

# Phase Separation Induced by Shear Quenching in Polymer Blends with a Diblock Copolymer

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**ABSTRACT:** The effects of adding A–B diblock copolymer to a polymer blend (A/B) on phase-separation kinetics and morphology have been investigated in a fixed shallow-quench condition ( $\Delta T = 1.5$  °C) by *in situ* time-resolved light scattering and phase-contrast optical microscopy. A shear-quench technique was used in this study instead of a conventional temperature-quench method. Mixtures of nearly monodisperse low relative-molecular masses of polybutadiene ( $M_w = 2.8$  kg/mol), polystyrene ( $M_w = 2.6$  kg/mol), and a near-symmetric butadiene–styrene diblock copolymer ( $M_w = 6.3$  kg/mol) as an interfacial modifier were studied. We observed that the addition of the diblock copolymer could either retard or accelerate the phase-separation kinetics depending on the concentration of the diblock copolymer in the homopolymer blends. In contrast to the conventional temperature quench, we observed complex phase-separation kinetics in the intermediate and late stages of phase separation by the shear-quench technique.

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**Keywords:** phase separation; shear quench; block copolymer; PB; PS; blend; interfacial modification

## INTRODUCTION

One of the important applications of block copolymers is their use as interfacial modifiers or compatibilizers in polymer blends.<sup>1,2</sup> Block copolymers can be viewed within this application as an analog to a nonionic surfactant in microemulsions of oil/water.<sup>3</sup> The interfacial activity of a block copolymer added to homopolymer blends is displayed by the reduction of the interfacial tension between two coexisting phases caused by the ac-

cumulation of diblock copolymer at the interface between the immiscible homopolymer phases. This has been demonstrated by the experimental measurement of interfacial tension<sup>4</sup> and has also been predicted from the theoretical considerations in equilibrium.<sup>5–7</sup>

The phase-separation kinetics in polymer mixtures is an important topic from both fundamental and practical points of view. Phase separation in ternary blends containing a block copolymer (A–B) as well as two homopolymers (A and B) was first studied by Roe and Kuo<sup>8</sup> as well as Park and Roe.<sup>9</sup> They demonstrated that the addition of a higher relative-molecular mass block copolymer than that of the homopolymers retards the kinetics of phase separation. Most experimental works

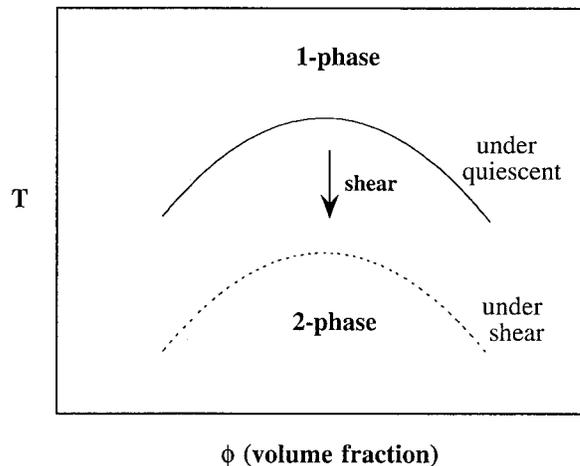
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on mixtures of two homopolymers as well as a block copolymer have indicated that the addition of a block copolymer slows down the phase-separation kinetics because of the decrease in the interfacial tension between the two homopolymers<sup>8–12</sup> except for the results of Lin et al.<sup>13</sup> Their kinetic study demonstrated that the addition of the polyethylbutylene–polymethylbutylene (PEB–PMB) diblock copolymer to the PEB–PMB homopolymer blends leads to an acceleration of phase-separation kinetics. Recently, Jeon et al.<sup>14</sup> and Lee et al.<sup>15</sup> investigated the effect of the diblock copolymer (polyethylene–polypropylene) concentration on the phase separation of the polyethylene–polypropylene homopolymer blends. These experiments indicated a specific concentration of a block copolymer in the homopolymer blends exhibits characteristics of both microphase and macrophase separation. The change in phase-separation kinetics is therefore complex and presumably depends on the concentration, molecular mass, and composition of the diblock copolymer.<sup>8</sup> Often, the results of the phase-separation experiments were interpreted as evidence that the diblock copolymer accumulates at the interfaces lowering the interfacial tension and slowing the rate of coarsening.

If the diffusion of block copolymers to the interfaces is relatively slow compared to the phase-separation kinetics, then the effects of the diblock copolymer addition in a shear-quenched system will not be easily recognized. It is not clear what the important thermodynamic and hydrodynamic parameters are that determine the diffusion rate of the block copolymer relative to the rate of the growth of the phase-separated structure that eventually determines the interfacial dynamics of the phase-separating system. The addition of a block copolymer, therefore, does not always lead to retardation in phase-separation kinetics especially when the phase separation occurs by shear quench instead of the conventional temperature quench.

In the present article, we studied the effects of diblock copolymer addition on the phase-separation kinetics and the morphology changes in the ternary blends of two homopolymers—polybutadiene (PB) and polystyrene (PS)—as well as a PB–PS diblock copolymer. This system has been investigated for a fixed shallow-quench condition [ $\Delta T = (1.5 \pm 0.1)^\circ\text{C}$ ] by using *in situ* light scattering (LS) and phase-contrast optical microscopy (PCOM) techniques. We conducted the experiments on three blends with a fixed ratio of the homopolymer mass fraction,  $\omega_{\text{PB}}/\omega_{\text{PS}} = 1.5$ , which



**Figure 1.** A schematic phase diagram for the shear-induced homogenization and phase separation in a PB–PS binary blend, where  $\phi$  is the volume fraction of PS in the PB–PS blend and  $T$  is the temperature (the critical temperature of a binary PB–PS blend under quiescent conditions is  $134.2 \pm 0.1^\circ\text{C}$ ; the critical point moves up and down with the adjusting shear rate).

is a near-critical composition based on cloud-point measurements for the binary homopolymer blends (PB/PS), where  $\omega_i$  is the mass fraction of component  $i$  in the PB/PS blends. Three blends containing PB–PS at mass fractions of diblock copolymer 0, 2.5, and 5% are designated as B0, B2.5, and B5, respectively. The binary homopolymer blend without the addition of a block copolymer exhibited an upper critical-solution temperature (UCST) phase behavior with a cloud point  $T_c = (134.2 \pm 0.1)^\circ\text{C}$ .

Our shear-quench technique is described with a generic-phase diagram of a binary blend with the UCST in Figure 1. First, we brought the sample to the one-phase region from the two-phase region by shear-induced mixing.<sup>16–18</sup> Then we removed the shear field and allowed the sample to quench back to the two-phase region abruptly. There are two main advantages of this technique: (1) the quench process is fast; and (2) the starting time of the phase separation is well defined. Moreover, the induction of the phase separation via shear quench will serve as a new technique to study the phase-separation kinetics in various polymeric systems.

## EXPERIMENTAL

Nearly monodisperse model PS used in the present study was purchased from Tosoh Corp.

**Table I.** The Compositions and Cloud Points of the Blends Used in this Study

Blend Designation	Components			Compositions		Cloud Points (°C)
	A	B	A-B	$\omega_A/\omega_B$	$\omega_{A-B}$	
B0	PB	PS	—	2/3	0	134.2 ± 0.1
B2.5	PB	PS	PB-PS	2/3	0.025	128.2 ± 0.1
B5	PB	PS	PB-PS	2/3	0.050	119.7 ± 0.1

with a weight-average molecular mass  $M_w = 2.63$  kg/mol and polydispersity index  $M_w/M_n = 1.05$ . PB with  $M_w = 2.80$  kg/mol and  $M_w/M_n = 1.2$  was purchased from Goodyear Chemical.<sup>19</sup> The PB-PS diblock copolymer (the mass fraction of the PS block is 55%, and the total  $M_w = 6.30$  kg/mol,  $M_w/M_n = 1.04$ ) was synthesized by J. W. Mays, University of Alabama, Birmingham.

The blends used in the present study were prepared by solution blending. First, the polymers were dissolved in dichloromethane separately and filtered with a 0.45- $\mu\text{m}$  poly(tetrafluoroethylene) filter. The purified polymers were dried in a vacuum oven at 40 °C. A mixture containing the appropriate amount of the purified polymers was then dissolved in dichloromethane at room temperature with a mass fraction of 0.05% Goodyear Wingstay No. 29 as an antioxidant. To remove all the solvents and air bubbles, the samples were dried in a vacuum oven at 40 °C for several days before use. The B0, B2.5, and B5 blends were annealed at 140 °C for 3 h under a vacuum. The annealing temperature was at least 6 °C higher than the cloud point of the prescribed blends. After annealing, the sample was transferred into the preheated sample compartment of the LS/optical microscopy instrument. The cloud points of the blends were determined by PCOM using a step-heating method.<sup>20</sup> The compositions and cloud points of the blends explored in the present article are listed in Table I.

In the shear cell, the sample compartment is composed of two electrically heated quartz plates, and the temperature of each plate is controlled to within  $\pm 0.1$  K by a 100  $\Omega$  platinum resistance-temperature-detector element in conjunction with a 1-mA constant current source. We fixed the quench depth of  $(1.5 \pm 0.1)$  °C for all blends investigated in the present article. Time  $t = 0$  is defined as the time at which the shear flow was stopped after the system reached steady state under the simple shear flow in the single-phase region.

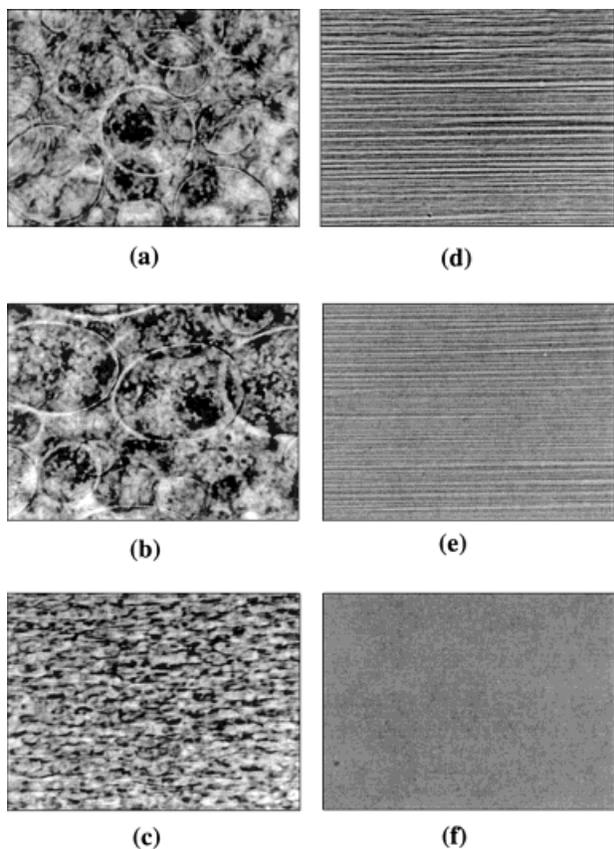
An *in situ* LS/optical microscopy instrument was designed and constructed for conducting the

LS and optical microscope measurements under simple shear flow.<sup>21</sup> The instrument has the capability to obtain two-dimensional LS data and real-time microscopic images. A beam of light from a 15-mW He-Ne laser with a wavelength of  $\lambda = 632.8$  nm was directed through the sample held between two electrically heated quartz disks. The Fourier image of the scattered light in the angular range from 4 to 27° (corresponding to  $q$  values ranging from 0.69 to 4.64  $\mu\text{m}^{-1}$ ) was focused onto a thermoelectrically cooled two-dimensional charge-coupled device (CCD) by using a pair of spherical condensers. The array of data from the  $256 \times 256$  pixels of a CCD camera was transferred to a personal computer via an optical fiber link. The microscopic images were collected by a video CCD camera (Dage MTI, model 72) and recorded on a super-VHS tape for subsequent analysis. A frame grabber from Data Translation (DT 3851) was used to digitize the captured images. Details of the instrument itself are described elsewhere.<sup>21</sup>

## RESULTS AND DISCUSSION

Phase separation in near-critical polymer blends occurs via the growth of concentration fluctuations when the blends are quenched into the unstable region of the phase diagram. We observed two kinds of coarsening mechanisms. The first is the intermediate stage of phase separation wherein both the composition of the coexisting phases as well as the size of the phase-separated domains change with time. The second is the late stage where the compositions of the coexisting phases have reached equilibrium, and only the size of the phase-separated domain changes with time.

The kinetic data of the phase separation in the B0, B2.5, and B5 blends (see Table I) were obtained by time-resolved *in situ* LS and PCOM.<sup>22</sup> At high shear rates, for example, 250  $\text{s}^{-1}$ , no significant LS images and microscopic structures were observed for all three blends, indicating a



**Figure 2.** Typical PCOMs of the B0 blend at various shear rates for the shear-induced homogenization. The dimension of each micrograph is  $200 \times 150 \mu\text{m}^2$ . The homogenization was observed at a shear rate =  $250 \text{ s}^{-1}$ : (a) shear rate =  $0.02 \text{ s}^{-1}$ , (b) shear rate =  $1 \text{ s}^{-1}$ , (c) shear rate =  $1 \text{ s}^{-1}$ , (d) shear rate =  $50 \text{ s}^{-1}$ , (e) shear rate =  $100 \text{ s}^{-1}$ , and (f) shear rate =  $250 \text{ s}^{-1}$ .

shear-induced homogenization within the measurement sensitivity of LS ( $\xi \approx 1.2 \mu\text{m}$ ) and optical microscopy ( $\xi \approx 1.0 \mu\text{m}$ ), where  $\xi$  is the characteristic length scale. Figure 2 shows the PCOMs of the B0 blend as a typical example at various shear rates for the shear-induced homogenization. The size of the micrographs is  $200 \times 150 \mu\text{m}^2$ . At very low shear rates [shown in Fig. 2(a)], the shapes of the dispersed droplets are isotropic with minimal deformation because of the relatively high interfacial tension. With an increasing shear rate, the dispersed domains elongate and coalesce [see Fig. 2(b)] and then break up and/or elongation occurs [see Fig. 2(c)]. The stringlike patterns with extremely high aspect ratios appeared at high shear rates [shown in Figs. 2(d,e)]. With a further increase in shear rate, the stringlike patterns almost disappear, and the micrograph shows no structure at  $250 \text{ s}^{-1}$

as shown in Figure 2(f). This indicates that the composition difference between two phases (PB-rich domain and PS-rich matrix) is negligible within an optical microscopic level ( $>1 \mu\text{m}$ ).

The isotropic LS patterns of the B0, B2.5, and B5 blends were obtained after shear quench. Because the scattering patterns are isotropic, we can use a circular averaged-scattered intensity. The  $q$  dependence of the circular averaged-scattered intensities obtained from the B0 blend at various times after the shear quench is shown in Figure 3(a). The scattering profile is flat at early times ( $t < 10 \text{ s}$ ). A peak is clearly observed at  $q = 3.8 \mu\text{m}^{-1}$  for  $t = 10 \text{ s}$ , and the scattering peak moves to a lower  $q$  and grows in intensity as time progresses, which is the defining feature of systems in the intermediate and late stages of phase separation. The time dependence of the scattering profiles obtained from the B2.5 and B5 blends is shown in Figures 3(b,c), respectively.

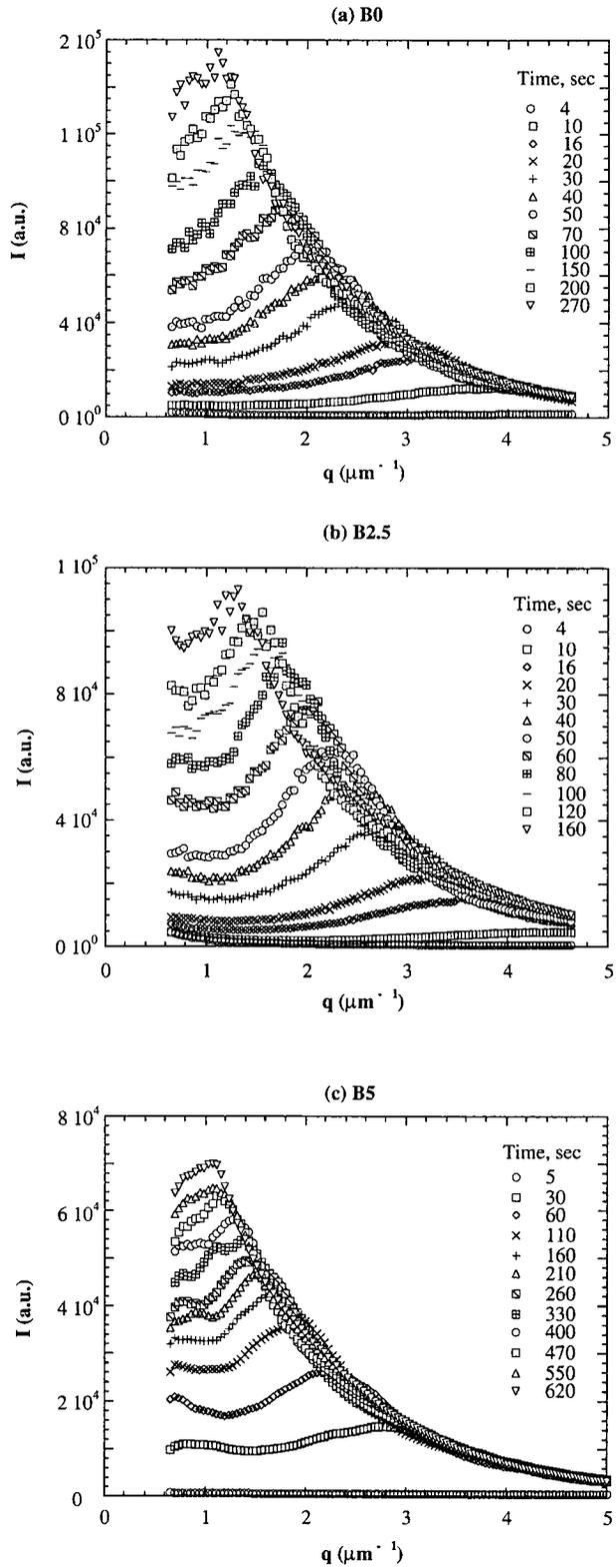
Coarsening processes in the intermediate and late stages of phase separation are inherently nonlinear, and analytic solutions to the governing equation are not yet known. The time dependence of the scattering-intensity maximum ( $I_{\text{max}}$ ) and wavevector maximum ( $\mathbf{q}_m$ ) in the intermediate and late stages of the phase separation in a binary blend is often expressed as scaling laws<sup>23,24</sup> in

$$\mathbf{q}_m = t^{-\alpha} \quad (1)$$

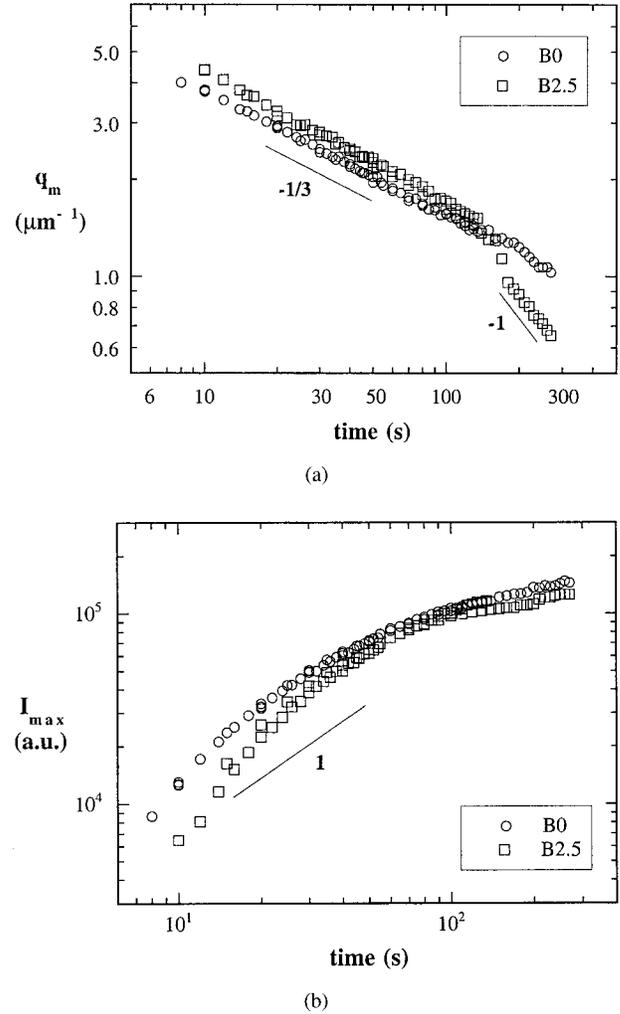
$$I_{\text{max}} = t^{\beta} \quad (2)$$

The exponential values of eqs 1 and 2 have a relationship  $\beta = 3\alpha$  as a result of dimensionality arguments. The exponent  $\alpha$  has a typical value around  $1/3$  in the intermediate stage and  $1$  in the late stage of phase separation.<sup>23–28</sup>

In Figures 4(a,b), we show the effect of adding block copolymer PB/PS to the PB–PS blend by displaying the time dependence of  $I_{\text{max}}$  and  $\mathbf{q}_m$  with  $\mathbf{q}_m = 2\pi/\xi$ , where  $\xi$  is the characteristic length scale of the phase-separated structure after cessation of shear. The characteristic length scale of our PB–PS blend in the intermediate stage of phase separation is about 10 times larger than that of the similar PB–PS blend obtained from the conventional temperature-quench method with a similar quench depth.<sup>20</sup> Because of the presence of a block copolymer, the interfacial free-energy density is lowered, and thus a small energy penalty is required to form a large concentration gradient at the interfaces between the



**Figure 3.** Time-resolved LS profiles at various times after shear quench with quench depth  $\Delta T = (1.5 \pm 0.1)^\circ\text{C}$ : (a) B0, (b) B2.5, and (c) B5 (the standard uncertainty in the measurement is smaller than the size of the symbol).



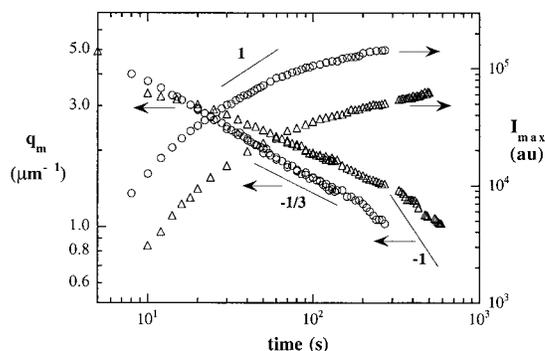
**Figure 4.** (a). The location of LS maximum  $q_m$  versus time for the B0 and B2.5 blends. The solid lines represent the scaling predictions of Akcasu et al.<sup>23</sup> for the intermediate and late stages of spinodal decomposition. The open circles refer to the B0 blend, and the open squares refer to the B2.5 blend. The standard uncertainty in the measurement is smaller than the size of the symbol. (b). The maximum of LS intensity  $I_{max}$  versus time for the B0 and B2.5 blends. The solid line represents the scaling prediction of Akcasu et al.<sup>23</sup> for the intermediate stages of spinodal decomposition. The open circles refer to the B0 blend, and the open squares refer to the B2.5 blend. The standard uncertainty in the measurement is smaller than the size of the symbol.

coexisting phases. This may affect the sequence of the conventional temperature-quench phase-separation mechanism in binary systems. Siggia<sup>26</sup> identified three stages of size growth in the phase separation of binary blends: (1) diffusion, (2) hydrodynamic flow, and (3) coalescence. The compositions of the phase-separated structures reach to the coexistence compositions, form co-continuous

structures through molecular diffusion, form discrete domains through hydrodynamic flow, and then grow in domain size through coalescence. Large concentration fluctuations can exist and develop relatively quickly because of the fact that the block copolymer will concentrate at the interfaces between coexisting regions having the steepest concentration gradient.<sup>29</sup> In other words, relatively large domains ( $\xi < 1 \mu\text{m}$ ) that could not be detected by LS and PCOM may start to be formed from the inhomogeneous structures (or large fluctuations) left behind by shear quench. Also, the shear-quench technique is relatively faster to get into the unstable region of the phase diagram than the conventional temperature-quench technique. It takes a while for thermal equilibrium in the conventional temperature-quench experiments so that the phase-separation process at the beginning is relatively slower than that of the shear-quench technique.

In Figure 4(a), we see that the B2.5 blend has a larger  $\mathbf{q}_m$  until  $t = 150$  s. This means that the blend containing 2.5% of the block copolymer has a smaller domain size than that of B0 until this time. For  $t < 150$  s the experimental scattering data obtained from the B0 and B2.5 blends are consistent with  $\alpha = 1/3$ , which implies that both blends are still in the intermediate stage of phase separation. In contrast, the scattering data from the B2.5 blend are well consistent with  $\alpha = 1$  after 150 s. This implies that the coarsening process in the B2.5 blend containing 2.5% of the block copolymer enters the late stage relatively early, and the domain growth is accelerated by the hydrodynamic flow for  $t > 150$  s. However, the B0 blend is still in the intermediate stage of phase separation within this time range. For the B2.5 blend, we can thus conclude that the addition of a block copolymer retards the coarsening processes in the intermediate stage but accelerates the coarsening mechanism when entering into the late stage of phase separation in the shear-quench experiments.

In Figure 4(b), it is evident that the addition of a block copolymer suppresses the scattering intensity especially in the intermediate stage, but the scattering-maximum data are not consistent with  $\beta = 1$  and 3 in the intermediate and late stages of phase separation, respectively. This discrepancy indicates that the time dependence of the scattering maximum in the shear-quenched phase separation on the B0 and B2.5 blends does not seem to follow the theoretical scaling predictions.<sup>26–28</sup> We can consider possible reasons for this discrepancy in our PB–PS system. First, rel-



**Figure 5.** The time dependence of  $\mathbf{q}_m$  and  $I_{\max}$  for the B0 and B5 blends. The solid lines represent the scaling predictions of Akcasu et al.<sup>23</sup> for the intermediate and late stages of spinodal decomposition. The open circles refer to the B0 blend, and the open triangles refer to the B5 blend. The standard uncertainty in the measurement is smaller than the size of the symbol.

atively large-scale structures ( $\xi < 1 \mu\text{m}$ ) can exist at the time of shear quench although the amplitude of composition fluctuations may be small enough that it does not give an observable LS signal with our detector. Additionally, the micrographs of shear-induced single-phase blends at  $t = 0$  represent texture-free images. Therefore, we realize that there are no detectable structures within the capability of our LS and PCOM instruments. Second, large-size ( $\xi \approx 2 \mu\text{m}$ ) composition fluctuations are observed in the LS data at a short time ( $t = 10$  s) after cessation of shear flow. On the other hand, the micrographs of the homopolymer blends at  $t = 30$  s seem to be co-continuous structures that lead to the conclusion that the slopes of  $\alpha = 1/3$  and  $\alpha = 1$  correspond to the intermediate and late stages of phase separation in a shear-quenched system, respectively. Therefore, the discrepancy of  $\beta < 3\alpha$  may be due to either the addition of the block copolymer, the low transmission of the sample caused by the large refractive-index differences of PB and PS ( $n_{\text{PB}} = 1.516$  and  $n_{\text{PS}} = 1.595$ ), and/or the very different phase-separation mechanisms caused by the shear-quench technique.

Figure 5 compares the phase-separation kinetics between B0 and B5 and shows the concentration effect of the block copolymer on the time dependence of  $\mathbf{q}_m$  and  $I_{\max}$ . As we increase the mass fraction of the block copolymer from 2.5 to 5%, the kinetics of phase separation seems to change significantly. The maximum scattering intensity is significantly suppressed as the concentration of the block copolymer increases. We find that the B5 blend has a smaller  $\mathbf{q}_m$  in the early

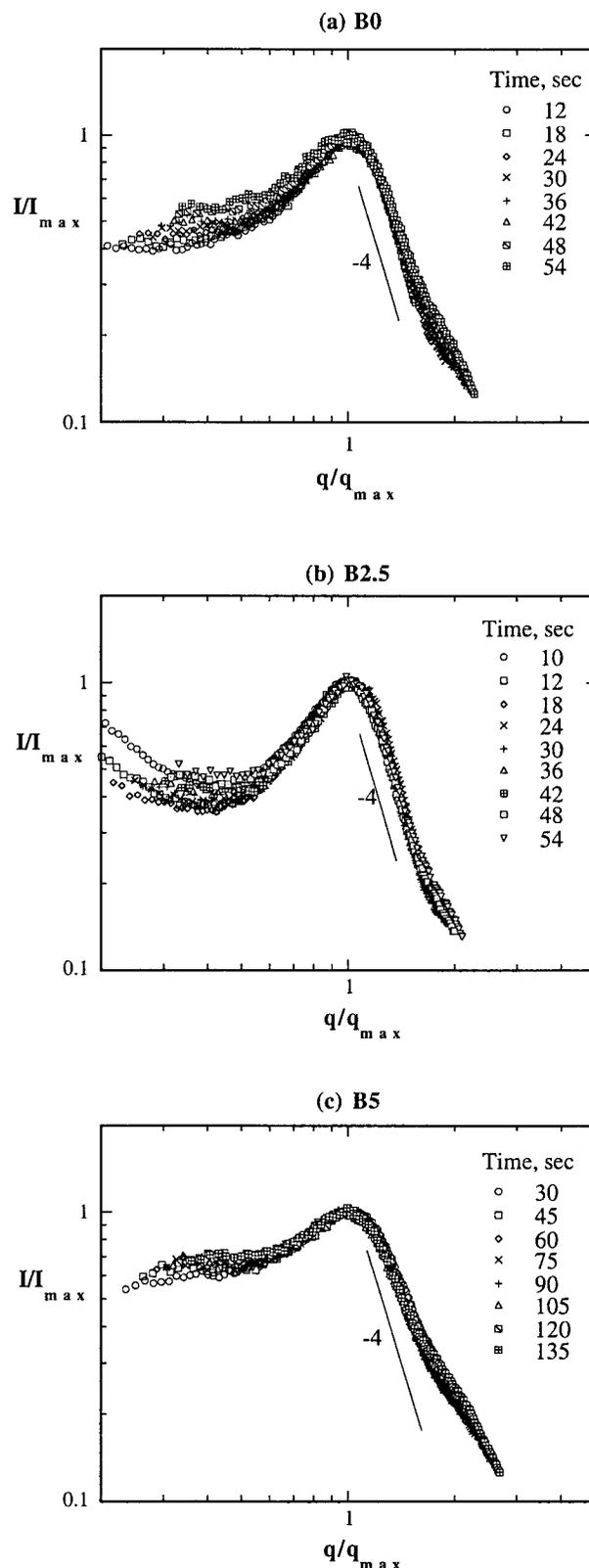
period of the phase separation ( $t < 20$  s). This means that the blend containing 5% of the block copolymer has a larger characteristic length scale than that of blend B0 at the beginning of the shear quench. The block copolymer probably tends to reside at the steepest gradient location when the mass fraction of the block copolymer reaches a certain critical level,<sup>29</sup> and this stabilizes the large fluctuation and gives a larger domain size at the beginning of the shear quench. The overall kinetics, however, slows down later because the accumulation of block copolymers at the interfaces slows down the transport of homopolymers across the interfaces. Therefore, the dimensional growth is retarded. As the block copolymers accumulate at the interfaces, the formation of an interfacial layer could induce a strong inhibition mechanism of droplet coalescence similar to that in thin film.<sup>30</sup>

Figure 6 illustrates the concentration effect of a block copolymer on the time dependence of the scattering intensity. For a clear comparison, the normalized scattering intensities ( $I/I_{\max}$ ) of the B0, B2.5, and B5 blends are plotted as a function of a normalized wavevector ( $\mathbf{q}/\mathbf{q}_m$ ). We introduce the scaled structure function of Furukawa<sup>27</sup> that suggests the domain structure formed in the two-phase state to explain the scattering profiles

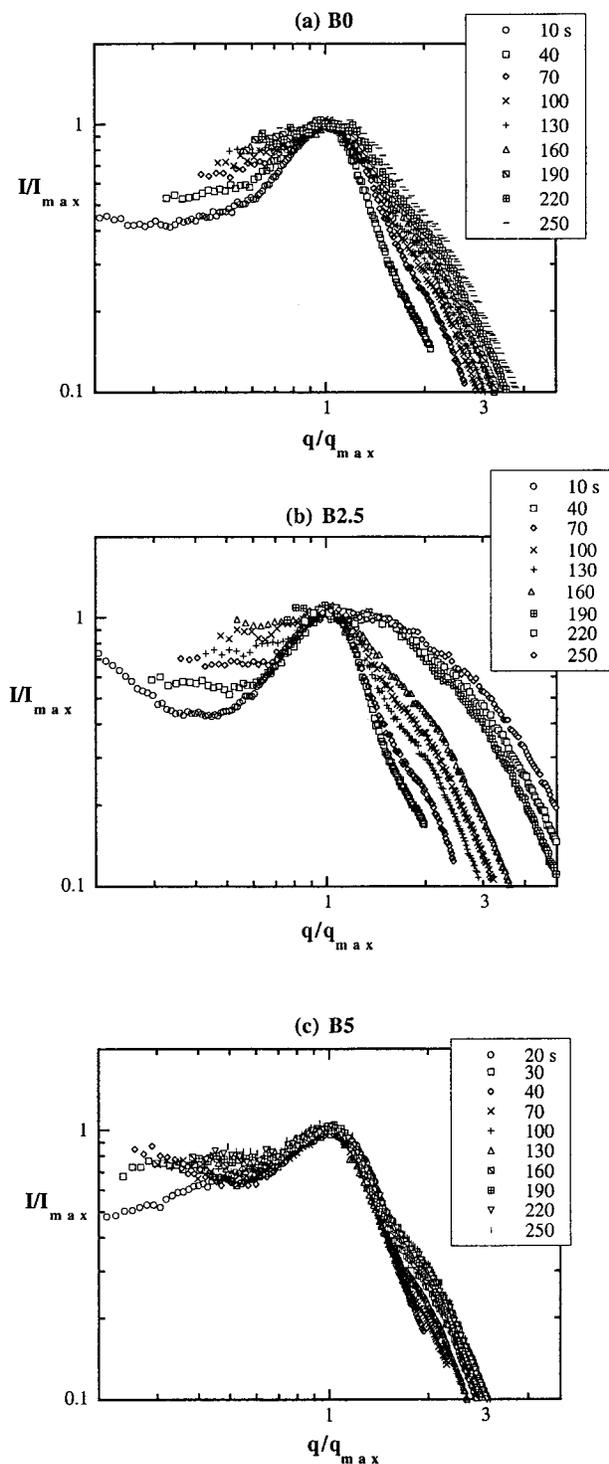
$$\frac{I}{I_{\max}} = \frac{c_1(\mathbf{q}/\mathbf{q}_m)^2}{c_2 + (\mathbf{q}/\mathbf{q}_m)^6} \quad (3)$$

where  $c_1$  and  $c_2$  are constants. For all three blends, the normalized scattering profiles in the intermediate stage are self-similar and collapsed onto a single master curve as a function of time, as shown in Figure 6. In the case of the B0 and B2.5 blends, the scattering-intensity profiles show the slope of  $-4$  for  $\mathbf{q}/\mathbf{q}_m > 1$ . On the other hand, when more of the block copolymer is added (i.e., 5%), the slope becomes less steep than the slopes of the two previous cases (B0 and B2.5). This may be interpreted as an indication of the formation of fuzzy boundaries caused by the accumulation of diblock copolymers at the interfaces of the phase-separated domains or by the growth of small new domains formed in the original domains as well as in the original matrix.

At later times after the shear quench, each blend represents its own characteristic behavior in the scattering profiles as shown in Figures 7(a–c). The broadening of the normalized LS profiles in the B0 blend was observed in Figure 7(a). This implies that the distribution of the domain



**Figure 6.** The time dependence of normalized scattering intensity  $I/I_{\max}$  in the early stage of phase separation: (a) B0, (b) B2.5, and (c) B5. The relative standard uncertainty in  $I/I_{\max}$  is less than 5%.

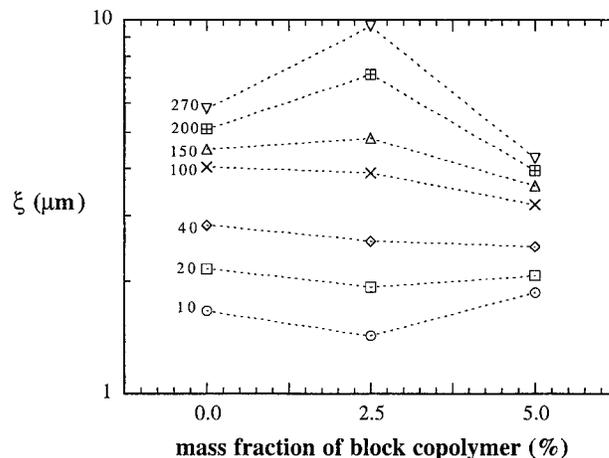


**Figure 7.** The time dependence of normalized scattering intensity  $I/I_{\max}$ : (a) B0, (b) B2.5, and (c) B5. The relative standard uncertainty in  $I/I_{\max}$  is less than 5%.

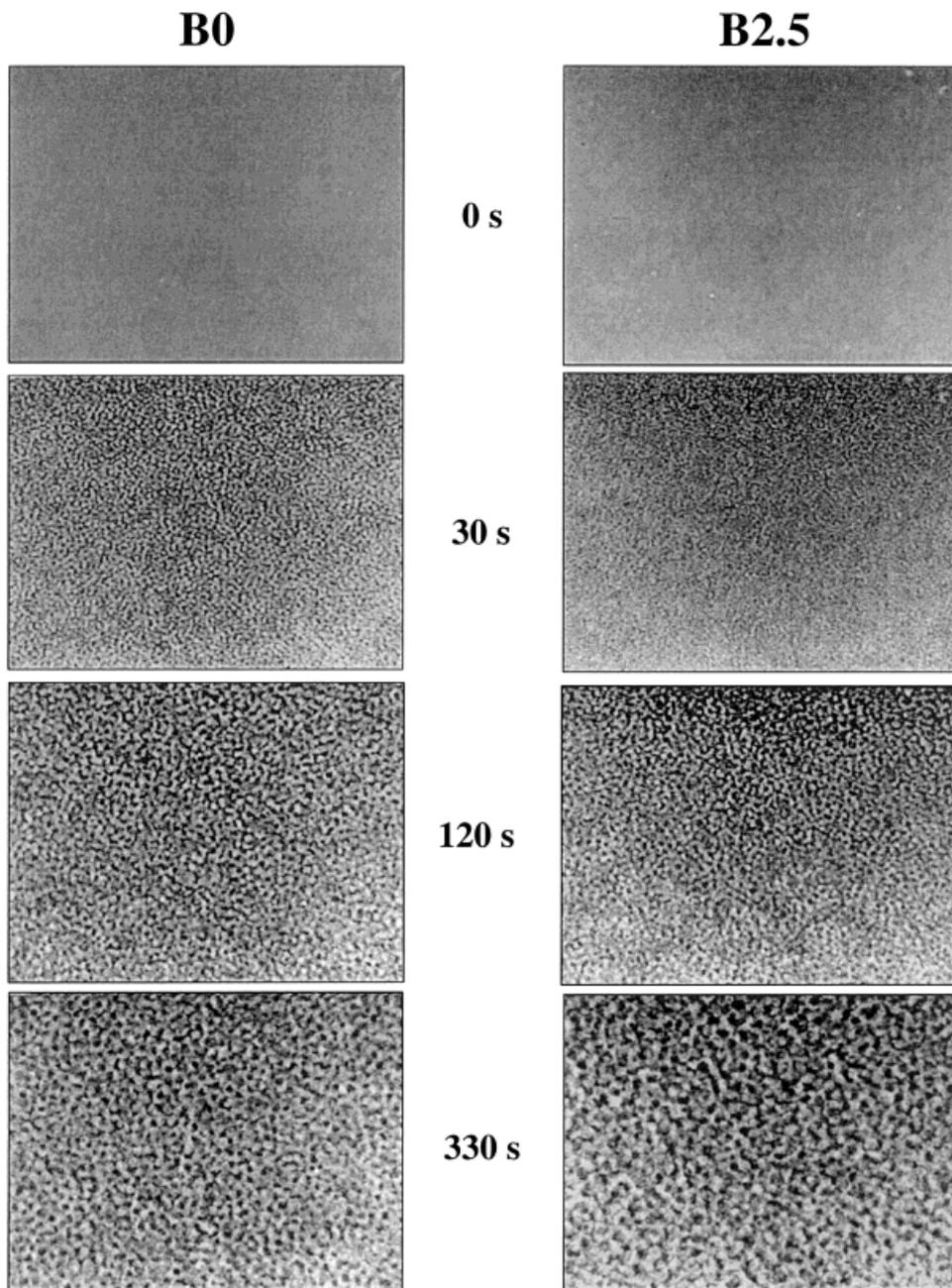
size is gradually broadened with time. The B2.5 blend also shows that the distribution of the domain size is gradually broadened with time as shown in Figure 7(b). However, we see a big jump

in the peak width as the time increases from 160 to 190 s after cessation of shear. This discontinuity is directly correlated to the transition from the intermediate to the late stages of phase separation where the slope  $\alpha$  changes from 1/3 to 1. Although there is a little broadening of the normalized LS profiles of the B5 blend as shown in Figure 7(c), the characteristic length scale is much smaller than that of the B0 blend at any given time except very early times,  $t < 20$  s (see Fig. 5). The amount of block copolymers accumulated at the interfaces could have lowered the interfacial tension, which may prevent a clear transition from the thermodynamic coarsening, such as diffusion, to the hydrodynamic coarsening, such as liquid flow or coalescence. The transition depends on the pinch off the co-continuous structure into discrete droplets as well as the recoil back into more spherical droplets because of instability and the interfacial tension of the two coexisting phases.<sup>11,30</sup>

In Figure 8 we compare the characteristic length scale of the phase-separated structures,  $\xi$ , obtained from the LS data at selected times for the B0, B2.5, and B5 blends. It is evident that the characteristic length scale in the B2.5 blend is smaller than that of homopolymer blend B0 until  $t = 100$  s, but it becomes larger for  $t \geq 150$  s corresponding to the transition time from the intermediate to the late stages of phase separation. In the case of the B5 blend, the characteristic length scale is always smaller than that of the B0



**Figure 8.** The dependence of a characteristic length scale,  $\xi$ , on the concentration of diblock copolymer in the binary PB-PS blend. The numbers in the figure represent the times after cessation of shear. The curves are drawn through the data point for guide to the eye. The standard uncertainty in the measurement is smaller than the size of the symbol.

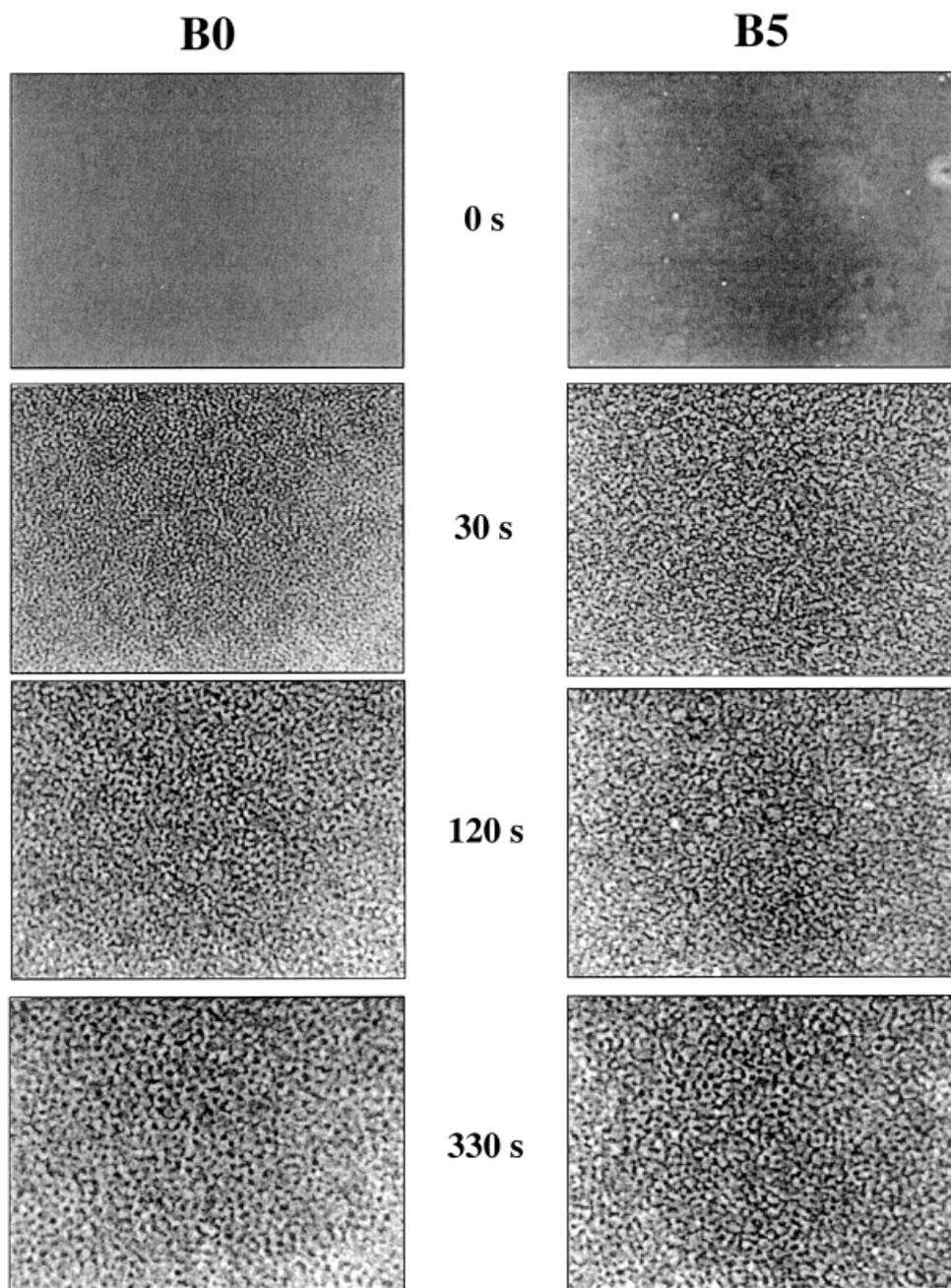


**Figure 9.** Comparison of the optical micrographs of the B0 and B2.5 blends at the selected times after shear quench. The dimension of each micrograph is  $200 \times 150 \mu\text{m}^2$ .

blend except  $t = 10$  s corresponding to the early stage of the phase separation (see Fig. 5). Thus, the scattering results imply that the addition of the block copolymer can accelerate or retard the phase-separation kinetics, and the mechanism of phase separation depends on the concentration of the block copolymer in the blends. This differs from the previous results<sup>8–12</sup> obtained from the temperature-quench experiments in which the addition of the block copolymer to the binary

blends resulted in the suppression of the coarsening rate except for the PEB/PMB/PEB–PMB blend.<sup>13</sup> Therefore, simultaneous experiments on the kinetics of phase separation based on *in situ* microscopy and LS techniques conducted in the present study are an attempt to distinguish some subtle phase-separation mechanisms caused by shear quench.

We compare the micrographs of the B0 and B2.5 blends in Figure 9. The acceleration of do-



**Figure 10.** Comparison of the optical micrographs of the B0 and B5 blends at the selected times after shear quench. The dimension of each micrograph is  $200 \times 150 \mu\text{m}^2$ .

main growth observed in the late stage of phase separation by LS is also readily identified in the micrographs of Figure 9. The size of the domains in the B2.5 blend is smaller than that of the B0 blend until  $t = 120$  s, and then becomes bigger in the later stage ( $t = 330$  s). This implies that the addition of 2.5% of the block copolymer accelerates the phase-separation kinetics, meaning the blend containing 2.5% of the block copolymer en-

ters the late stage earlier than the B0 blend. This conclusion is consistent with the data shown in Figure 4(a), where we show the time dependence of  $q_m$  and  $I_{\text{max}}$  for the B0 and B2.5 blends.

Finally, we compare the micrographs of the B0 and B5 blends in Figure 10. We can see bigger domain sizes from the B5 blend at least up to 120 s after shear quench. This is inconsistent with the LS data shown in Figure 5 where the

scattering results imply that the addition of the block copolymer suppresses the domain growth in the B5 blend. The  $q_m$  is larger at all times for the B5 blend except for the first 10 s, which implies that the domain size of the B5 blend is smaller than that of the B0 blend in the LS measurement. However, in the microscopic measurement the droplet size of the B5 blend grows bigger than that of the B0 blend at least up to 120 s after cessation of shear as shown in Figure 10. The discrepancy between the LS and the microscopic data in the B5 blend can be explained as follows. Although this is beyond the sensitivity of the LS and PCOM, we know from the other study<sup>30</sup> that the phase-separated structures at high block copolymer concentrations may be stabilized under shear with the block copolymers aggregated at the steepest gradient region. Therefore, before shear quenching at a shear rate of  $250 \text{ s}^{-1}$ , the domains in either a droplet or stringlike shape much smaller than a micron in length scale may still exist,<sup>31</sup> which initiates the phase separation both inside and outside (in the matrix phase) of the pre-existing structures. In other words, there will be phase separation in the original domains (into new small domains embedded in the original large domain that become a matrix of the new small domain) as well as in the original matrix with complementary compositions. The composition of the phase-separated domains within the original domains will be the same as the composition of the matrix of the phase-separated matrix phase. In this second phase separation, because the new minority domains separated out within the original domains will have the same compositions as the majority matrix parts within the original matrix region, the LS measurement could be dominated by the phase-separation process within the original phase-separated structures. In contrast, the PCOM is only measuring the outside parameters of the original domains that have been growing from the pre-existing structures at the time of shear quench. As small domains grow inside the original larger domains in the B5 blend, the larger domains gradually break up into smaller domains and merge with the new matrix part of the phase-separated matrix. That is the why the LS detects the growth of smaller structures in the B5 blend even smaller than that of the B0 blend.

## CONCLUSION

We have studied the effects of the diblock copolymer (PB-PS) addition to the binary homopoly-

mer blend (PB/PS) on the phase-separation kinetics and morphology obtained from the shear-quench technique using *in situ* LS and PCOM. It has been reported that the domain size in the blends containing a block copolymer becomes smaller as a result of the slowing down of the phase separation in the temperature-quench experiment. In this shear-quenched experiment, we found that the domain size as well as the kinetics of phase separation depend on the quench methods such as temperature jump or shear quench and the amount of the diblock copolymer added to the homopolymer blend. We also observed that the addition of 2.5% of the block copolymer results in a smaller characteristic length scale than that of the homopolymer blend (B0) until the late stage of phase separation. On the other hand, the addition of 5% of the block copolymer results in a very complicated mechanism of phase separation within the phase-separated structures and the breakup of large domains at the late stage. Thus, in a limited sense, we conclude that the addition of the block copolymer to the binary blend in the shear-quenched experiment could affect the kinetics of phase separation in the following ways: First, the domain size of the blend containing 2.5% of the block copolymer is smaller than that of the homopolymer blend B0 in the intermediate stage of phase separation; however, it becomes larger than that of B0 in the late stage of phase separation. The reason is that it takes a shorter time for the B2.5 blend to enter the late stage than that of the B0 blend. Second, for the B5 blend, very unusual phase-separation kinetics in the intermediate and late stages (compared to the temperature-induced phase separation studied either only by LS or microscopy) could be obtained with the combination of using the shear-quench technique and the block copolymer as an interfacial modifier. We think that the combination of the *in situ* LS, optical microscopy, and the shear-quench technique can reveal new and complex mechanisms in the study of phase-separation kinetics in polymer systems. It may be useful especially for the systems containing compatibilizer (or interfacial modifier), external shear fields, or even chemical reactions.

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- The references to commercial equipment or materials do not imply recommendation or endorsement by the National Institute of Standards and Technology. According to ISO 31-8, the term *molecular weight* has been replaced by "relative molecular mass",  $M_r$ . The older, more conventional, notation for number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights is utilized in the present article.
- The cloud points of the polymer blend were measured as follows. The blend is loaded in the shear cell and the temperature is raised to the one-phase region and then mixed by the shear field to make the blend become homogenous. The shear field works as a good tool for mechanical mixing. Then we lowered the temperature of the shear cell 1 °C at a time until phase-separated domains appeared on the monitor screen of our shear LS/microscopy instrument. As soon as the phase-separated domains appeared on the screen, we raised the temperature by 2 °C. After making sure the blend was in the one-phase region, we lowered the temperature 0.1 °C at a time until phase-separated domains appeared and then raised the temperature by 0.1 °C to see if it would go into one phase again. By repeating the preceding procedure, we determined a cloud point for a blend with an accuracy of  $\pm 0.1$  °C.
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