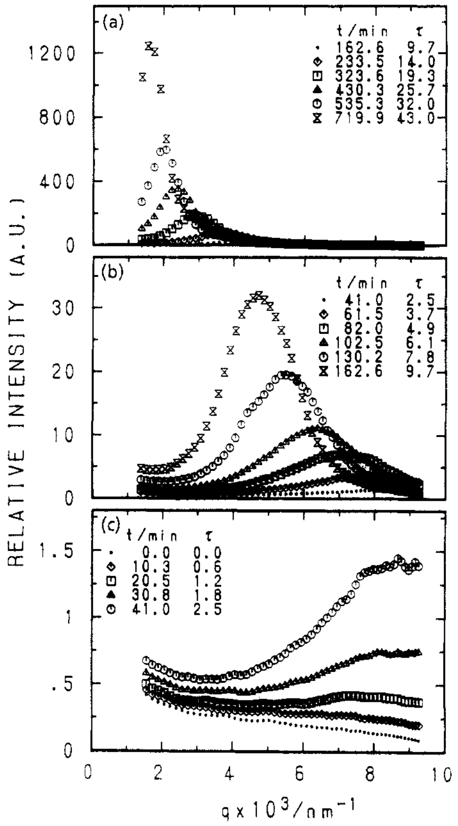

Figure 1. Time evolution of the light scattering profile for B0 during the spinodal decomposition at 50 °C. Time elapses in the order of (c) to (a).

It is worth noting the the compatibilization effect of the copolymer in a weak segregation limit is also an interesting research theme. However, this is beyond the scope of our present study and left open to a future study.

III. Experimental Results

Figures 1–3 show time-resolved light scattering profiles during SD at 50 °C for the blends B0, B3, and B6, respectively. In each figure, time elapses in the order of (c) to (a). With increasing time after phase separation, the scattering maximum appears at the large q limit

Table III. Characteristic Parameters Obtained from the Analysis of the Early-Stage Spinodal Decomposition

specimen code	w_{block}/(wt %)	temp/°C	ϵ_T	D_{app}/(nm^2 s^{-1})	$q_m(0) \times 10^3$/nm^{-1}	$t_c \times 10^{-3}$/s	$D_{app}q_m^{-2}(0) \times 10^{-5}$/(nm^4 s^{-1})
B0	0	50	2.8	10	10	1.0	1.0
		60	2.7	20	9.5	0.54	2.2
		70	2.6	34	10	0.28	3.3
B3	3.0	50	2.8	8.0	10	1.2	0.77
		60	2.7	16	10	0.62	1.6
		70	2.6	31	10	0.32	2.9
B6	6.0	50	2.8	5.7	11	1.6	0.51
		60	2.7	12	10	0.84	1.1
		70	2.5	23	10	0.44	2.3

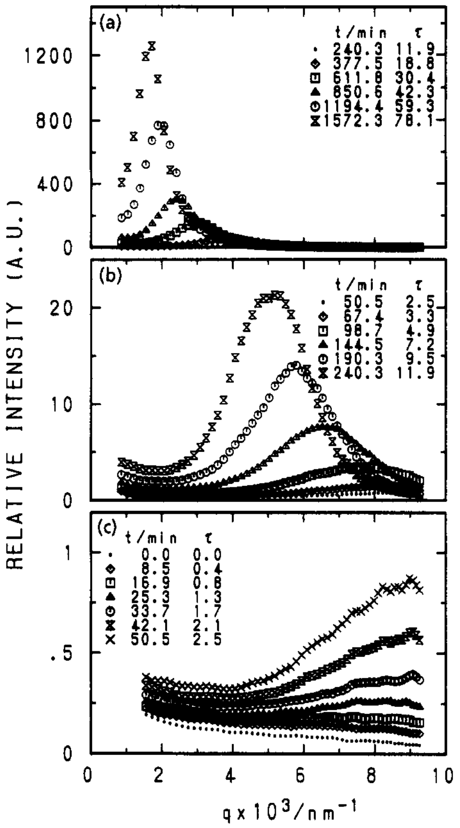

Figure 2. Time evolution of the light scattering profile for B3 during the spinodal decomposition at 50 °C. Time elapses in the order of (c) to (a).

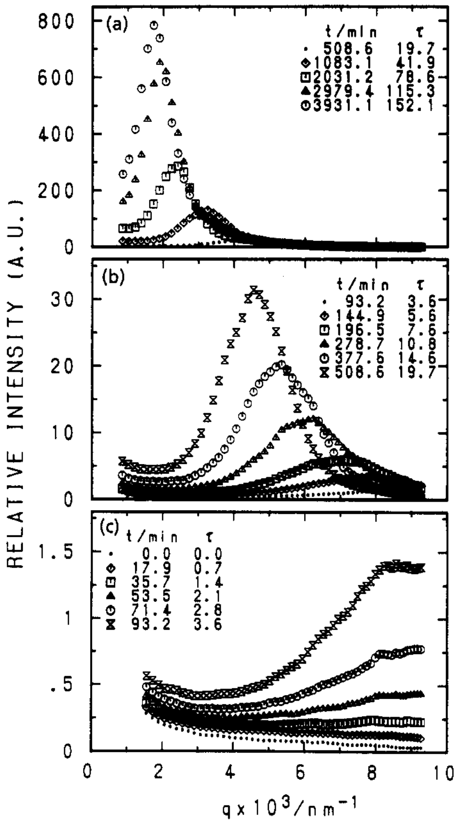

Figure 3. Time evolution of the light scattering profile for B6 during the spinodal decomposition at 50 °C. Time elapses in the order of (c) to (a).

covered in our experiment, and this maximum shifts toward smaller q and the peak intensity increases, indicating the onset of SD and coarsening of the structure self-assembled via SD. Close observation of the results clearly indicates that the coarsening process is slowed on addition of the block copolymer. Later we will show that the early-stage SD persists up to about 40, 50, and 60 min at 50 °C for B0, B3, and B6, respectively. Thus, part c in each figure (Figures 1–3) approximately corresponds to the profiles in the early-stage SD.

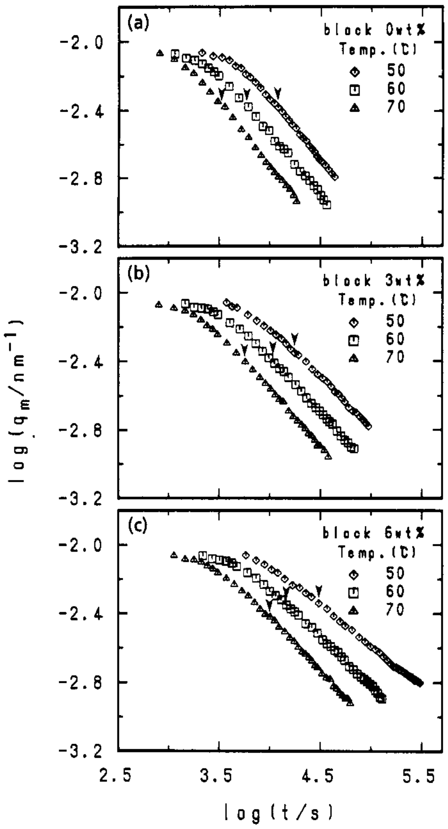

Figure 4. Time change of the characteristic wavenumber $q_m(t)$ for (a) B0, (b) B3, and (c) B6 at the three phase separation temperatures.

Time changes of the peak scattering vector $q_m(t)$ and the peak intensity $I_m(t)$ are shown in Figures 4 and 5, respectively. In each figure, parts a–c present, respectively, effects of temperature on the coarsening behavior of the blends B0, B3, and B6. For each blend the higher the temperature the shorter the time required to reach given levels of $q_m(t)$ and $I_m(t)$, indicating a faster coarsening rate. This is because, in this low temperature range, the coarsening is controlled by the transport process rather than the thermodynamic driving force associated with the quench depth. At each temperature the coarsening rate is found to systematically decrease with an increasing amount of the block copolymer. This suppression of the coarsening rate in the later-stage SD (i.e., the intermediate-stage and late-stage SD[4]) is consistent with the results reported by Roe and Kuo[5] and Kawakatsu et al.[6,8] It may also be consistent with the results reported by Ohta et al.[11] and Enomoto and Watanabe.[12]

IV. Analysis and Discussion

A. Early-Stage Spinodal Decomposition. In our previous papers,[10,13] we reported that the early-stage SD for the same polymer mixture without block copolymers (the blend B0) is well approximated by the Cahn–Hilliard linearized theory of SD.[3] This theory predicts that

$$I(q,t) = I(q,t=0) \exp[2R(q)t] \quad (2)$$

where $R(q)$ is the growth rate of the q-Fourier mode of

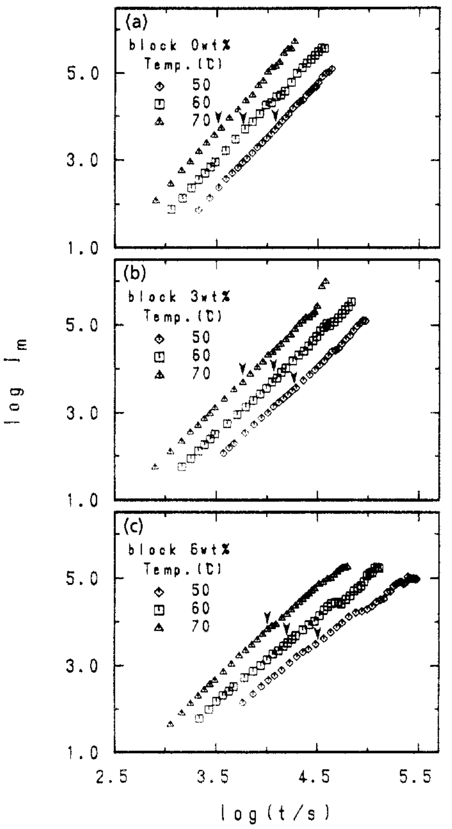

Figure 5. Time change of the maximum scattered intensity $I_m(t)$ for (a) B0, (b) B3, and (c) B6 at the three phase separation temperatures.

concentration fluctuation given by

$$R(q) = q^2 D_{app}\{1-q^2/[2q_m^{\ 2}(0)]\} \tag{3}$$

D_{app} is the mutual diffusivity and $q_m(0)$ is the wavenumber of the mode having the maximum growth rate $R(q)$. Far from the critical point, these parameters were found[10] to be well approximated by the mean-field theory,

$$D_{app} = D_c \epsilon_T \tag{4}$$

and

$$q_m^{\ 2}(0) = (18/R_0^{\ 2})\epsilon_T \tag{5}$$

where D_c and R_0 are the self-diffusivity and root-mean-squared end-to-end distance for unperturbed polymer chains. It should be noted in eq 4 that, at least in the early-stage SD, the contribution of the hydrodynamic interaction[14,15] to D_{app} is assumed to be insignificant for the polymer melts far below the critical temperature.

The linear analysis was attempted here for the mixtures containing block copolymers B3 and B6. The results are shown in Figures 6 and 7 and summarized in Table III. As show in Figure 6 for B3 and B6, logarithms of the scattered intensity linearly increase with time t in the early stage, in the small q range ($3.58 \times 10^{-3} \leq q \leq 9.09 \times 10^{-3}$ nm^{-1}) and at these deep quenches of T = 50 (a), 60 (b), and 70 °C (c) covered in our experiment. At a given q and T, the time scale for the linear behavior becomes longer with an increasing amount of the block copolymer. The deviation from the linearity at a later time is due to the effect of coarsening on the time change of the scattered intensity, driven by the nonlinear nature of the time evolution equation.[1,14-17]

The analysis based upon eq 2 yielded the q-dependent growth rate $R(q)$. The results are summerized in Figure 7 which includes the data obtained at the three different T of 50, 60, and 70 °C for B0 (a), B3 (b), and B6 (c). They were well fitted to eq 3 given by the linearized theory. The best fit yielded the characteristic parameters D_{app} and $q_m(0)$ as summarized in Table III. The table also contains the value $D_{app}/q_m^{\ 2}(0)$ and the characteristic time t_c determined from the analysis of the early-stage SD, where t_c is defined by

$$t_c^{-1} = q_m^{\ 2}(0)D_{app} = 2R_m \tag{6}$$

where R_m is the value $R(q)$ at $q = q_m(0)$, i.e., the maximum growth rate. It should be pointed out that the success of the linear analysis is primarily based upon the following two factors: (i) observation in the small q modes ($q \ll q_c = (\sqrt{2})q_m$) and (ii) observation at the low temperatures or deep quenches. These factors made the effects of the thermal noise on $I(q,t)$ less significant and the rate of SD slow.

For each blend, the higher the temperature, the faster the growth rate $R(q)$ or the larger the diffusivity D_{app}, indicating that the growth rate is diffusion-controlled, i.e., controlled by D_c rather than by ϵ_T(eq 4). On the other hand $q_m(0)$ hardly depends on T, since ϵ_T does not change significantly in the narrow temperature range covered in this experiment (see section II).

At each temperature, D_{app} or R_m ($\sim t_c^{-1}$, eq 6) decreases significantly with an increasing amount of the block copolymer (w), while $q_m(0)$ hardly changes. The decrease of D_{app} or $R_m(\sim t_c^{-1})$ on addition of the copolymer implies the suppression of the growth rate in the early-stage SD, i.e., in the regime which was not covered by Roe and Kuo. The suppression of the growth rate is consistent with the result obtained from the computer experiment[7] which takes into account the excluded volume effect of the surfactant molecules.

The change of D_{app} with w is determined by the changes of D_c and ϵ_T with w (eq 4), whereas the change of $q_m(0)$ with w is determined by the changes of "effective" R_0 and ϵ_T (eq 5). The change in ϵ_T can be evaluated by the RPA analysis discussed in the Appendix. Thus, the effect of w on ϵ_T should be factored out from that on D_c and R_0. From eqs 4 and 5, one obtains the quantity related to the Onsager coefficient in the zero wavenumber limit,

$$D_{app}/q_m^{\ 2}(0) = D_c R_0^{\ 2}/18 \tag{7}$$

which is independent of ϵ_T. This quantity decreases with increasing w as seen in Table III. The RPA analysis in the Appendix predicts that ϵ_T at a given T tends to decrease only slightly with increasing w. Thus, this effect of w turns out to little affect D_{app}. Our experimental result showing the decrease of D_{app} with increasing w is therefore interpreted to be due to the decrease of D_c with increasing w. This decrease of the diffusion coefficient with an increasing amount of block copolymer may be due to the fact that the block copolymer has a molecular weight higher than those of the constituent polymers SBR1 and PB2.

B. Scaling Analysis on the Later-Stage SD. The effects of the block copolymer on the coarsening process in the later-stage SD (i.e., the intermediate- and late-stage SD) were investigated on the basis of a power law analysis,

$$q_m(t;T,\phi) \sim t^{-\alpha} \tag{8}$$

and

$$I_m(t;T,\phi) \sim t^{\beta} \tag{9}$$

For each mixture with a given volume fraction of the block copolymer ϕ ($\phi \simeq w$ for our systems) and at a given temperature T, the dynamical exponents α and β are

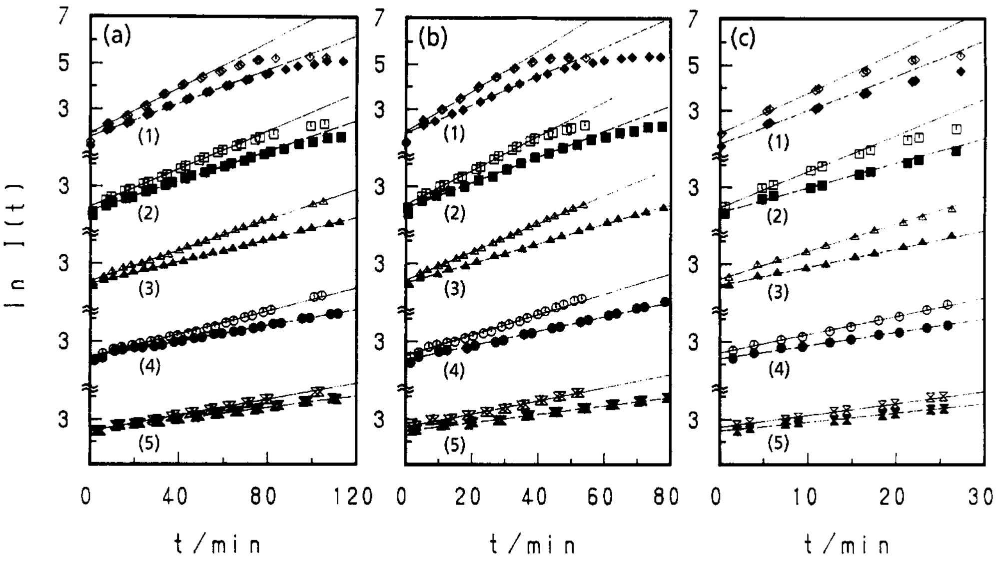

Figure 6. Time evolution of the scattered intensity at various q (q = 9.09, 7.99, 6.67, 5.19, and 3.58 × 10^{-3} nm^{-1} for the curves numbered 1–5, respectively) in the early stage of the spinodal decomposition of B3 (solid lines and unfilled symbols) and B6 (broken lines and filled symbols) at (a) 50, (b) 60, and (c) 70 °C.

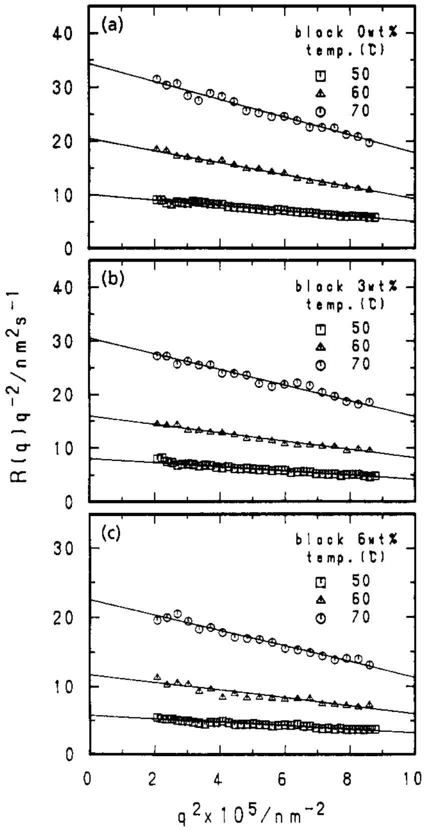

Figure 7. $R(q)/q^2$ vs q^2 at 50, 60, and 70 °C for (a) B0, (b) B3, and (c) B6.

Table IV. Results of Scaling Analysis in the Late-Stage Spinodal Decomposition

specimen code	w_{block}/(wt %)	temp/°C	α	β	β/α	τ_{cr}
B0	0	50	0.78	2.4	3.0	12
		60	0.77	2.4	3.0	11
		70	0.80	2.5	3.1	12
B3	3.0	50	0.66	2.1	3.1	15
		60	0.68	2.1	3.1	18
		70	0.70	2.1	3.0	18
B6	6.0	50	0.54	1.6	3.0	20
		60	0.60	1.8	3.0	18
		70	0.65	2.0	3.0	22

observed to satisfy

$$\beta > 3\alpha \tag{10}$$

in the time scale t shorter than the crossover time t_{cr} between the intermediate- and late-stage SD. The crossover time is shown by arrows in Figures 4 and 5. On the other hand, in the late stage at $t > t_{\text{cr}}$, the relationship

$$\beta \simeq 3\alpha \tag{11}$$

is observed, indicating that the mean-squared refractive index fluctuation $\langle\eta^2\rangle$ between the domains and matrix reaches an equilibrium value $\langle\eta^2\rangle_e$ and the scaled structure factor $F(x)$ becomes essentially universal with time (see eqs 3.4–3.6 of ref 4a, for example). Table IV summarizes the exponents α and β in the late stage and the crossover time τ_{cr} reduced by the characteristic time t_c listed in Table III,

$$\tau_{\text{cr}} \equiv t_{\text{cr}}/t_c \tag{12}$$

The blend B0 without the block copolymer has $\tau_c \simeq 10$ and $\alpha \simeq 0.8$ in the late stage, consistent with the earlier results reported.[10] At a given temperature, τ_{cr} tends to increase and α in the late stage tends to decrease with increasing ϕ, indicating that the coarsening in the later-stage SD is slowed with the small amount of the copolymer.

Next we test the scaling postulate[16,17] on the growth of domains in the late-stage SD. We define the reduced wavenumber Q_m, reduced intensity $\tilde{I}_m$, and reduced time τ:

$$Q_m = q_m(t;T,\phi)/q_m(0;T,\phi) \tag{13}$$

$$\tilde{I}_m = I_m(t;T,\phi)\, q_m^{\,3}(0;T,\phi)/\langle\eta^2(T,\phi)\rangle_{\text{eq}} \tag{14}$$

$$\tau = t/t_c(T,\phi) \tag{15}$$

where $q_m(0;T,\phi)$ and $t_c(T,\phi)$ were determined from the analysis of the early-stage SD (Table III), and $\langle\eta(T,\phi)^2\rangle_{\text{eq}}$ is the mean-squared fluctuation of the refractive index of the system at thermal equilibrium. In our analysis, $\langle\eta^2(T,\phi)\rangle_{\text{eq}}$ was assumed to be a constant independent of temperature, since the temperature range covered is very narrow and far from the critical point; i.e., ϵ_T is almost independent of T. The results are shown in Figures 8 and 9.

For the blend B0 without the block copolymer, the data $Q_m(\tau)$ and $\tilde{I}_m(\tau)$ obtained at the three different T fall on

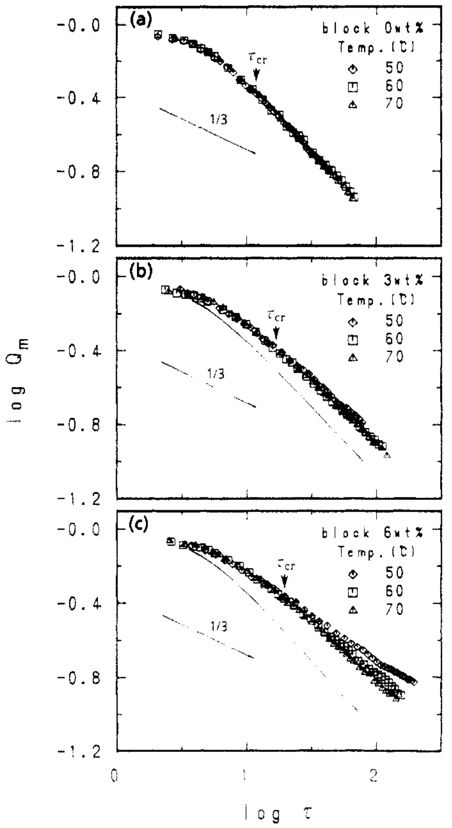

Figure 8. Reduced characteristic wavenumber Q_m plotted against reduced time τ in double logarithmic scales for (a) B0, (b) B3, and (c) B6. The solid line in parts b and c shows $Q_m(\tau)$ for B0 for comparison.

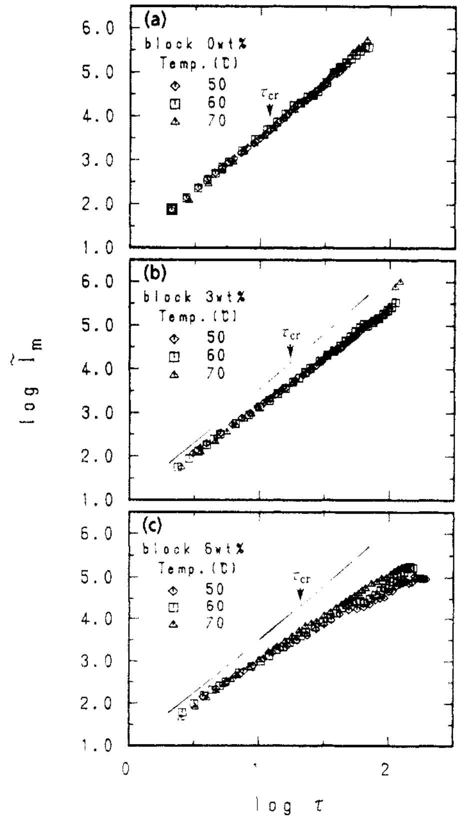

Figure 9. Reduced maximum scattered intensity $\tilde{I}_m$ plotted against reduced time τ in double logarithmic scales for (a) B0, (b) B3, and (c) B6. The solid lines in parts b and c show $\tilde{I}_m(\tau)$ for B0 for comparison.

a master curve (Figures 8a and 9a), satisfying the dynamical scaling postulate;[16,17] i.e., the temperature affects the spatial and temporal scales of the ordering process through $1/q_m(0)$ and t_c, respectively, but not the ordering mechanism. The postulate is found to be essentially valid for B3 over the time and temperature ranges covered in our work (Figures 8b and 9b). However, the postulate tends to break down for B6, the mixture having the highest amount of the block copolymer, as seen in the branches at the long τ limit in Figures 8c and 9c, although the effect is not very large. The branch (denoted hereafter as "T-branching") occurs in such a way that the lower the temperature the slower the growth rate on the reduced plot, i.e., the larger the reduced wavenumber Q_m and the smaller the reduced intensity $\tilde{I}_m$.

Figures 8b, 8c, 9b, and 9c include $Q_m(\tau)$ and $\tilde{I}_m(\tau)$ for B0 for comparison. The comparison of the behaviors of $Q_m(\tau)$ and $\tilde{I}_m(\tau)$ for B6 with those for B0 clearly indicates that the block copolymer tends to slow the coarsening even in the reduced scales. This means that the *T-branching* occurs in such a way that the lower the temperature the larger the effect of the block copolymer. Before we discuss a possible origin of this T-branching, let us first look at the effect of the block copolymer concentration ϕ on the reduced quantities.

It is clear from Figures 8 and 9 that $\tilde{I}_m(\tau)$ and $Q_m(\tau)$ for the mixtures with a different block copolymer concentration do not fall onto a master curve. This branching due to block copolymer concentration, called hereafter *B-branching* with B denoting block copolymer, is much larger and more significant than the T-banching. The nonuniversal nature of the coarsening behavior with ϕ, as observed with $Q_m(\tau)$ and $\tilde{I}_m(\tau)$, indicates that the block copolymer affects not only the time and spatial scales of the ordering process, as clearly seen in its effect on the early-stage SD, but also the mechanism of the ordering process. As the concentration fluctuations grow, and the interface between the two domains is formed, the copolymer chains tend to diffuse into the interfaces and to localize there. The localized copolymer then reduces the interfacial tension, which in turn affects the interface dynamics[14,15,18] and hence the coarsening rate. This reduction of the coarsening rate cannot be obviously scaled with the ϕ dependence of $q_m(0)$ and t_c. The reduction depends directly on the number density of the copolymer at the interface and hence explicitly on ϕ. This may be a key for interpreting the *B-branch*. A similar explanation may be legitimate for the *T-branching*; the lower the temperature, the higher the number density of the copolymer at the interface at a given reduced time τ. However, a clarification of this point deserves further investigation.

In the coarsening process, the interfacial area is reduced,[20,25] which increases the number density of the copolymer at the interfaces. The interfaces may be eventually saturated with the copolymer molecules, and further coarsening may be hindered, leading to the pinning of the domain growth. The nonuniversality of the reduced variables as observed in the coarsening process, i.e., B-branch or T-branch, seems to correspond to the crossover stage leading to this pinning process. The experiments at a longer time scale are crucial to confirm this postulate.

We discuss below the B-branching effect in terms of the nonlinear time evolution equation. The fact that the exponent α (in eq 8) is greater than 1/3 in the late-stage SD, as seen in Figure 8, suggests that the hydrodynamic effect[4,14,15,18,19] should be taken into account in the coarsening process. Moreover, this effect appears to be switched on even at a surprisingly early time in the late-stage SD. This feature of the coarsening behavior will be highlighted elsewhere.[20,21] In binary critical mixtures of fluids (i.e., purely viscous mixtures), the hydrodynamic effect was incorporated[14,15] in the time-dependent Ginzburg–Landau equation,

$$\partial S(\mathbf{r},t)/\partial t = L\nabla^2\mu\{S(\mathbf{r},t)\} + f_T - \nabla S(\mathbf{r},t)\cdot\int T(\mathbf{r}-\mathbf{r}')\ \nabla' S(\mathbf{r}',t)\ \mu\{S(\mathbf{r}',t)\}\ \mathrm{d}\mathbf{r}' \quad (16)$$

where $S(\mathbf{r},t)$ is the spatial concentration fluctuation at a given time t, L is the Onsager kinetic coefficient, μ is the chemical potential which is a functional of the order parameter $S(\mathbf{r},t)$, f_T is the contribution of the random thermal force on the time evolution of $S(\mathbf{r},t)$, and $T(\mathbf{r})$ is the Oseen tensor given by

$$T(\mathbf{r}) = (1/8\pi\eta)[1/r + \mathbf{rr}/r^3] \quad (17)$$

Here η is the shear viscosity of the system and 1 is the unit tensor. The first two terms of the right-hand side (rhs) of eq 16 describe the time evolution of the order parameter $S(\mathbf{r},t)$ through individual molecular motions driven by the thermodynamic driving force (the first term) and the random thermal noise (the second term), whereas the third term of the rhs of eq 16 describes the time evolution of S through the local velocity field (i.e., the hydrodynamic effect).

The block copolymer affects the time evolution equation through the interfacial tension γ. The interfacial tension affects the equation through the following two terms: (i) the hydrodynamic term (the third term on the rhs of eq 16) which depends explicitly on γ/η,[18] and (ii) the term associated with individual molecular motion $\nabla^2\mu$ (the first term on the rhs of eq 16) in which the free energy F of the system (the variational derivative of which with S gives μ, i.e., $\mu = \delta F/\delta S$) contains the square-gradient term $(\nabla S)^2$ which depends on the interfacial tension.[3]

Our data shown in Figures 8 and 9 suggest qualitatively that the B-branching becomes increasingly noticeable in the later stage of the SD process where the hydrodynamic effect becomes increasingly important. The time evolution equation of the order parameter S expressed in terms of the reduced wavenumber Q_m, reduced intensity $\tilde{I}_m$, and reduced time τ is expected to become nonuniversal with the amount of copolymer ϕ, primarily due to the hydrodynamic effect which depends explicitly on the interfacial tension γ and η.[18] It becomes nonuniversal even with T in the long time limit in the case when $\phi \neq 0$ because of the same reason as stated above.

It should be noted that this nonuniversality may occur even in the absence of the hydrodynamic interaction for the systems containing block copolymers or surfactants. This fact is clearly indicated by the computer experiments by Kawakatsu et al.[8] and may be interpreted as a consequence of the reduction of the interfacial tension induced by the localization of the copolymers or surfactants at the interface. The localization affects the square-gradient term $(\nabla S)^2$ in the free energy functional $F\{S(\mathbf{r},t)\}$ of our system[3] and hence $\mu\{S(\mathbf{r},t)\}$ given by the variational derivative of F with S in the first term of the rhs of eq 16. However, the hydrodynamic term appears to give a bigger contribution in our system, simply because the T- and B-branches appear to occur in the time scale where the hydrodynamic interaction dominates the coarsening processes.

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Appendix. RPA Estimation of the Change of the Thermodynamic Driving Force ϵ_T for Spinodal Decomposition of Blends with an Addition of Block Copolymer

We can estimate the change of ϵ_T on addition of a block copolymer on the basis of the random phae approximation.[22-24] The thermodynamic force $F(q)$ required to generate the q-Fourier mode of the concentration fluctuation for the two-component systems in the single phase is generally given by

$$F(q) = S(q)/W(q) - 2\chi \quad (A1)$$

where

$$S(q) = S_{SS}(q) + S_{BB}(q) + 2S_{SB}(q) \quad (A2)$$

$$W(q) = S_{SS}(q)\ S_{BB}(q) - S_{SB}^{\ 2}(q) \quad (A3)$$

and $S_{KJ}(q)$ (K, J = S or B) are the Fourier transform of the density–density correlation for K and J monomers in a given polymer chain. Here S and B denote styrene and butadiene monomers, respectively. This force is associated with the elastic scattering intensity of the systems at the scattering vector q by

$$I(q) \sim F(q)^{-1} \quad (A4)$$

The component polymers SBR1, PB2, and SBR-*b*-PB have degrees of polymerization (DP) N_1, N_2, and N_b, respectively, and volume fractions ϕ_1, ϕ_2, and ϕ_b, respectively, where

$$\phi_1 + \phi_2 + \phi_b = 1 \quad (A5)$$

The SBR and PB chains in the copolymer SBR-*b*-PB have relative DP f and $1 - f$, respectively, where f is defined by

$$1-f = N_{PB}/N_b \quad (A6)$$

with N_{PB} being the DP of polybutadiene block chains. We define the fraction of styrene monomers in SBR1 as ψ_1 and that in SBR of SBR-*b*-PB as ψ_b. Then S_{KJ} are given by

$$S_{SS} = \phi_1\psi_1^{\ 2}N_1g(1,N_1) + \phi_b\psi_b^{\ 2}N_bg(f,N_b) \quad (A7)$$

$$S_{BB} = \phi_1(1-\psi_1)^2N_1g(1,N_1) + \phi_2N_2g(1,N_2) + \phi_b\{(1-\psi_b)^2N_bg(f,N_b) + N_bg(1-f,N_b) + (1-\psi_b)N_b[g(1,N_b) - g(f,N_b) - g(1-f,N_b)]\} \quad (A8)$$

$$S_{SB} = \phi_1\psi_1(1-\psi_1)N_1g(1,N_1) + \phi_b\{\psi_b(1-\psi_b)N_bg(f,N_b) + (1/2)\psi_bN_b[g(1,N_b) - g(f,N_b) - g(1-f,N_b)]\} \quad (A9)$$

$$g(f,N) = (2/x^2)[\mathrm{f}x - 1 + \exp(-fx)] \quad (A10)$$

and

$$x = q^2Na^2/6 \quad (A11)$$

The spinodal point χ_{s,ϕ_b} for a given blend having a volume fraction of the block copolymer ϕ_b can be estimated by

$$2\chi_{s,\phi_b} = \lim_{q\to 0}[S(q)/W(q)] \quad (A12)$$

Here it is useful to note that

$$\lim_{q\to 0} g(f,N) = f^2 \quad (A13)$$

Let us define the effective χ parameter at a given phase separation temperature T to be χ_{eff}. Then the thermodynamic driving force ϵ_{T,ϕ_b} after an addition of a small amount of the block copolymer ϕ_b is given by

$$\epsilon_{T,\phi_b} = (\chi_{\mathrm{eff}} - \chi_{s,\phi_b})/\chi_{s,\phi_b} \qquad \text{(A14)}$$

The results of the estimated thermodynamic driving force for the phase separation ϵ_T are summarized in Table III.

References and Notes

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