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Phase separation dynamics of polycarbonate/polymethyl methacrylate blends. I. Temperature jumps into an immiscibility loop

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Time-resolved light scattering was employed to elucidate the dynamics of phase separation in mixtures of polycarbonate (PC) and polymethyl methacrylate (PMMA). Blends of PC and PMMA of moderately low molecular weight reveal the coexistence of an upper critical solution temperature (UCST) and a lower critical solution temperature (LCST), forming an immiscibility loop. Temperature jump (T jump) experiments were conducted on the 40/60 PC/PMMA composition from a single phase (150 °C) to a two-phase immiscibility loop region (180 and 190 °C). Phase separation takes place through spinodal decomposition (SD). The early stage of SD is explicable in terms of the linearized Cahn–Hilliard theory. The late stage of SD follows the power law relationship with the exponents of $-1/3$ and 1 as predicted by the cluster theory of Binder and Stauffer. The universal curve with reduced variables Q_m and τ was established. The late stage data were analyzed in accordance with the recent scaling law of Furukawa. The temporal phase decomposition appears to be self-similar. The shape of the structure function can be scaled with slopes of 2 and -6 for $q < q_m$ and $q > q_m$ regions, respectively.

INTRODUCTION

It has been generally known that most metal alloys, low molecular weight oligomer and solution mixtures reveal an upper critical solution temperature (UCST).¹ On the contrary, most high molecular weight polymer blends exhibit an inverted phase diagram known as a lower critical solution temperature (LCST).² This contrasting behavior has been attributed to the small entropy of mixing of long chain molecules. Intuitively, if one selects an appropriate polymer pair with intermediate molecular weight, both UCST and LCST might appear in the phase diagram. This idea has led to the miscibility studies of polycarbonate (PC) and polymethyl methacrylate (PMMA) of moderately low molecular weight.³ Another interesting feature with this PC/PMMA mixture is the very small interaction parameter χ which would undoubtedly play an important role for observing both LCST and UCST. That is to say, if χ has a large positive value, the mixtures will be completely immiscible. On the other hand, if χ has a large negative value, the system may be miscible or may occasionally show an LCST behavior. When χ is close to zero or slightly positive, the coexistence of LCST and UCST might occur, as predicted in the equation of state theory by MacMaster.⁴

Recently, we observed an immiscibility loop phase diagram in the PC/PMMA mixture, in that the UCST is located above the LCST curve.⁵ A similar phase diagram has been reported for poly(ethylene glycol)/water mixtures⁶ and also for aqueous poly(vinyl alcohol-co-vinyl acetate) solution.⁷ The immiscibility loop has been predicted for polymer blends in the lattice fluid theory of Sanchez and co-workers.^{8,9} However, no experimental evidence has ever been found for polymer mixtures until recently. Our pre-

vious work may be the first experimental evidence to identify the immiscibility loop in homopolymer blends.⁵

In this paper, we focus our attention on the dynamic aspects of phase segregation at the composition of 40/60 PC/PMMA. Several T jump experiments were conducted from a single phase (150 °C) to a two-phase (180 and 190 °C) immiscibility loop region. The results were analyzed in the context of linear^{10,11} and nonlinear theories.¹²⁻¹⁷

EXPERIMENTAL

Reagent grades of bisphenol-*A* polycarbonate ($M_w \sim 64\,000$ and $M_w/M_n \sim 2.1$) and polymethyl methacrylate ($M_w \sim 30\,000$ and $M_w/M_n \sim 2.4$) were purchased from the Scientific Polymer Product Co. and Aldrich Chemical Co., respectively. The polymers were dissolved in a mutual solvent (tetrahydrofuran) at a polymer concentration of 2 wt %. Thin films (5–10 μm) were cast on glass slides at low temperatures of approximately 5 °C. The films were dried in a vacuum oven at 70 °C for at least 72 h and kept in a desiccator prior to use.

Time-resolved light scattering was employed to follow the dynamics of phase separation. The scattering setup consists of a 2 mW He–Ne laser light source with a wavelength of 632.8 nm. The scattering profile was monitored by a two-dimensional Vidicon camera interlinked with an Optical Multichannel Analyzer (OMA III, EG & G Princeton Applied Research Co.). The post data treatment was undertaken on an off-line microcomputer (IBM-PC). The detailed descriptions of the light scattering setup and the heating cell were reported elsewhere.¹⁸ T jumps experiments were carried out using a set of heating cells; one was controlled at the experimental temperatures (180 and 190 °C), while the other was used for preheating, typically at 150 °C for about a minute.

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RESULTS AND DISCUSSION

In a previous paper,⁵ we have demonstrated the immiscibility loop in moderately low molecular weight PC/PMMA blends. Figure 1 shows such a cloud point phase diagram of PC/PMMA blends obtained by annealing the mixtures for 2 h at each temperature (1 °C interval). Both UCST and LCST curves were located at appreciably lower temperatures than those obtained previously at a heating rate of 0.5 °C/min.⁵ Because of a strong heating rate dependence of the cloud point temperatures (Fig. 2), it is very difficult to establish a true equilibrium phase diagram from such nonisothermal experiments. However, the observed cloud point temperature (156 °C) for 40/60 PC/PMMA, as will be explained in a succeeding paper,¹⁹ is very close to the spinodal temperature obtained from isothermal T jump studies. In view of the lengthy procedure in the T jump experiments, the determination of spinodal temperatures for all blend compositions is no longer practical and therefore the true phase diagram was not established. In the case of PC/isotactic PMMA with comparable molecular weights, the blend exhibits an LCST and is reversible in character; hence, the establishment of a true phase diagram is relatively straight forward.²⁰ There is no doubt that PC/PMMA is a miscible pair, but it exhibits a variety of phase diagrams which makes the present study interesting.

Thermogravimetric analysis (TGA) studies show that the blends are thermally stable up to about 250 °C. The specimens after heating and cooling from 220 °C are completely transparent without any change in color or polymer degradation. As demonstrated previously, the phase separated domains in the two-phase region are interconnected which are familiar characteristics of spinodal decomposition.

Early stage of spinodal decomposition

We first carried out temperature jump experiments from a single phase (150 °C) to a two-phase region of 180

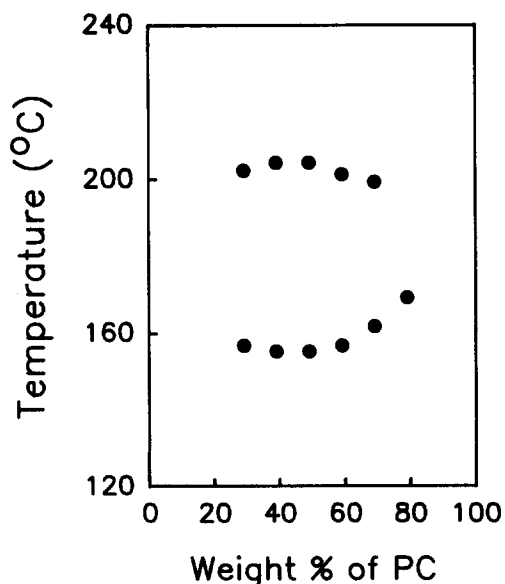


FIG. 1. A cloud point phase diagram of PC/PMMA blends obtained by annealing for 2 h at each temperature (1 °C interval).

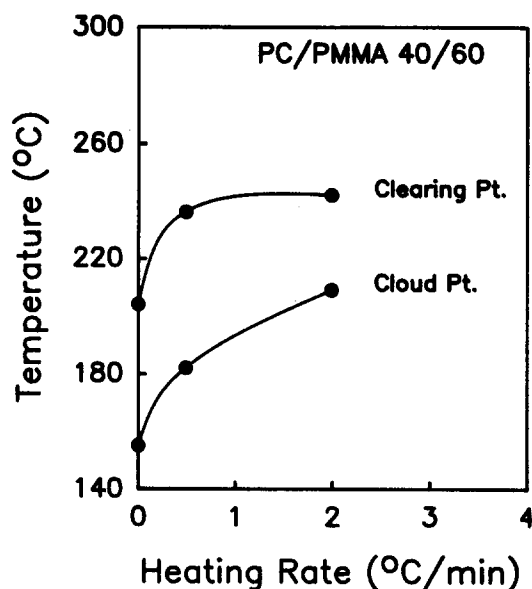


FIG. 2. The heating rate dependence of cloud point temperature for 40/60 PC/PMMA. The points on the temperature axis represent the cloud points obtained by 2 h annealing.

and 190 °C using time-resolved light scattering. Figure 3 shows a typical time evolution of scattering curves following a T jump to 190 °C. The scattered intensity increases very gradually at the beginning without revealing a scattering maximum. Then, a scattering peak appears at a large scattering wave number and remains stationary for a considerable period (about 90 min). Subsequently, the peak position moves to lower scattering wave numbers while the intensity increases immensely. The behavior of peak invariance is one of the features predicted in the linearized theory of Cahn–Hilliard¹⁰ in which the scattered intensity has been predicted to increase exponentially as follow:

$$I(q,t) = I(q,t=0)\exp\{2R(q)\cdot t\} \quad (1)$$

where t is the phase separation time and q is a scattering wave number which is equal to $(4\pi/\lambda)\sin\theta/2$ with λ and θ being the wavelength of incident light and a scattering angle measured in the medium. $R(q)$ is an amplification factor representing the growth rate of composition fluctuations which may be further expressed as

$$\begin{aligned} R(q) &= -Mq^2\left\{\left(\frac{\partial^2 f}{\partial c^2}\right) + 2\kappa q^2\right\} \\ &= D_{\text{app}}q^2\{1 - q^2/2q_m(0)^2\}, \end{aligned} \quad (2)$$

where M is an Onsager-type mobility, f is the local free energy density, c is the concentration, and κ is the coefficient of concentration gradient. D_{app} is the apparent diffusivity and $q_m(0)$ is the wave number, where $R(q)$ is maximum at $t=0$, which may be further expressed as

$$D_{\text{app}} = -M\left(\frac{\partial^2 f}{\partial c^2}\right) \quad (3)$$

and

$$q_m(0)^2 = q_c^2/2 = -\left(\frac{\partial^2 f}{\partial c^2}\right)/4\kappa, \quad (4)$$

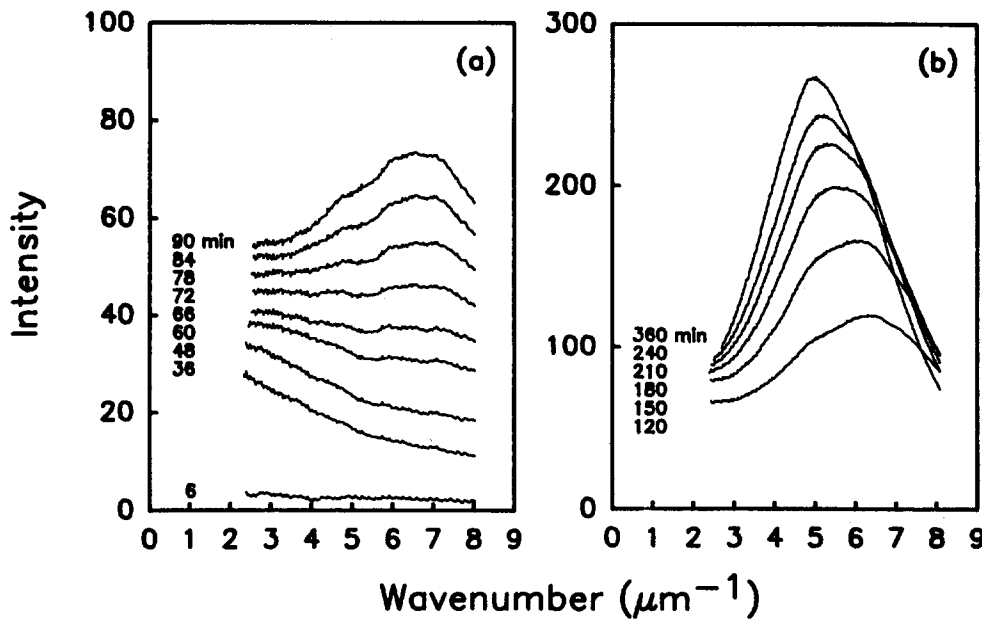


FIG. 3. Time evolution of scattering curves of the 40/60 PC/PMMA blend, following a T jump from a single phase (150°C) to a two-phase immiscibility loop region (190°C).

where q_c is the crossover wave number at which $R(q)$ becomes zero. The deficiency of Cahn-Hilliard theory was first pointed out by Cook¹¹ who proposed a structure factor $S(q,t)$ by incorporating the contribution from thermal fluctuations of a single phase, viz.,

$$S(q,t) - S_s(q) = [S(q,t=0) - S_s(q)] \exp\{2R(q) \cdot t\}, \quad (5)$$

where $S_s(q)$ is a virtual structure factor, i.e., an extrapolated structure factor into the two-phase region assuming analytical continuity in the mean-field approximation. The significance of this structure factor has been thoroughly discussed by Binder²¹ and Han *et al.*^{22,23} In the present case, the temperature jump is considerably large that the contribution from thermal fluctuations to the scattering may be negligibly small, thus Eq. (1) may be operative. In practice, the measured intensity needs to be corrected for parasitic scattering, dark current, and thermal fluctuations. These contributions were lumped together into background scattering which can be measured at the onset of phase separation. To obtain the true intensity, the background scattering was subtracted

from the experimentally observed intensity.

The corrected scattered intensity, $I(q,t) \sim S(q,t)$, was plotted in semilogarithmic form against phase separation time in Fig. 4 for various scattering wave numbers. In conformity with the prediction of the linearized theory, there is a considerable period where $\log I$ varies linearly with t . However, at a later time, the intensity deviates from the linear slope and levels off. The amplification factor, $R(q)$, was determined from the linear slope. The value of $R(q)/q^2$ was plotted against q^2 in Fig. 5 to test the validity of the linearized Cahn-Hilliard theory. As can be seen in Fig. 5, the data can be approximated by linear slopes for both T jumps of 180 and 190°C . In the literature,²⁴⁻²⁷ such plots tend to show a curvature rather than a linear slope, especially when the scattering peak appears at low angles due to the large initial fluctuation size. In the present case, since the initial fluctuation size is very small, the scattering maxima appears at relatively wide scattering angles. The scattering data at low wave numbers (below $q = 2.5 \mu\text{m}^{-1}$) are not necessarily contributed by the phase separation process, but affected by

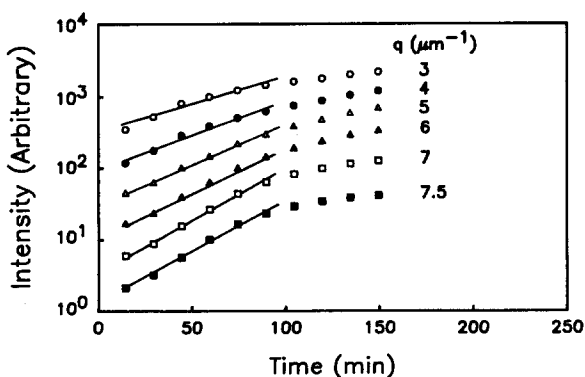


FIG. 4. The variation of logarithmic scattered intensity as a function of phase separation time for the 40/60 PC/PMMA at various wave numbers.

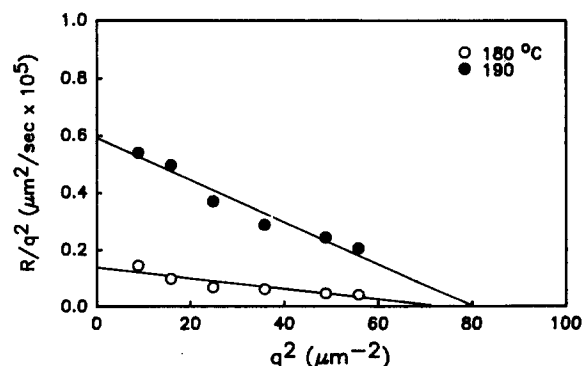


FIG. 5. The Cahn's plot of $R(q)/q^2$ vs. q^2 .

parasitic scattering. Thus, the validity of the linearized theory should be further checked with Eq. (4). As shown in Fig. 5, this relation holds for both T jumps of 180 and 190 °C, thereby confirming the validity of the linearized theory. Similar observations were made by Hashimoto *et al.*²⁸ and Okada and Han²² in the blends of polystyrene (PS)/polyvinyl methyl ether (PVME). Very recently, Bates²⁹ demonstrated the existence of linear region in the early stage of spinodal decomposition (SD) in the mixtures of deuterated/protonated polybutadiene (PB).

Late stages of spinodal decomposition

As described before, the scattering peak shifts to low scattering angles with elapsed time as a result of phase growth. This nonlinear phase growth in the late stages of SD is not explicable by the linearized Cahn–Hilliard theory.¹⁰ It may be best explained in terms of the time evolution of the maximum peak position $q_m(t)$ and the corresponding intensity $I_m(t)$. Contrary to the early stage of SD, there is no period in which the structure function $S(q,t)$ or the scattering function $I(q,t)$ increases at an exponential rate, but rather varies according to a power-law scheme, namely,

$$q_m(t) \sim t^{-\varphi} \quad (6)$$

and

$$I_m(t) \sim t^\psi, \quad (7)$$

where the exponents φ and ψ have been predicted in a number of nonlinear theories.^{12–15} On the basis of the nonlinear statistical consideration, Langer, Baron and Miller (LBM)¹² estimated a value of 0.21 for φ . Another notable theory is the cluster dynamics of Binder and Stauffer (BS),¹³ in that the clusters aggregate and coalesce into larger domains in order to minimize the surface free energy. The BS theory predicts that $\varphi = 1/3$ and $\psi = 1$ with $3\varphi = \psi$. From a completely different approach, Siggia¹⁴ obtained an equivalent expression, but with the values of $\varphi = 1/3$ and $\psi = 1$ for the early growth process and $\varphi = 1$ and $\psi = 3$ at the late flow stage. His approach is based on the percolation mechanism in that the coarsening occurs as the materials diffuse through interconnected channels due to surface tension. On the other hand, Kawasaki and Ohta¹⁵ argued on the basis of hydrodynamic consideration that there is no kinetic exponent for the entire spinodal process.

The time evolution of the maximum wavenumber was plotted in log–log scale as shown in Fig. 6. In the early period, the q_m remains constant, then decrease at a later time with a slope of $-1/3$. As can be seen in Fig. 7, the corresponding maximum intensity I_m vs time plot gives a slope of 1 for both T jumps. These exponents are exactly the values predicted by Binder and Stauffer¹³ for the coalescence of clusters to a larger domain to minimize the surface free energy. This process has been observed by Hashimoto *et al.*²³ for PS/PVME mixtures and Nojima *et al.*²⁵ for PS/poly(methylphenyl siloxane) (PMPS) mixtures.

At very late stages of SD, a number of studies indicate that q_m and I_m vary with the slopes of -1 and 3, respectively. This stage is identified to be a percolation regime, where

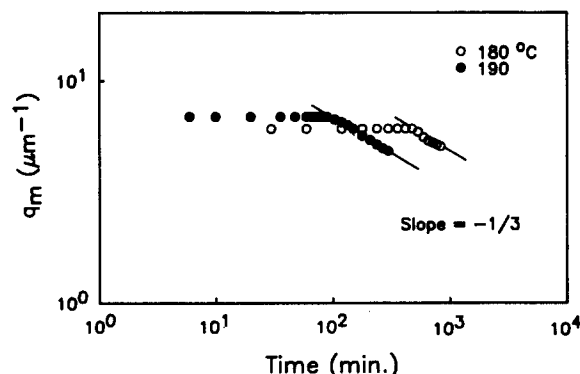


FIG. 6. The log–log plot of maximum peak wave number vs phase separation time for the 40/60 PC/PMMA blend.

coalescence of domains has been dominated by surface tension. We also observed the same phenomenon in the blends of high molecular weight PC/PMMA in which the T jump was carried out deeply into the immiscible region. In the present case, the phase separation obviously does not reach the percolation regime, although the experimental time is over 6 h. As will be demonstrated in a succeeding paper,¹⁹ if the T jump is too high, phase dissolution can occur due to the UCST at elevated temperatures.

Since there is an appreciable period at which q_m remains invariant, the correlation length (ξ) in the single phase may be approximated as the initial fluctuation size of spinodal at $t = 0$,

$$\xi = 1/q_m(0). \quad (8)$$

The universal curve may then be established with dimensionless reduced variables,

$$Q_m = q/q_m(0) = q\xi \quad (9)$$

and

$$\tau = D_{\text{app}} \xi^{-2} t, \quad (10)$$

where D_{app} and ξ were already known from Figs. 5 and 6. The universal curve with reduced variables Q_m vs τ shows a good superposition as shown in Fig. 8. Although the time scale is rather short, the trend is similar to those reported by Snyder and Meakin³⁰ and Hashimoto *et al.*³¹ for PS/PVME blends.

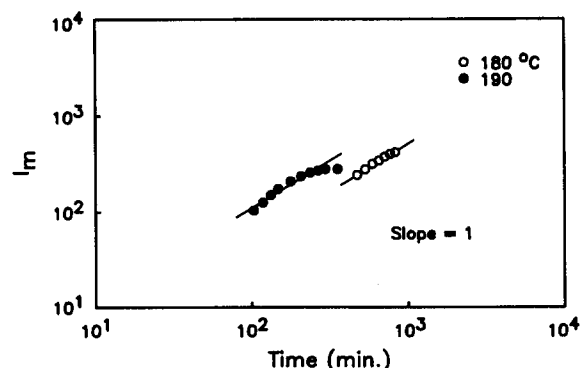


FIG. 7. The log–log plot of the maximum intensity vs phase separation time for the 40/60 PC/PMMA blend.

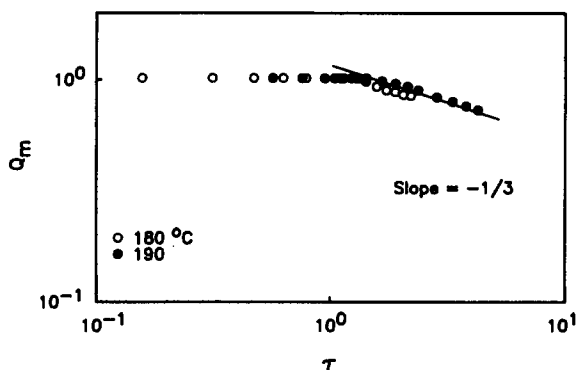


FIG. 8. The universal curve for reduced variables Q_m vs τ , showing a good superposition.

Scaling tests of self-similarity and structure function (Refs. 16 and 17)

Now we shall turn our attention to the scaling tests of late stages of SD. The evolution of the scattered intensity for different time scales during the coarsening process may be examined in terms of a scaled structure factor $S(z)$ with a single length parameter $\xi(t)$, i.e.,

$$I(q,t) \sim V^2 \langle \eta^2 \rangle \xi(t)^3 S(z), \quad (11)$$

where V is the scattering volume, $\langle \eta^2 \rangle$ the mean square fluctuation of refractive index and $z = q\xi(t)$. Here, $\xi(t)$ is related to the wavelength of periodic structure $\Lambda(t)$ by the relation

$$\xi(t) = \Lambda(t)/2\pi. \quad (12)$$

From Eqs. (11) and (12), the structure factor can be described as

$$S(z) \sim I(q,t)q_m^3 \quad (13)$$

with

$$z = q/q_m. \quad (14)$$

In the early stage of SD, the $\langle \eta^2 \rangle$ term does not reach its limiting value, therefore it cannot be scaled with a single length parameter $\xi(t)$. Hence, only the data of late stages of SD were used in the scaling tests. Figure 9 shows the plots of $S(z)$ vs z for various phase separation time. The superposition of scaled scattering curves is reasonably good for the late stages of SD where the coalescence of phase domains occurs, suggesting that the structure function is universal with time in this growth process of SD.

The dynamical scaling of the shape of the structure factor $S(q,t)$ proposed by Furukawa is of interest in examining the behavior of the critical and off-critical mixtures. He described the structure factor in terms of the cluster size $R(t)$,

$$S(q,t) \sim R(t)^d \tilde{S}(X), \quad (15)$$

where $\tilde{S}(X)$ is a universal scaling function which may be expressed as

$$\tilde{S}(X) \sim X^2/(\gamma/2 + X^{2+\gamma}), \quad (16)$$

where $X = qR(t)$ and d is the dimensionality of growth. γ is defined as

$$\gamma = \begin{cases} d + 1 & \text{for the off-critical mixture} \\ 2d & \text{for the critical mixture} \end{cases} \quad (17)$$

For the three dimensional growth, the structure function is predicted to vary with an exponent of 2 at $q < q_m$ and -4 or -6 at $q > q_m$ depending on whether the mixture is off-critical or critical one. The validity of this dynamic scaling has been demonstrated in the demixing of Al-Zn and Al-Zn-Mg metal alloys,³² polystyrene (PS)/poly(methylphenyl siloxane) oligomer mixtures³³ and aqueous hydroxypropyl cellulose systems.³⁴ In the above cases, slopes of 2 and -4 were obtained which is in conformity with the prediction for off-critical quenches. In the case of the critical composition of PS/PVME blends, Hashimoto and co-workers³⁵ reported

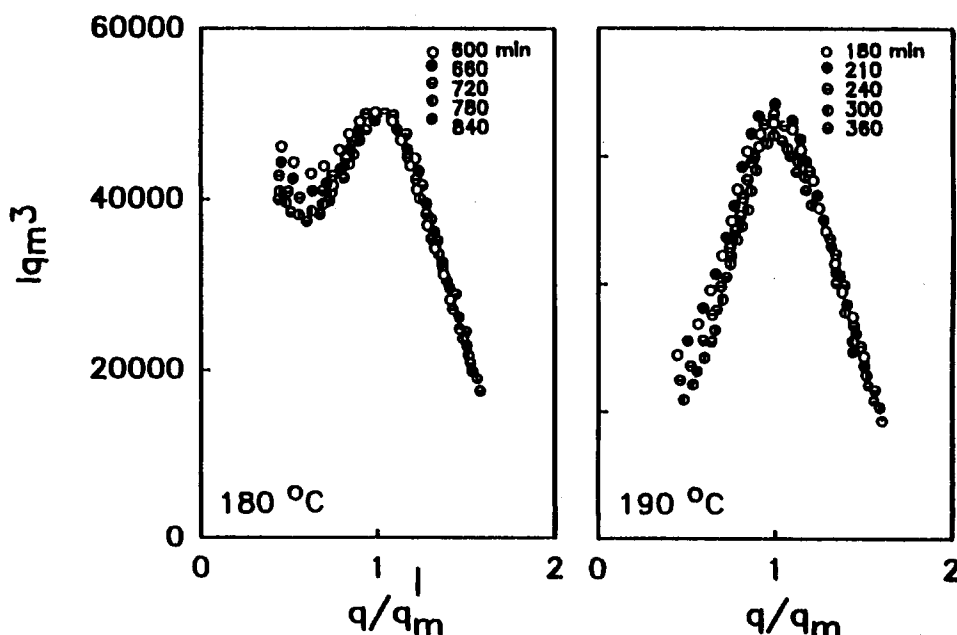


FIG. 9. $I(q,t)q_m^3$ vs q/q_m plots for the self-similarity test.

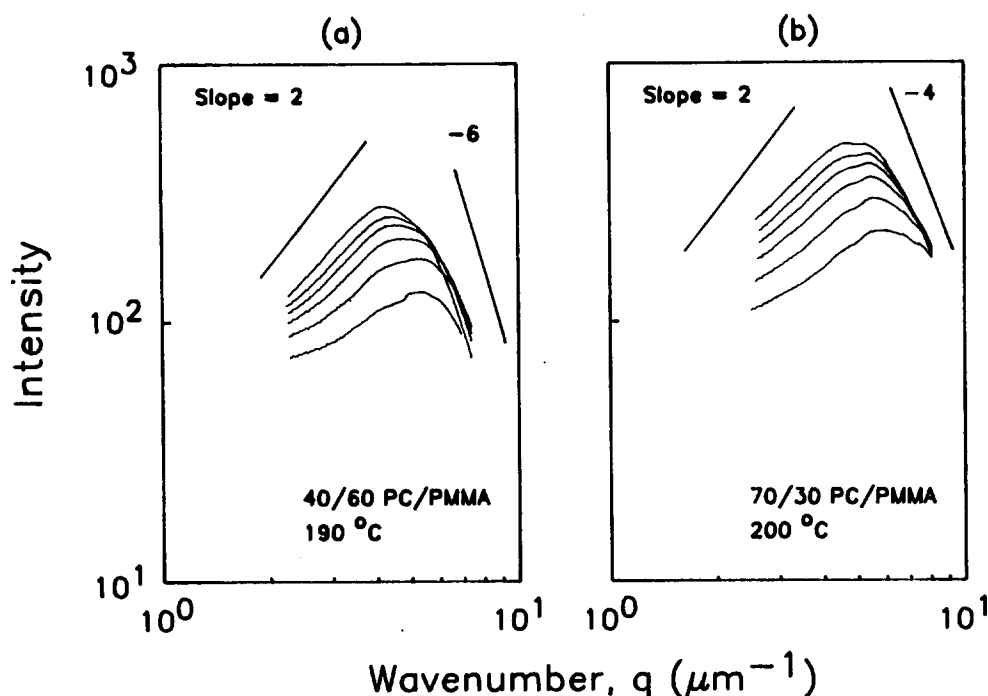


FIG. 10. (a) The log-log plot of scattered intensity against scattering wave number for the 40/60 PC/PMMA composition and (b) for the 70/30 PC/PMMA composition.

the values of 2 and -6 as predicted by the theory. In the present case, the experiment covers limited q range. It is difficult to conclude from this data alone, although the 40/60 PC/PMMA blend shows the slopes of 2 and -6 at $q < q_m$ and $q > q_m$ regions [Fig. 10(a)]. As will be demonstrated in the succeeding paper,¹⁹ the slopes of 2 and -6 were obtained for the same blend in the T jumps above the immiscibility loop. Furukawa³⁶ further cautioned that the prediction of kinetic exponent $\gamma = 6$ has no physical significance, thus it may be valid only for intermediate wave numbers. He then conjectured that the exponent at large q may recover the Porod value of 4. The recovery of -4 slope has been confirmed experimentally in metal alloys³⁷ and in polymer blends.³⁸ Very recently, Oono and Puri³⁹ showed from their simulation that the slope could be much steeper than q^{-4} at intermediate wave numbers of the percolated regime.

In order to compare the dynamical behavior between the critical and off-critical mixtures, we have further examined an off-critical mixture of 70/30 PC/PMMA. The behavior of early to late stages of SD for the off-critical composition are similar to those of the critical mixture, except for the dynamical scaling of the shape of scattering profiles. Figure 10(b) shows the log-log plots of I vs q for 70/30 PC/PMMA. As predicted by Furukawa¹⁷ for the off-critical mixtures, slopes of 2 and -4 were obtained at $q < q_m$ and $q > q_m$, respectively. Hence, it may be concluded that the asymptotic behavior of the scaled function agrees very well between theory and experiment in this PC/PMMA blend.

CONCLUSIONS

The phase separation dynamics, following the T jumps into an immiscibility loop region, is similar to the behavior reported for most conventional LCST systems. The early

stage of SD is explicable in terms of the linearized Cahn-Hilliard theory, whereas the late stage follows the power law with exponents of $-1/3$ and 1. This late stage of SD has been identified to be the cluster regime, where the clusters coalesce to form a larger domain in order to minimize the surface free energy. Self-similarity was attained during the growth process of SD where the structure function is universal with time.

ACKNOWLEDGMENT

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