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Kyu, Thein and Lim, DS, "Phase-Separation Dynamics of Polycarbonate Polymethyl Methacrylate Blends. II. Temperature Jumps Above An Immiscibility Loop" (1990). *College of Polymer Science and Polymer Engineering*. 54. http://ideaexchange.uakron.edu/polymer_ideas/54

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Phase separation dynamics of polycarbonate/polymethyl methacrylate blends. II. Temperature jumps above an immiscibility loop

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(Received 14 August 1989; accepted 7 December 1989)

Blends of polycarbonate (PC) and moderately low molecular weight polymethyl methacrylate (PMMA) reveal an immiscibility loop in which an upper critical solution temperature (UCST) is located above a lower critical solution temperature (LCST). Temperature jump (T jump) experiments were conducted on a 40/60 PC/PMMA composition from a single phase (150 °C) to two-phase temperatures above the immiscibility loop (205–241 °C). Phase separation first occurs, then is accompanied by phase dissolution. The early stage of phase separation 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 was established with dimensionless variables of Q_m and τ . The late stage data were analyzed in accordance with the recent scaling laws of Furukawa. Time evolution of structure function exhibits universality in the late stages of spinodal decomposition. 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. At a later time, phase dissolution takes place and the system returns to a single phase.

INTRODUCTION

In a previous paper, we have demonstrated the immiscibility loop phase diagram in mixtures of polycarbonate (PC) and moderately low molecular weight polymethyl methacrylate (PMMA).¹ Subsequently, we have investigated the dynamical behavior of phase separation following temperature (T) jumps from a single phase (150 °C) to an immiscibility loop two-phase region (180 and 190 °C).² It was found that phase separation takes place through spinodal decomposition (SD). The linearized Cahn–Hilliard theory³ is valid to account for the early stage of spinodal decomposition (SD). The late stages of SD follow the power laws in conformity with the cluster theory of Binder and Stauffer.⁴ Hence, it was concluded that the dynamics of phase separation in the immiscibility loop is similar to that of conventional polymer blends.^{5–9}

Another interesting feature in this blend system is that phase dissolution occurs when temperature increases beyond the UCST, i.e., the mixture reverts to a single phase. It is unclear how the LCST and UCST affect each other. It is therefore of crucial importance in understanding the role of LCST and UCST in the dynamics of SD, i.e., when temperature is changed instantaneously from a low temperature single phase (below LCST) to a high temperature single phase (above UCST). If thermodynamics were to be dominant, it is not expected to see any phase changes because thermodynamics describes only the equilibrium properties of starting and final states, but does not depend on its path. However, if kinetic effects predominate, the path would be important, i.e., the blends would phase separate first, then revert to a single phase. It seems the competition between thermodynamic and kinetic contributions would determine the phase behavior.

In this paper, we continue our studies on the dynamical behavior of isothermal phase segregation and phase dissolution at a composition of 40/60 PC/PMMA. Several T jump experiments were conducted from a single phase (150 °C) to above immiscibility loop (205–241 °C). The results will be compared with those obtained for T jumps into the immiscibility loop.

EXPERIMENT

Blend specimen preparation, molecular weight and its distribution of PC and PMMA used in this study were the same as in the preceding paper.² The details of the time-resolved light scattering set-up were already described elsewhere.¹⁰ Temperature (T) jump experiments were carried out from a single phase (150 °C) to temperatures above immiscibility loop (205, 210, 220, 228, and 241 °C) using time-resolved light scattering.

RESULTS AND DISCUSSION

Figure 1 shows a typical time evolution of scattering curves following a T jump to 205 °C. As can be seen in Fig. 1(a), the scattered intensity increases gradually at the beginning without exhibiting a scattering maximum. Then, a scattering peak appears at a large scattering wave number and remains virtually stationary for some period (about 30 min). Subsequently, the peak position shifts to a lower scattering wavenumber while the intensity increases immensely [Fig. 1(b)]. The peak movement stops after 110 min, then the intensity decays while keeping the peak position constant [Fig. 1(c)]. In the case of T jumps to 210 and 220 °C, the evolution of scattering profile with time appears weakly non-linear, i.e., the peak shows a slight movement to lower scattering angles. At higher T jumps above 220 °C, the initial peak was not detected as it is located beyond the angle range

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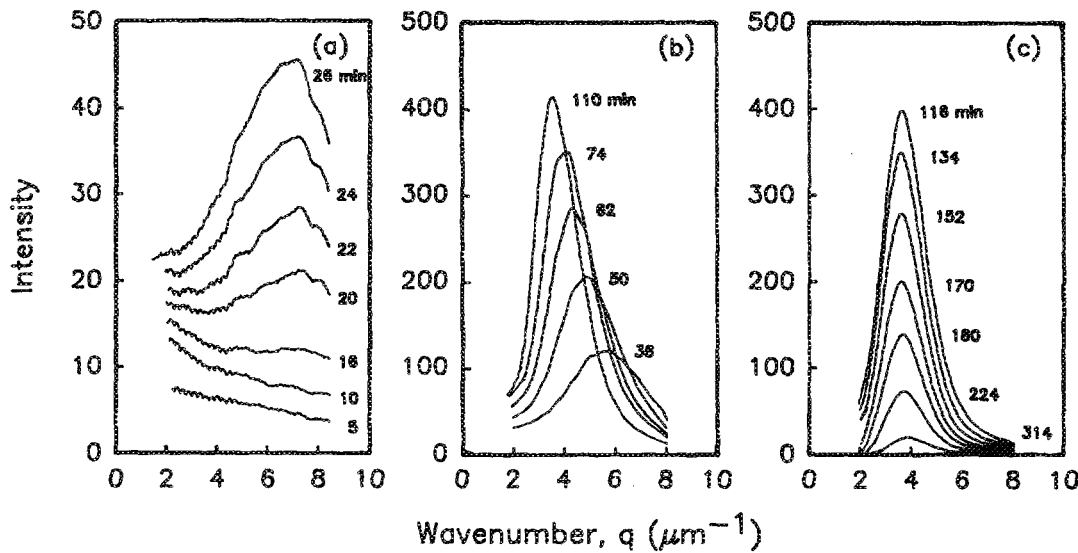


FIG. 1. Time evolution of scattering profiles of 40/60 PC/PMMA blends following a T jump from 150 to 205 °C; (a) initial stage of SD, (b) late stages of SD, and (c) phase dissolution.

covered in this experimental configuration. The behavior of subsequent decay of scattering curves during phase dissolution is similar for different T jumps with the exception that the time scale gets shorter with increasing temperature. These results were analyzed in four parts; (1) early stage of SD, (2) late stages of SD, (3) phase dissolution, and (4) scaling tests.

Early stage of SD

Similar to the previous T jumps into the immiscibility loop, the behavior of peak invariance above the immiscibility loop may be best explained in terms of the linearized theory of Cahn–Hilliard³ for early stages of SD, as described in the preceding paper.² In the context of mean field approximation, the apparent diffusivity D_{app} may be related to molecular parameters, i.e.,

$$D_{app} = -M \left(\frac{\partial^2 f}{\partial c^2} \right) = D_c \epsilon, \quad (1)$$

where, D_c is a translational diffusivity and ϵ is further given by

$$\epsilon = (\chi - \chi_s) / \chi_s, \quad (2)$$

where χ is the interaction parameter and subscript s stands for spinodal. Equation (2) may be expanded near the spinodal point as

$$\epsilon = - (1/\chi_s) \left[\frac{\partial \chi}{\partial T} \right]_{T_s} \Delta T + \varphi(\Delta T^2), \quad (3)$$

where, $\Delta T = T - T_s$ and $\varphi(\Delta T^2)$ are the higher order terms. Neglecting higher order terms and assuming the blends to have equal degree of polymerization,¹¹ one obtains,

$$q_m(0)^2 \sim \epsilon \sim \Delta T. \quad (4)$$

Figure 2 shows the typical semilogarithmic plot of corrected intensity against phase separation time for the T jump to 205 °C. In conformity with the prediction of the linearized theory,³ 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

$R(q)$ as determined from the linear slope, was plotted in the form of $R(q)/q^2$ vs q^2 to test the validity of the linearized Cahn–Hilliard theory.³ As can be seen in Fig. 3, the data can reasonably be approximated by linear slopes for most T jumps. In the literature,^{12–15} 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. The validity of the linearized theory was further checked with the relationship $q_m(0)^2 = q_c^2/2$. Again, this relation is operative for T jumps of 205, 210, 220 and 228 °C, thereby validating the linearized theory.

Since q_m can be determined experimentally, the correlation distance ξ in single phase may be estimated from q_m at $t = 0$, i.e., $\xi = 1/q_m(0)$. Moreover, the spinodal temperature may be estimated in the context of the mean field approximation by plotting $q_m(0)^2$ vs T . Figure 4 shows such a plot in which the data points can reasonably be fitted by a straight line. T_s as determined from the intercept corresponds to about 156 °C which is close to the cloud point temperature.

In fact, the translational diffusivity D_c in Eq. (1) is a

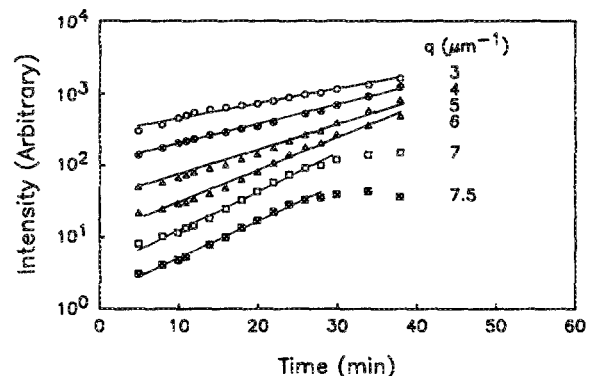


FIG. 2. The variation of logarithmic scattered intensity as a function of phase separation time for 40/60 PC/PMMA blends at 205 °C.

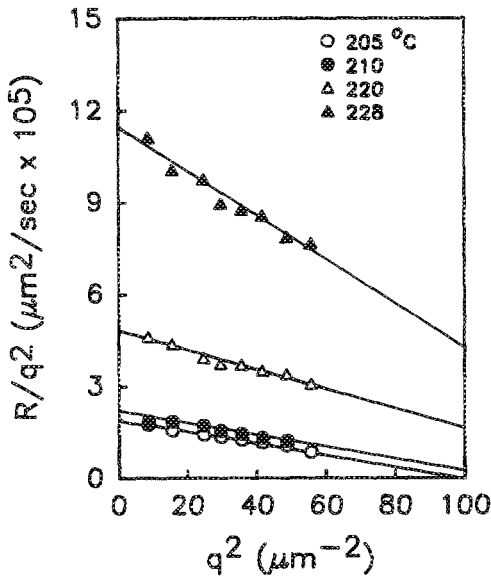


FIG. 3. The Cahn's plots of $R(q)/q^2$ vs q^2 for various T jumps.

temperature dependent function which is generally assumed to be an Arrhenius type, viz.;

$$D_c \sim \exp(-\Delta H_a/R_G T), \quad (7)$$

where ΔH_a is an apparent activation energy and R_G is the gas constant. From Eqs. (2) and (7), the activation energy may be evaluated by plotting $\log(D_{app}/\Delta T)$ against $1/T$. As can be seen in Fig. 5, a reasonably good linear slope was obtained. The activation energy as determined from the slope is approximately 30 kcal/mol, which is comparable to the reported literature values for PC and PMMA from viscoelastic measurements.^{16,17}

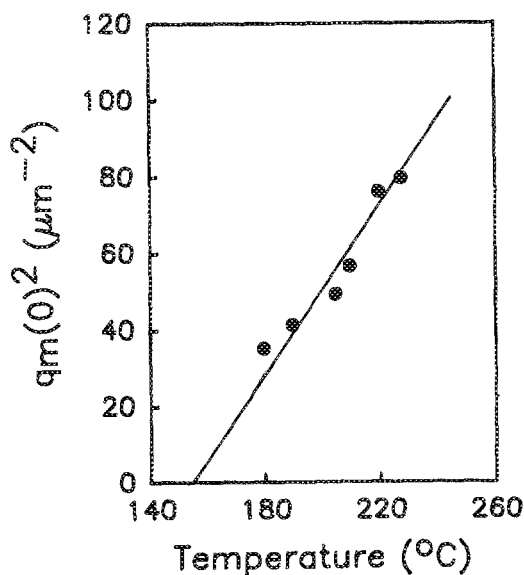


FIG. 4. The variation of the square of maximum wave number $q_m(0)^2$ as a function of temperature. From the intercept of temperature axis, a spinodal temperature T_s of 156 °C was obtained.

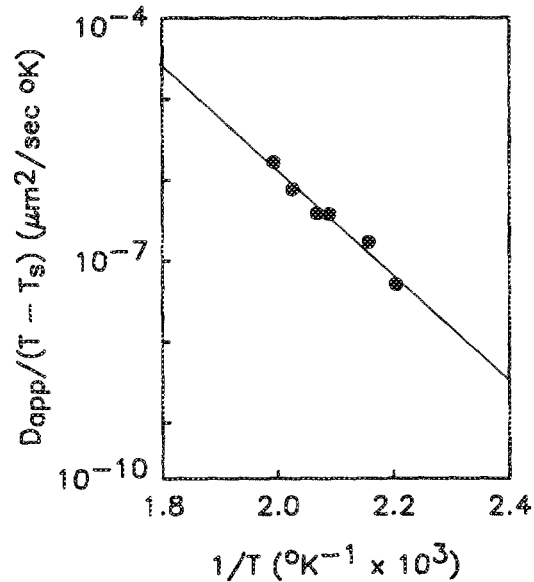


FIG. 5. Arrhenius plot of apparent diffusivity against reciprocal absolute temperature.

Late stages of SD

At the late stages of spinodal decomposition, the scattering peak moves to a lower wave number as a result of phase growth. This nonlinear behavior may be best explained in terms of the power law relationships.^{4,18,19} Figures 6 and 7 show the log-log plots of the maximum peak position q_m and the corresponding intensity I_m against elapsed time for phase separation. For a short period, the q_m appears constant, then rapidly decreases with a slope of $-1/3$. Concurrently, the I_m increases with a slope of 1 which is in good agreement with the prediction of the cluster theory of Binder and Stauffer.⁴

The dynamical behavior of SD up to this stage is similar to what was reported previously for the T jumps into the immiscibility loop.²

Since, the correlation length (ξ) in the single phase can be estimated from Eq. (8) of the preceding paper,² the universal curve may be established in terms of dimensionless reduced variables, Q_m and τ . Figure 8 shows a good superim-

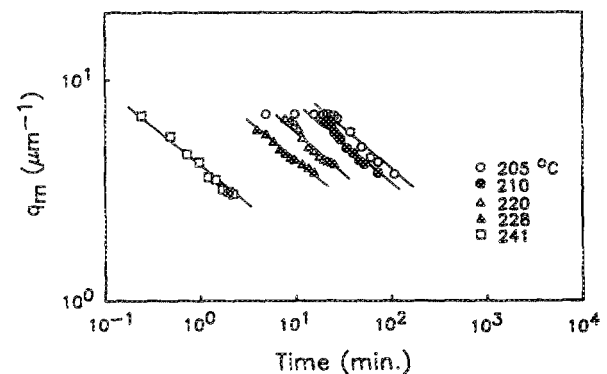


FIG. 6. The log-log plot of maximum wave number vs phase separation time for 40/60 PC/PMMA blend. The slope of $-1/3$ was provided for reference.

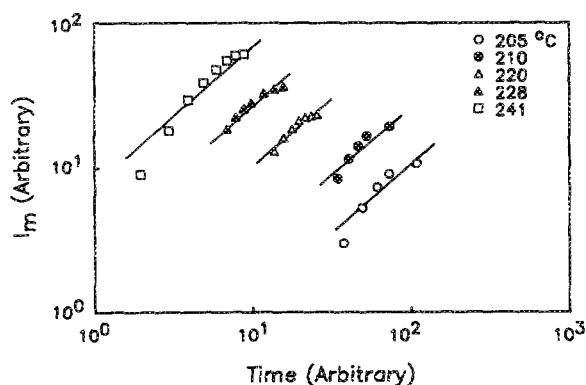


FIG. 7. The log-log plot of scattering maxima vs phase separation time for 40/60 PC/PMMA. The slope of 1 was provided for reference.

posed master curve. The curve consists of two distinct regions; the first is the linear region, where Q_m is invariant with time and the second is the cluster regime in which the slope becomes $-1/3$. In recent studies of metal alloys,^{20,21} the cross-over of slopes from $-1/6$ to $-1/3$ has been reported in the intermediate stage of SD. However, it cannot be identified in the present case. Although our experimental time for phase separation is sufficiently long, we are unable to reach the percolation regime (where the slope becomes -1) because of phase dissolution as will be discussed later. Nevertheless, the trend here is similar to those of metal alloys, solution mixtures and polymer blends.²²

Phase dissolution

Phase dissolution refers to the reversion of phase separated biphasic structure to a single phase. It should be borne in mind that phase dissolution in the present system is different from the conventional binary mixtures where the reversion of phase structure normally takes place by reversing the temperature across the phase boundary. In the present case, the two opposing processes, i.e., phase separation and dissolution, occur concurrently under isothermal condition which may be caused by LCST and UCST, respectively. As can be seen in Fig. 1(c), the scattering peak no longer moves

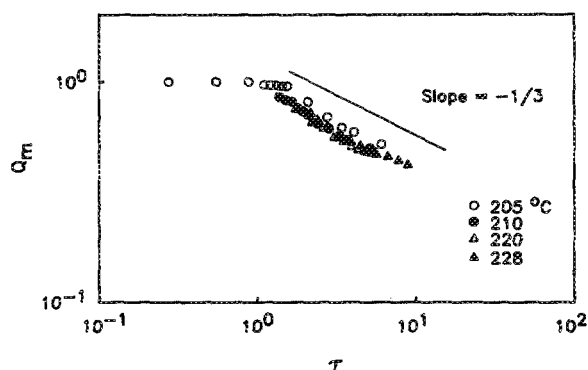


FIG. 8. The universal curve plotting reduced maximum wave number Q_m as a function of reduced time τ . The slope of $-1/3$ was provided for reference.

with further increase of time, instead the intensity diminishes and eventually disappears completely. Visually, the cloudy blend films turn transparent, i.e., the two-phase structure returns to a single phase. This observation was further supported by the DSC study, revealing a single T_g in the annealed blend.¹ This process is attributed to phase dissolution. It seems the competition between LCST and UCST dictates the behavior of phase separation and dissolution, i.e., the thermodynamic driving force associated with ΔT from LCST and from UCST may be of crucial importance.

The process of phase dissolution, if not more, is equally important as phase separation. However, there are only limited works in the literature dealing with phase dissolution kinetics. Kumaki and Hashimoto²³ treated this as a Fickian diffusion problem in which the diffusivity was evaluated from the slope of $R(q)$ vs q^2 . On the other hand, Sato and Han²⁴ pointed out the need for considering the decay of concentration gradient and consequently treated in terms of the reverse linearized Cahn-Hilliard model. The authors further cautioned that their approach is valid only if the fluctuation size is sufficiently small. In the present case, phase dissolution occurs right after intermediate stage of SD, thus it is obviously beyond the linear regime. Nevertheless, we attempt to analyze it as a simple diffusion process as well as by the reverse linearized theory.

In Fig. 9, the decay rate $-R(q)$ is plotted against q^2 for various temperatures. There appears a maximum in the q^2 dependence rather than a linear slope, which is contradictory to the Fick's law. On the other hand, the plot of $-R(q)/q^2$ vs q^2 in Fig. 10 is a curvature rather than a straight line, thereby pointing the deficiency of the reverse linearized theory. We have to admit that phase dissolution in the present case occurs where phase growth has considerably advanced beyond the linear regime. The phenomenon of phase dissolution appears to be more complex than that in the reversed quenching across the phase boundary as we have no control over the growth process. On the basis of the scattering data alone, it is unclear whether the average size of concentration fluctuations gets smaller with elapsed time or the gradient of concentration fluctuation becomes weaker. Optical micrographs in Fig. 11 suggests although by no means conclusive that the interdomain distance and the

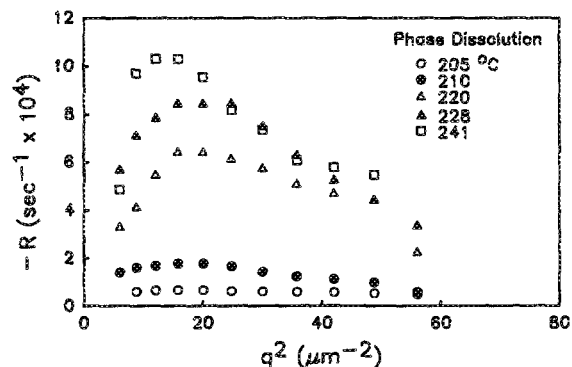


FIG. 9. q^2 dependence of the decay rate $-R(q)$ during phase dissolution at various temperatures for 40/60 PC/PMMA blend.

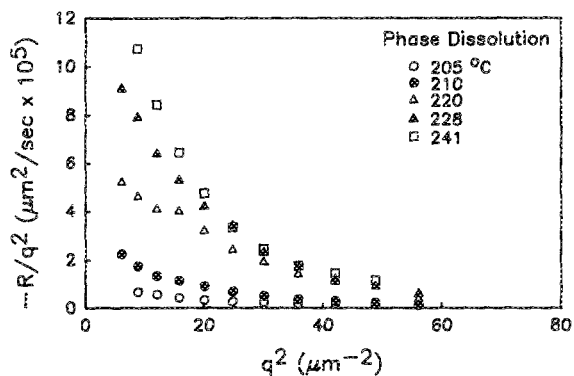


FIG. 10. The $-R(q)/q^2$ vs q^2 plots for the phase dissolution at various temperatures.

average size are not getting smaller during dissolution, but rather the contrast of phases diminishes. Hence, it seems necessary to take into consideration the concentration gradient term in the diffusion equation. However, the fluctuation size in the present case has actually grown beyond the linear regime; the linear theory might be operative otherwise.

Scaling tests of SD (Refs. 25 and 26)

In the preceding paper,² we found self-similarity in the late stages of SD where the structure function exhibits universality with time. We continue our efforts to examine self-similarity in the T jumps above the immiscibility loop. In Fig. 12 are shown the plots of $I(q,t)q_m^3$ against q/q_m for later

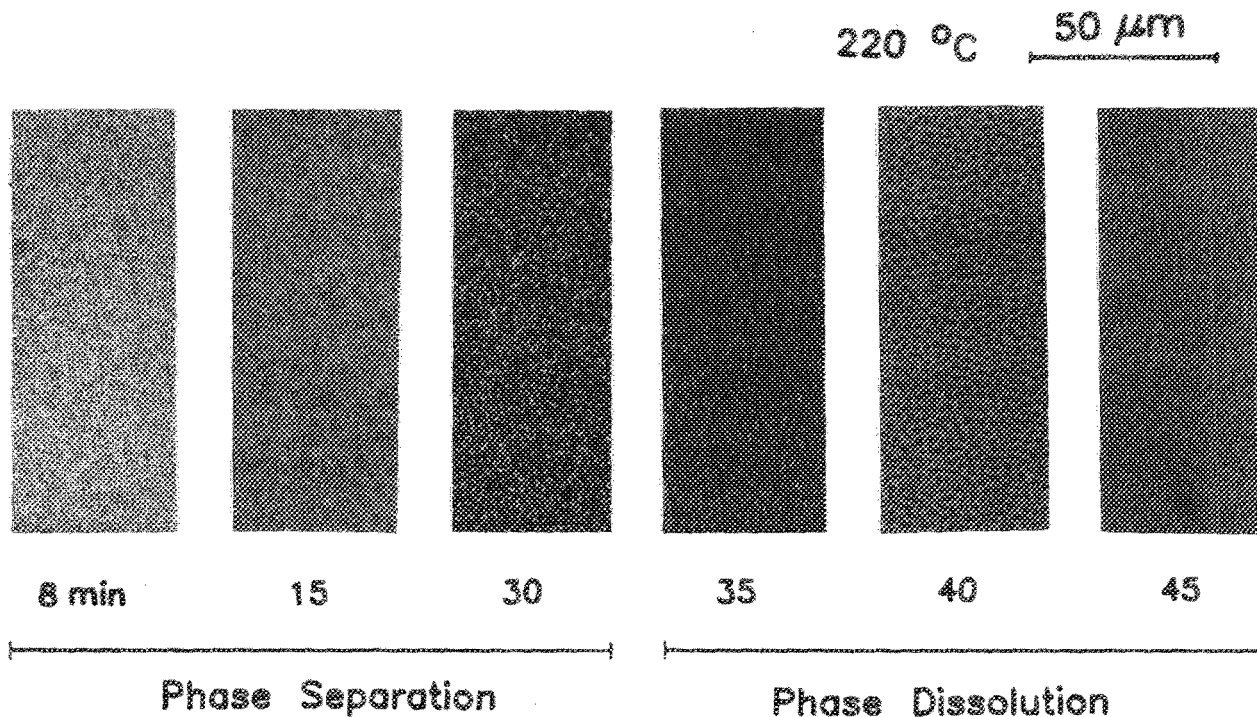


FIG. 11. Optical micrographs displaying the change of domain structure during phase separation followed by dissolution (after 30 min.) at 220 °C.

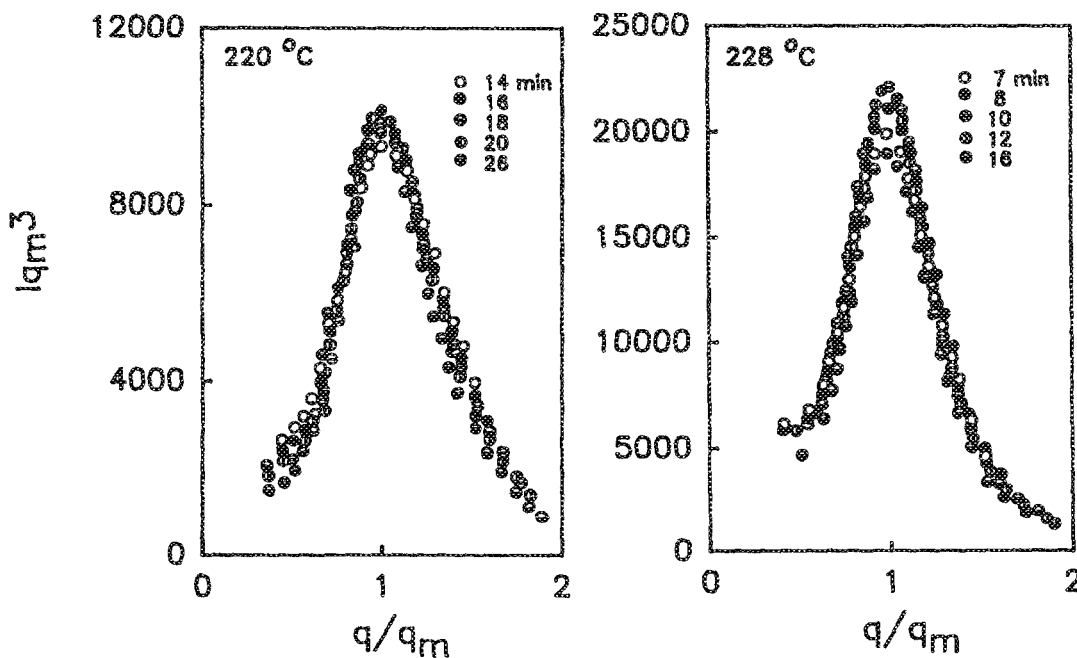


FIG. 12. $I(q) \cdot q_m^3$ vs q/q_m plots for self-similarity tests for 220 and 228 °C.

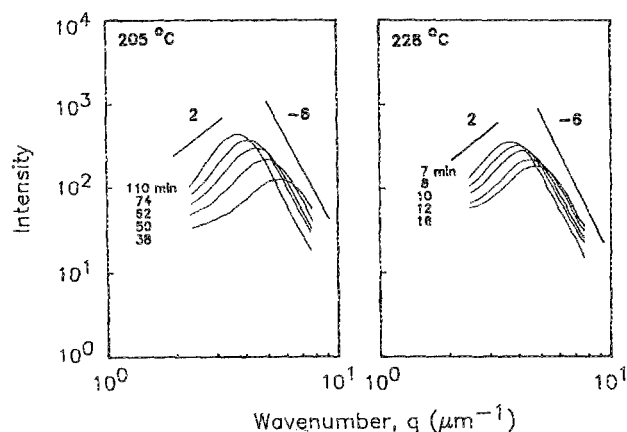


FIG. 13. The log-log plots of scattered intensity against scattering wave number for 40/60 PC/PMMA blends 205 and 228 °C. The slopes of 2 and -6 were provided for reference.

time following T jumps to 205, 210, 220, and 228 °C. All T jumps show excellent superposition of the curves for various time scale, suggesting that self-similarity has been attained. There is no difference in the behavior of scaled structure functions for different T jumps, as long as the time scale is in the universal region. This observation is consistent with the previous studies.²

In the case of the dynamical scaling for the shape of structure function,²⁶ we have demonstrated previously² that the slope of 2 and -6 was obtained at $q < q_m$ and $q > q_m$ for the 40/60 PC/PMMA composition, which has been predicted theoretically for the behavior of a critical quench. The same scaling analysis has been employed on the 70/30 PC/PMMA and the slopes of 2 and -4 were obtained as typical for off-critical mixtures. In contrast, the time evolution of scattering curves of the 40/60 PC/PMMA, as plotted in Fig. 13, indeed show the slopes about 2 and -6 which are predicted for the critical mixture in the percolation regime. However, our experiment never reaches the percolation regime because of the occurrence of dissolution.

CONCLUSIONS

We have demonstrated that isothermal phase separation and dissolution occur isothermally when the temperature of 40/60 PC/PMMA blend is rapidly increased from a low temperature single phase to a high temperature single

phase above the immiscibility loop. It seems the dynamical behavior of these two processes has been dictated by the competition between LCST (which favors phase separation) and UCST (which favors dissolution). The phase separation behavior appears to be the same for T jumps into immiscibility loop or above it, which is also in good accord with that generally observed in conventional polymer blends. Phase dissolution in the present case may be attributed to the decay of gradient of concentration fluctuations rather than its average size.

ACKNOWLEDGMENT

Support of this work by the Edison Polymer Innovation Corporation (EPIC) is gratefully acknowledged.

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