Scattering Studies of Self-Assembling Processes of Polymer Blends in Spinodal Decomposition

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Abstract

Structure self-assembling in the spinodal decomposition (SD) of polymer blends in its late stage has been explored for a near-critical mixture of polybutadiene and polyisoprene by a time-resolved light scattering technique, with a particular emphasis on the time evolution of the interface structure. By analysis of a scaled structure factor \( F(x, t) = I(q, t)q_m(t)^{\alpha} \) over wide ranges of a reduced scattering vector \( x = q/q_m(t) \) and time, it was found relevant to divide the late stage of SD into two stages, I and II. Here, \( I(q, t) \) denotes the scattered intensity as a function of the scattering vector \( q \) and time \( t \). In the intermediate stage preceding the late one, \( F(x, t) \) became sharper with its peak at \( x = 1 \) increasing with \( t \). However, as time elapsed, \( F(x, t) \) turned out to be universal for \( t \), first in the range of \( x \) smaller than about 2 and then over the entire range of \( x \) accessible by the present experiment. The time interval in which the former occurred is defined as late stage I and the one in which the latter was realized is called late stage II. In late stage I, the average thickness of phase-phase interfaces decreases towards an equilibrium value and the time evolution of the interfacial area density \( \Sigma(t) \) does not scale with \( q_m(t) \), i.e. the exponents \( \gamma \) and \( \alpha \) in the power laws \( \Sigma(t) \sim t^{-\gamma} \) and \( q_m(t) \sim t^{-\alpha} \) do not coincide (actually, \( \alpha < \gamma \)). Late stage II corresponds to the process in which these exponents become equal and the interface thickness reaches equilibrium. Such conditions probably ensure the establishment of a complete dynamical scaling law in the SD process.

1. Introduction

The mechanism and dynamics of spinodal decomposition (SD) processes of polymer blends have been extensively investigated from both theoretical (Gunton, San Miguel & Sahni, 1983) and experimental (Hashimoto, 1988) points of view. We have classified the SD of a critical mixture of polystyrene (PS) and poly(methyl vinyl ether) (PMVE) into three stages which we called early, intermediate and late (Hashimoto, Itakura & Hasegawa, 1986). The spatial composition distributions in these stages for a mixture of polymers \( A \) and \( B \) are shown in Fig. 1, where \( \varphi_A \) is the composition of polymer \( A \). In the early stage, the composition distribution is described well by linearized theory (Cahn, 1965; de Gennes, 1980; Binder, 1983). The wavelength \( \Lambda_m(t) \) of the dominant mode of composition variation is essentially independent of time \( t \), while the amplitude of composition fluctuation, \( \Delta \varphi(t) \), grows exponentially with increasing \( t \). The quantitative definition of \( \Lambda_m(t) \) is given below. The composition fluctuation grows continuously in time and nonlinear effects become important. Thus, an increase in \( \Lambda_m(t) \) occurs (from \( \Lambda_1 \) to \( \Lambda_2 \) in Fig. 1) (Langer, Bar-on & Miller, 1975; Grant, San Miguel, Viñals & Gunton, 1983).

![Fig. 1. Schematic diagram showing the spatial segmental density profile of component A in the early (a), intermediate (b) and late (c) stages of spinodal decomposition.](image-url)
This stage of SD can be divided into two substages, intermediate and late. In the intermediate stage, the growth of $\Delta \varphi$ is substantial, but its rate is progressively suppressed and eventually becomes negligible. In this latter state, $\Delta \varphi$ is no longer distinguishable from its equilibrium value $\Delta \varphi_e$ determined by the coexistence curve (Jinnai, Hasegawa, Hashimoto & Han, 1991), and the system enters the late stage. In this stage, well-defined interfaces develop between two coexisting phases having the equilibrium compositions and $\Lambda_m(t)$, characterizing the global size of the structure, increases with time.

As usual, we define $\Lambda_m(t)$ by $2\pi/q_m(t)$, where $q_m(t)$ is the scattering vector $q$ at which the scattered intensity $I(q, t)$ shows a maximum $I_m(t)$. It can be shown by scaling analysis of $q_m(t)$, $I_m(t)$ and the scale structure factor $F(x, t)$ that if SD reaches the stage where $F(x, t)$ for different $t$ are superimposable (i.e. universal for $t$) over the entire range of $x$, the following relation holds:

$$\beta = 3\alpha.$$  

Here, $\alpha$ and $\beta$ are the exponents defined by

$$q_m(t) \sim t^{-\alpha}$$  

$$I_m(t) \sim t^{-\beta}$$

and $F(x, t)$ is defined by

$$F(x, t) = I(q, t)q_m(t)^3$$

with

$$x = q/q_m(t).$$

\subsection*{2. Experimental}

A binary mixture of polybutadiene (PB) and polyisoprene (PI) with a near critical composition (50/50 wt/wt) was chosen for this work. Molecular characteristics of PB and PI are summarized in Table 1. The polymer mixture was dissolved in toluene to prepare a homogeneous solution containing 10 wt% polymer. The solution was first filtered through a Milipore film having an average pore size of 0.2 \( \mu \)m and then cast into thin films in a Petri dish by evaporating solvent slowly for 4 d. Each film obtained was further dried in a vacuum oven at room temperature until its weight became constant (about 3 d were needed). The as-cast film thus prepared was transferred onto a glass plate 0.5 mm thick and 13 x 13 mm in section, degassed under vacuum at room temperature for about 12 h and seal-covered with a glass plate. Both PB and PI had $N_e/N_c$ about 20, where $N$ and $N_e$ are the degrees of polymerization of the polymer chain and the chain between entangling points, respectively (Ferry, 1980).
Our polymer mixture was found to show phase separation behavior of the LCST (the lower-critical-solution-temperature) type, with the spinodal temperature $T_s = 299.1$ K. This $T_s$ was determined from the following observations. Temperature jump to $T = 298$ K from a lower temperature caused no measurable increase in scattered intensity over a period of time up to 4 d (see Fig. 3b), while there appeared a spinodal ring at $q_m = 10^{-4}$ nm$^{-1}$ 3 d after the temperature jump to 300 K (Fig. 3a). The data reported below are concerned with the SD behavior of our polymer blend observed by the previously described time-resolved light-scattering method for a temperature jump from 298 to 306 K, i.e. for a quench depth of $\Delta T_s = T - T_s = 7$ K.

3. Experimental results

Time evolution of light scattering profiles after the temperature jump mentioned above is shown in Fig. 4, where (b) concerns the change from the early to the intermediate stage of SD and (a) the change from the intermediate to the late stage. An intensity maximum appears some time after the onset of SD and it shifts towards smaller $q$ while the peak intensity increases. The early-stage SD occurred for about 20 min or about 2 in the reduced time $\tau$, which is defined below in (9).

Fig. 5 shows time changes in the scattered intensity $I(q, t)$ at various $q$ values in the early-stage SD. It is seen that $\ln I(q, t)$ at fixed $q$ increases linearly with $t$ at a $q$-dependent growth rate $R(q)$, yielding

$$ I(q, t) = I(q, 0)\exp[2R(q)t]. \quad (6) $$

This behavior agrees with the prediction from Cahn's linearized theory (Cahn, 1965). Departure of the data points from (6) after some period of time reflects nonlinear effects which arise from the increased amplitude of composition fluctuation.

Fig. 6 illustrates $R(q)/q^2$ plotted against $q^2$ and the behavior of the data points is consistent with the theoretically predicted relation

$$ R(q)/q^2 = D_{app}[1 - q^2/[2q_m(0)^2]]. \quad (7) $$

Table 2 shows the values of the characteristic parameters $D_{app}$ (the collective diffusivity) and $q_m(0)$ determined by fitting (7) to the data of Fig. 6. This table also gives the value of the characteristic time $t_c$ defined by

$$ t_c = [q_m^2(0)D_{app}]^{-1}. \quad (8) $$

Fig. 3. Scattering pattern leading to determination of the spinodal temperature.

Fig. 4. Time evolution of light scattering profiles after a temperature jump from 295 K in the single-phase state to 306 K inside the spinodal phase boundary; $\epsilon_f = 1/T - 1/T_s/(1/T_s) = 2.29 \times 10^{-2}$. (a) The late stage and (b) the early and intermediate stages. The intensity is in arbitrary units.
In Fig. 7, the time changes in $q_m(t)$ and $I_m(t)$ are shown. Here, the arrow for $t_{cr1}$ indicates the crossover between the intermediate stage in which $\beta$ was larger than $3\alpha$ and the late stage in which $\beta$ became equal to $3\alpha$ (in fact, these conditions are our definition for the intermediate and late stages). Table 2 includes the value of $t_{cr1}$. The arrow for another crossover time $t_{cr2}$ points to the boundary between late stage I and late stage II, which are defined in the following section. At the longest time limit that could be attained by the present experiment, the exponent $\alpha$ reached 0.92. We believe the system would ultimately go into the regime where $\alpha$ is equal to unity. In fact, we have observed this regime at higher temperatures (Takenaka & Hashimoto, 1991).

Table 2. Characteristic parameters for spinodal decomposition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavenumber of the dominant mode of fluctuations in early-stage SD as determined from $R(q)/q^2$ versus $q^2$.</td>
<td>$q_m(0)$</td>
<td>nm$^{-1}$</td>
<td>4.23</td>
</tr>
<tr>
<td>Collective diffusivity in early-stage SD as determined from $R(q)/q^2$ versus $q^2$.</td>
<td>$D_{apf}$</td>
<td>nm$^2$ s$^{-1}$</td>
<td>6.13</td>
</tr>
<tr>
<td>Characteristic time for early-stage SD, $t_{cr1}$ = $[q_m(0)D_{apf}]^{-1}$.</td>
<td>$t_{cr1}$</td>
<td>s</td>
<td>613</td>
</tr>
<tr>
<td>Characteristic time for late stage I, $t_{cr2}$ = $[q_m(0)D_{apf}]^{-1}$.</td>
<td>$t_{cr2}$</td>
<td>s</td>
<td>9.2 x 10$^4$</td>
</tr>
<tr>
<td>Reduced crossover time $\tau_{cr1}$ = $t_{cr1}/t_1$.</td>
<td>$\tau_{cr1}$</td>
<td>s</td>
<td>5.5 x 10$^4$</td>
</tr>
<tr>
<td>Reduced crossover time $\tau_{cr2}$ = $t_{cr2}/t_1$.</td>
<td>$\tau_{cr2}$</td>
<td>s</td>
<td>15</td>
</tr>
</tbody>
</table>

4. Scaling analysis

The time changes in $q_m(t)$ and $I_m(t)$ are replotted in Fig. 8 using the reduced variables defined by

$$\tau = t/t_1,$$

$$Q_m(\tau) = q_m(\tau)/q_m(0),$$

$$I_m(\tau) = I_m(\tau)q_m(0)^2 \int_0^{q'} q^2 dq,$$

where $q'$ and $q''$ denote the $q$ values at which $I(q, t)$ almost vanishes. The arrows in the figure indicate the reduced times $\tau_{cr1}$ and $\tau_{cr2}$ corresponding to $t_{cr1}$ and $t_{cr2}$, respectively, and give $\tau_{cr1} = 15$ and $\tau_{cr2} = 90$. In the time scale of our experiment, $\alpha$ varied from 0.56 to 0.92 and $\beta$ from 2.4 to 2.8 as $\tau$ increased. In the long time limit of SD, the theory predicts either $\alpha = 1/3$ and $\beta = 1$ (bulk diffusion) or $\alpha = 1/4$ and $\beta = 3/4$ (surface diffusion) in the nonhydrodynamic regime and $\alpha = 1$ and $\beta = 3$ in the hydrodynamic regime (see e.g. Gunton et al., 1983). Thus, our results suggest that, in the period from the intermediate stage to an early time of late stage I, the hydrodynamic interaction is less significant, while, in late stage II, the system enters the hydrodynamic regime.
Fig. 9 presents the data for the scaled structure factor $F(x, t)$ [see (4)] in the intermediate stage (a), late stage I (b) and late stage II (c). The scattered intensity $I(q, t)$ can be generally expressed as

$$I(q, t) \sim \langle \eta^2 \rangle \Lambda_m(t)^3 S(x, t),$$

(12)

where $\langle \eta^2 \rangle$ is the mean square of refractive-index fluctuations and $S(x, t)$ is a scaling function which varies between zero and unity when $x$ is increased from zero to infinity. This characterizes the $q$ dependence of the scattered intensity and hence the pattern self-assembled during SD. $\langle \eta^2 \rangle$ is proportional to $\Delta \varphi(t)^2$ and can be determined experimentally from the integrated scattered intensity,

$$\langle \eta^2 \rangle = \int I(q, t)q^2dq.$$

The scaling function may generally depend on time because the self-assembling pattern may change with time. However, in late-stage SD in which the pattern grows with dynamical self-similarity, the function becomes independent of time.

Comparing (12) with (4) and noting the definition of $q_m(t)$, we find that the scaling function $S(x, t)$ is related to $F(x, t)$ by

$$F(x, t) = \langle \eta^2 \rangle S(x, t).$$

(13)

In the intermediate stage, $F(x, t)$ increases with time, primarily due to an increase of $\Delta \varphi(t)^2$ and hence $\langle \eta^2 \rangle$. At the same time $F(x, t)$ becomes sharper with increasing time. This sharpening is clearly observed by vertically shifting the profiles $F(x, t)$ at different times. The sharpening of $F(x, t)$ reflects that of $S(x, t)$. Thus, in the intermediate stage, $\langle \eta^2 \rangle$ increases and $S(x, t)$ becomes sharper with time, so that $F(x, t)$ becomes nonuniversal with time.

Fig. 9(b) shows that when SD enters the late stage, $F(x, t)$ at $x$ comparable to 1 becomes time independent. This implies that the global structure corresponding to $q = q_m(t)$ becomes scalable with a single time-dependent length parameter $\Lambda_m(t) = 2\pi/q_m(t)$. However, this figure reveals that $F(x, t)$ for $x$ above 2 [i.e. $q > 2q_m(t)$] differs for different $t$. We define late stage I as the interval of time in which $F(x, t)$ for high $q$ remains unscalable with $\Lambda_m(t)$ only. Thus, though self-similar globally, the self-assembled structure at different times is not yet self-similar locally. Fig. 9(c) shows that $F(x, t)$ at $t > 90$ turned out to be scalable only with $\Lambda_m(t)$ over the entire range of $x$ covered in the present work. We define late stage II as the time interval in which this complete universality of $F(x, t)$ is observed.

Interestingly, $F(x, t)$ in the late stage exhibits a shoulder or a second-order maximum at $x = 3$. In another work on a mixture of PB and styrene–butadiene random copolymer (SBR), we observed a similar shoulder in $F(x, t)$ at $x = 2$ (Hashimoto, Takenaka & Izumitani, 1989; Takenaka, Izumitani & Hashimoto, 1990). We tentatively consider that such a shoulder has something to do with a local structure probably consisting of stacked lamella-type domains.
According to this idea, depending on whether the effective volume fractions of $A$-rich and $B$-rich domains are 50/50 or deviate from this, the shoulder should appear at either $x = 3$ or $x = 2$ (Hashimoto, Nagatoshi, Todo, Hasegawa & Kawai, 1974; Hashimoto, Shibayama & Kawai, 1980). We note that the shoulder was found experimentally, almost at the same time, by Nose (1989) and Bates & Wiltzius (1989), and predicated by simulations by Puru & Oono (1988) and Chakrabarti, Toral, Gunton & Muthukumar (1989) and theoretically by Ohta & Nozaki (1989).

In late stage I, if the data for $F(x, t)$ at $x > 2$ are fitted to a relation of the kind

$$F(x, t) \sim x^{-n},$$

the exponent $n$ decreases from 7.2 to 4 with increasing time. This is a kind of dynamical crossover. A similar change in $n$ is expected to occur for $F(x, t)$ at a given time when $x$ is increased. This may be referred to as spatial crossover. In fact this spatial crossover is confirmed in late stage II. The origin of these crossover phenomena has been discussed elsewhere (Takenaka et al., 1990).

Bates & Wiltzius (1989) studied the SD on a nearly symmetric critical mixture of deuterated and protonated polybutadiene and divided the observed process into four stages: early, intermediate, transition, and final. It is worth comparing their four-stage classification with ours: early, intermediate, late I, late II.

(i) In both cases, the early stage ($0 < \tau < 2$ in our case) refers to the time interval in which the SD dynamics follows Cahn’s linearized theory.

(ii) In both cases, the relation $\beta > 3 \alpha$ ($\alpha = 0.77$ and $\beta = 2.5$ in our system) holds in the intermediate stage ($2 < \tau < 15$ in our case). In the experiment of Bates & Wiltzius, $\alpha$ depends on the phase-separation temperature, so that plots of $Q_m(\tau)$ versus $\tau$ at different temperatures do not fall on a single curve, differing from our PB/PI mixture (Takenaka & Hashimoto, 1991) for which they definitely fell onto a master curve.

(iii) Either in our late stage I ($15 < \tau < 89$) or in the Bates–Wiltzius transition stage ($15 < \tau < 200$), the amplitude of concentration fluctuation reaches equilibrium. However, in the former, the relation $\beta = 3 \alpha$ holds ($\alpha = 0.91-0.92$ and $\beta = 2.7-2.8$), while, in the latter, $\beta$ is still larger than $3 \alpha$ and, in addition, $\alpha$ is not only independent of temperature but also surprisingly as small as 0.28. Bates & Wiltzius consider that even after the amplitude of composition fluctuation reaches equilibrium, the interface thickness is initially comparable to $A_m(t)$ and decreases to an equilibrium value while $A_m(t)$ increases. This substantial decrease in the interface thickness must have a considerable effect on the dynamics in which the global structure is self-assembled during SD and hence on the relation between $\alpha$ and $\beta$. Thus, Bates & Wiltzius concluded that the relation $\beta = 3 \alpha$ will not be established soon after the amplitude of composition fluctuation reaches equilibrium. We directly evaluated the interface thickness as a function of time and found it to be about 350 nm in the initial period of late stage I. This value is only one seventh the value of $A_m(t)$ at the same time, suggesting that the local dynamic process towards the equilibrium interface does not greatly affect the self-assembling of the global structure so that the relation $\beta = 3 \alpha$ will hold as a good approximation once the amplitude of composition fluctuation reaches equilibrium. Thus, our late stage I is not always the same as that which Bates & Wiltzius call the transition stage.

(iv) Our late stage II ($89 < \tau < 210$) and the final stage of Bates & Wiltzius are the same. In both, SD is characterized by a single length parameter $A_m(t)$ and the composition distribution self-similarly varies with time, with its amplitude maintained at the equilibrium value.

(v) Finally, though interesting, the paper of Bates & Wiltzius did not go into a detailed discussion about either the time change in the scaled structure factor $F(x, t)$ or the nonuniversality of $F(x, t)$ at large $x \geq 2$. Thus, it is difficult to judge if there is a one-to-one correspondence between our late stage I and their transition stage.

5. Time evolution of interface structure

The scattered intensity $I(q, t)$ at large $q$ for a self-assembled structure with a diffuse interface approaches the so-called Porod region, in which we have

$$I(q, t) \sim \langle \eta(t)^2 \rangle \Sigma(t) q^{-4} \exp[-\sigma(t)^2 q^2].$$

Here, $\sigma(t)$ is a time-dependent parameter characterizing the spread of the segmental density profile $\rho(z)$ across the interface, which is described by

$$\rho(z) = \rho_0(z) * h(z)$$

with

$$h(z) = (2\pi \sigma^2)^{-1/2} \exp(-z^2/2\sigma^2),$$

where $z$ is a coordinate normal to the interface, $\rho_0(z)$ is the segmental density profile for the sharp interface and $*$ signifies a convolution product. We note that $\sigma$ is related to the characteristic interface thickness $t_f$ defined as the integral width of the Gaussian curve $h(z)$ by

$$t_f = \int_0^\infty h(z) dz/h(z = 0) = (2\pi)^{1/2} \sigma.$$
With (15) we obtain
\[
\tilde{I}(q, t) = I(q, t) / \int_q^\infty I(q, t) q^2 dq \\
\sim \Sigma(t) q^{-4} \exp[-\sigma(t) q^2],
\]
(19)
which shows that \( \ln [\tilde{I}(q, t) q^4] \) at fixed \( t \) plotted against \( q^2 \) follows a straight line and the parameters \( \Sigma(t) \) and \( \sigma(t) \) can be evaluated from the intercept at \( q = 0 \) and the slope of the line. Fig. 10 presents this plot at various \( t \) in late stages I and II. We observe that the data points at relatively small \( t \) exhibit a minimum. This feature is associated with the appearance of a shoulder in \( P(x, t) \) at \( x = 3 \) and makes the determination of the parameters somewhat ambiguous. However, as time elapses, the shoulder shifts to lower \( q \) and, as a result, the linear region is expanded and the parameters can be evaluated more accurately. The resulting values of \( \Sigma(t) \) and \( \sigma(t) \) are listed in Table 3, along with those of \( t_{fr} \).

Fig. 11 shows how \( \Sigma(t) \) and \( \Sigma(t) t_{fr} \) vary with time. The interface thickness decreases with time in late stage I but stays constant at \( t_{fr} = 256 \) (20) nm in late stage II. If we fit the \( \Sigma(t) \) data to a power law,
\[
\Sigma(t) \sim t^{-\gamma},
\]
(20)
we find that \( \gamma \) decreases systematically in late stage I and stays at about 1 in late stage II (note the location for \( t_{cr,2} \) indicated by an arrow on the horizontal axis). Since, as has been shown above, the exponent \( \alpha \) was found to be 0.77-0.90 in late stage I and 0.9-0.92 in late stage II, we see \( \gamma > \alpha \) and \( \gamma = \alpha \) in late stage I and II respectively. The inequality implies that, in the late stage, the local structure corresponding to higher-\( q \) modes relaxes to the equilibrium faster than the global structure corresponding to lower-\( q \) modes. It should be noted here that our previous analysis of the late-stage SD for a near-critical mixture of PB and SBR yielded \( \gamma < \alpha \), i.e. a conclusion quite opposite to that obtained here (Takenaka et al., 1990). We considered it necessary to re-examine this, because the previous analysis was based on the assumption that \( \sigma(t) q_{m}(t) \ll 1 \).

Fig. 12 illustrates the changes with time in \( \Sigma(t)/q_{m}(t) \), i.e. the interfacial area density relative to \( q_{m}(t) \) scaling the global structure, and also in \( t_{fr}(t) \Sigma(t) \), i.e. the volume fraction of the interface region. With (2) and (20), we can write
\[
\Sigma(t)/q_{m}(t) \sim t^{-(\gamma - \alpha)}
\]
and find \( \gamma - \alpha \) to be 0.23 and 0 for late stages I and II, respectively. On the other hand, the power law
\[
\Sigma(t) t_{fr}(t) \sim t^{-\delta}
\]
(22)
gives \( \delta = 1.3 \) and 1.0 for the late stages I and II, respectively. These results lead us to the following conclusions. (i) In late stage I, the time change in \( \Sigma(t) \) and \( q_{m}(t) \) follow different laws and \( t_{fr}(t) \) keeps decreasing with time. (ii) In late stage II, the time...
Table 3. Time evolution of the interfacial structure in late stages I and II

<table>
<thead>
<tr>
<th>Time t (min)</th>
<th>Reduced time τ*</th>
<th>Σ(t) x 10^2*†</th>
<th>σ†</th>
<th>t~t) (nm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>336.5</td>
<td>32.9</td>
<td>1.29</td>
<td>138.6</td>
<td>347.4</td>
<td>Late stage I</td>
</tr>
<tr>
<td>363.8</td>
<td>35.5</td>
<td>1.08</td>
<td>137.5</td>
<td>344.7</td>
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<tr>
<td>392.6</td>
<td>38.4</td>
<td>1.06</td>
<td>125.0</td>
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<td>42.1</td>
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<td>112.2</td>
<td>281.2</td>
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<tr>
<td>465.6</td>
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<td>96.5</td>
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<td>271.2</td>
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<td>267.7</td>
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<tr>
<td>948.9</td>
<td>92.7</td>
<td>0.24</td>
<td>112.2</td>
<td>281.2</td>
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<td>274.5</td>
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<tr>
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<td>101.8</td>
<td>0.22</td>
<td>110.9</td>
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<tr>
<td>1136.0</td>
<td>111.0</td>
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<td>102.5</td>
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<td>91.6</td>
<td>229.7</td>
<td></td>
</tr>
<tr>
<td>1992.3</td>
<td>194.7</td>
<td>0.11</td>
<td>105.4</td>
<td>264.2</td>
<td></td>
</tr>
<tr>
<td>2179.7</td>
<td>213.0</td>
<td>0.10</td>
<td>108.2</td>
<td>271.2</td>
<td></td>
</tr>
</tbody>
</table>

* τ = t/t_c.
† Interfacial area density.
‡ Parameter characterizing the interface thickness [see (17)].
§ Characteristic interface thickness [see (18)].

change in Σ(t) and q_m(t) follow the same power law and t~t) reaches an equilibrium value. Thus, in late stage II, it turns out that the time evolution of the self-assembled structure is scaled with a single length parameter over the entire length scale from local to global. The radii of gyration of our PB and PI samples can be estimated to be 8·8 and 10·4 nm, respectively, so that if their arithmetic mean is denoted by R_g, t~/R_g is 27 at AT = 7 K or ε_T = (1/T - 1/T_s)/(1/T_s) = 2.29 x 10^-2.

6. Universal nature of F(x, t) and crossover

As mentioned above, the nonuniversality of F(x, t) at large x (> 2) in late stage I can be attributed to the fact that q_m(t) and Σ(t) follow different dynamical scaling laws and t~t) still decreases in late stage I. From (4) and (15) it follows that F(x, t) at large x in the late stage, where t~t) becomes independent of time, is represented by

\[ F(x, t) \sim Σ(t)q_m(t)^{-1}x^{-4}\exp[-σ(t)q_m(t)^2x^2] \]

or

\[ F(x, t) \sim t^{-(γ-α)}x^{-4}\exp[-σ(t)q_m(t)^2x^2]. \]  

Since the term t^{-(γ-α)} decreases and the exponential term in this equation increases with time, the increase in F(x, t) at x > 2 in late stage I can be explained as being due to the outweighing of the latter over the former. The crossover from the nonuniversal to the universal F(x, t) occurs at t > t_c,2 at which γ = α and σ, q_m(t) ≪ 1, where σ is the equilibrium interface thickness.

We compare our value for t_c,2 with the theoretical prediction by Joanny & Leibler (1978) for a polymer/polymer mixture near the critical point. On the assumption of the hyperbolic-tangent-type segment density profile across the interface, they derived

\[ t_{c,2} = 2L, \]

where

\[ L = 2^{1/2}ξ = (9N_0ε_T/N_A/N_Bd^3)^{-1/2}, \]

ξ is the thermal correlation length and

\[ \bar{N} = N_0φ_{A,C} + N_B(1 - φ_{A,C}), \]

\[ d^3 = a_A^2(1 - φ_{A,C}) + a_B^2φ_{A,C}, \]

\[ ε_T = (χ - 1)/(χ_s). \]
Here, \( \varphi_{K,C}, a_K \) and \( N_K \) denote the volume fraction at the critical point, the Kuhn statistical segment length, and the degree of polymerization of polymer \( K (K = A \text{ or } B) \), respectively, and \( \chi \) is the Flory interaction parameter, with the subscript \( s \) specifying the value at the spinodal point. We assume our 50/50 wt/wt mixture of PB and PI to have the critical composition. Then, since \( N_{PB} = 1070, a_{PB} = 0.656 \text{ nm}, N_{PI} = 1490, a_{PI} = 0.656 \text{ nm} \) and, as noted above, \( \varepsilon_T = 2.29 \times 10^{-2} \), we obtain \( t_{r, \text{theory}} = 102 \text{ nm} \) from (25). Though our experimental value is larger than this by a factor of 2, the agreement may be considered satisfactory.

7. Comparison with theoretical scaled structure factors

Theories so far presented for \( F(x, t) \) are all concerned with the nonhydrodynamic regime \( (\alpha = 1/3 \text{ in (2)}) \) and are thus not applicable to the late stage in our experiment \( (\alpha = 1) \). Nonetheless, in Fig. 13, our experimental \( F(x, t) \) curve in late stage II is compared with the theory of Ohta & Nozaki (1989) (Fig. 13a) and the simulation work of Chakrabarti et al. (1989) (Fig. 13b). Though not shown here, the latter gives nonuniversal \( F(x, t) \) for \( x > 2 \), which decreases with increasing time. We interpret this behavior as being due to the overweighting of the term \( t^{-1(\gamma-\alpha)} \) over the term \( \exp[-\sigma(t)^2 q_m(t)^2 x^2] \) [see (24)].

The agreement of the experimental curve with the calculated one of Ohta & Nozaki is quite good. It is worth noting that both show a shoulder at \( x = 3 \). The experimental result is also consistent with the numerical one of Chakrabarti et al. (1989) though the shoulder is less apparent in the latter. This fine agreement between the experimental curve obtained in the hydrodynamic regime \( (\alpha = 1) \) and the calculated ones obtained in the nonhydrodynamic regime \( (\alpha = 1/3) \) may imply that the behavior of \( F(x, t) \) is rather insensitive to the detailed coarsening mechanism. On the contrary, the time change in the characteristic length scale \( A_m(t) \) [or \( 1/q_m(t) \)] is quite sensitive to the mechanism. Bates & Wiltzius (1989) made a similar comparison for a mixture of deuterated and protonated polybutadiene. Though exhibiting a shoulder at \( x = 2 \) instead of \( x = 3 \), their data are also consistent with the curve of Ohta & Nozaki (1989).

8. Concluding remarks

The demixing processes occurring in a spinodally decomposing mixture of PB and PI with a near-critical composition was studied over wide ranges of time scale and length scale by time-resolved light scattering. It was found that the process consists of four stages we call early, intermediate, late I and late II and that the self-assembled structure scalable over the entire length scale appears in late stage II. In this stage, the interface thickness becomes independent of time and the global and local self-assembled structures follow the same dynamical scaling law. Further work will be required to check the present conclusion by changing the quench depth (Takenaka & Hashimoto, 1991).

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