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Phase Separation by Spinodal Decomposition in Polycarbonate/Poly(methyl methacrylate) Blends

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ABSTRACT: Early and late stages of phase separation by spinodal decomposition in mixtures of polycarbonate (PC) and poly(methyl methacrylate) (PMMA) were investigated by time-resolved light scattering. The PC/PMMA blend reveals a miscibility window reminiscent of an LCST (lower critical solution temperature) character. A high level of interconnectivity in the domain structure was observed in optical microscopic investigations. The time evolution of scattering halo was followed as a function of temperature jump (ΔT). The early stage of spinodal decomposition at low ΔT reasonably follows the linearized Cahn–Hilliard's theory; however, deviations are seen at large temperature jumps. The evolution of the maximum intensity (I_m) and the corresponding wavenumber (q_m) obey the power-law scheme ($I_m \propto t^\beta$ and $q_m \propto t^{-\alpha}$). A relation of $\beta = 3\alpha$ is obtained with $\beta \cong 3$ and $\alpha \cong 1$. The exponent $\alpha \cong 1$ is exactly the value that was predicted by Siggia for late stages of spinodal decomposition. This is identified to be a coarsening process driven by surface tension.

Introduction

The field of phase separation in polymeric mixtures has recently gained considerable interest among material scientists because of its interdisciplinary nature.[1-3] The theory of phase separation by spinodal decomposition in critical mixtures, although having a relatively short history, has made a remarkable progress.[4,5] Spinodal decomposition refers to phase separation in an initially unstable system associated with an infinitesimal composition fluctuation.[4] Because of the shallow energy barrier, even the smallest fluctuation can grow in spinodal regime, which contrasts the conventional nucleation process. The process of nucleation is a rare occurrence associated with metastability in which the system is stable at infinitesimal concentration fluctuations but unstable at sufficiently large concentration fluctuations.

The theory of spinodal decomposition was first introduced by Cahn,[4] who predicted exponential growth of a scattering peak characteristic of phase-separated regions induced by periodic concentration fluctuations. Behavior similar to this has been found in metal alloys, glasses, and liquids, and recently in polymeric mixtures.[3-16] Most studies found that the prediction of Cahn–Hilliard's theory hardly holds even at the early stage of phase separation. At a late stage, the time-dependent scattering significantly deviates from exponential growth but follows a power-law scheme.[8-10] Newer theories have been introduced on the basis of a statistical thermodynamic approach, notably by Langer,[8] Binder and Stauffer,[9] Kawasaki and Ohta,[11] and very recently by Furukawa.[12]

Van Aartsen[17,18] extended the theory of spinodal decomposition to polymer mixtures by taking into consideration the Flory–Huggins free energy[19] in the Cahn–Hilliard's equations. Recently, de Gennes[20] and later, Pincus have modified the existing Cahn–Hilliard theory on the basis of reptation model of polymeric chains. There exist a limited number of experiments in the literature dealing with the kinetic aspects of phase separation in polymeric mixtures.[22-30] The most notable systems are polystyrene (PS)/poly(vinyl methyl ether) (PVME),[22-24] poly(methyl methacrylate) (PMMA)/styrene acrylonitrile (SAN),[25] low molecular weight PS/poly(methylphenylsiloxane) (PMPS),[27] PS/polybutadiene (PB) oligomers,[28] etc. The number of such studies continues to increase as can be witnessed in recent publications.[29,30]

The phase separation studies of polymeric mixtures are not limited to the classical light scattering technique. Small angle X-ray scattering by synchrotron radiation has been recently applied to PS/PB oligomers[28] and PMMA/chlorinated polyethylene (CPE) systems.[29] The behavior of labeled molecules during phase separation has been probed by neutron scattering techniques.[31,32] The above techniques are complementary to each other and address different structural dimensions.

We recently found a new polymer blend system, i.e. polycarbonate (PC)/PMMA system, which shows a miscibility window reminiscent of a lower critical solution temperature (LCST).[33] This polymer pair was originally reported by others to be immiscible or at best partially miscible.[34,35] In this paper, the dynamic aspect of phase separation in PC/PMMA as obtained by time-resolved light scattering is presented.

Experimental Section

Various mixtures of polycarbonate (Lexan 141, $M_w \cong 58\,000$, $M_w/M_N \cong 2.7$, General Electric) and poly(methyl methacrylate) (V811, $M_w \cong 84\,000$, M_w/M_N 2.13, Rohm and Haas Co.) were prepared by dissolving in a common solvent, tetrahydrofuran (THF). The concentration was 2% by weight. The blend samples were cast on glass slides at 47 °C in an oven. The cast films were very thin (about 10 μm) and transparent and scattered no light, characteristic of one phase structure. These films were subsequently dried at 70 °C in a vacuum oven for at least 24 h and kept in a desiccator.

Differential scanning calorimetry (DSC) runs were carried out on a Du Pont DSC 9900 at a heating rate of 20 °C/min. A Leitz optical microscope (Laborlux 12 POL) was used for taking micrographs. A photographic light scattering pattern was taken with a Polaroid instant camera (Land film holder 545). A 2-mW He–Ne laser light source with a wavelength of 6328 Å was used. Time-resolved light scattering scans were acquired by a two-dimensional Vidicon camera (Model 1252B, EG&G) coupled with an Optical Multichannel Analyser (OMAIII, EG & G). The details of the SALS set up is reported in a previous paper.[33] Two sets of heating cells were used: one was preheated to a temperature below the cloud point while the other was controlled at an experimental temperature. The temperature jump was performed by rapidly transferring from one to the other. A programmable temperature controller (Omega, Model CN2012) with an accuracy of 1 °C was utilized.

Results and Discussion

The transparent PC/PMMA blends cast from THF solutions at an elevated temperature (47 °C) exhibit a pronounced single glass transition in all compositions. The glass transition temperatures (T_g) are plotted against composition in Figure 1, varying systematically in accordance with Fox prediction[36] for miscible blends. In the subsequent runs, after quenching from the melts (300 °C),

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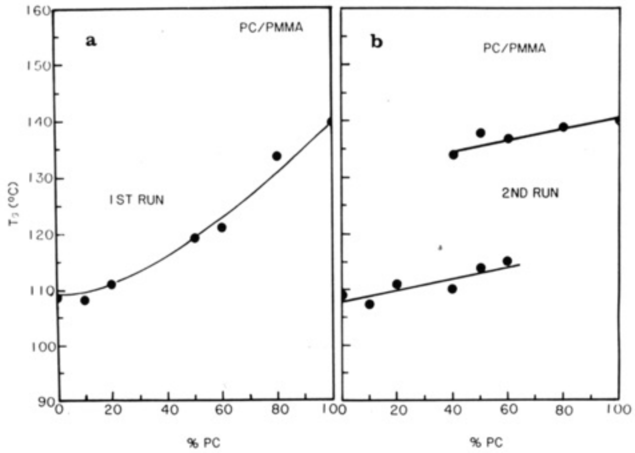

Figure 1. Variations of glass transition temperature (T_g) with blend compositions: (a) first runs and (b) second runs.

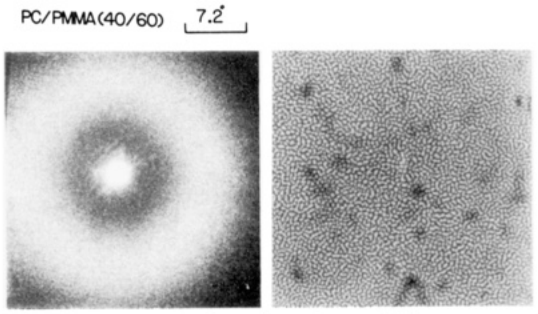

Figure 2. Structure of phase domains and the corresponding scattering halo of 40/60 (PC/PMMA) composition developed at 261 °C.

the intermediate blends show dual glass transitions corresponding to those of pure polymers. As can be seen in Figure 1, both T_gs of the second runs are well separated and vary slightly with composition, implying that thermally induced phase separation must occur during heating in the first runs.

The occurrence of thermally induced phase separation was confirmed independently by optical microscopy and light scattering studies. Figure 2 shows a photomicrograph and the corresponding scattering image of the PC/PMMA (40/60) composition heated to 261 °C. A high level of interconnected domains can be discernible while the corresponding scattering shows a diffused halo. The radius of this scattering ring collapses to smaller diameters as phase separation proceeds with continued heating while the intensity immensely increases. The development of interconnected domains and a diffused scattering halo are the familiar characteristics of spinodal decomposition.

The phase diagram was subsequently established based on the cloud point determination reported earlier.[33] Figure 3 shows the cloud points versus composition plot obtained at 2 °C/min. An attempt was made to determine the equilibrium phase separation temperature at zero-heating rate. As can be noticed from Figure 4, the heating rate dependence of the cloud points is a curve; thus the extrapolation to zero heating rate may be ambiguous. It appears that the low heating rate involves a large contribution from isothermal phase separation while such contribution may be insignificant at high heating rates. On the other hand, the cloud point determination at fast heating rates tends to show higher phase separation temperatures than that at the equilibrium state. Both PC and PMMA used in this study are the typical commercial grades; the polydispersity may affect their phase behavior. Due to the uncertainty of the extrapolation procedure, the equilibrium phase diagram was not established. Nevertheless, it should be mentioned that the phase diagram in Figure 3 is reminiscent of an LCST. This kind of an LCST phase diagram was recently obtained by Chiou et al.[37] and Kambour et al.[38] for PC/PMMA blends. Both groups concluded that PC/PMMA blends are miscible over the whole blend composition range when prepared by appropriate blending techniques. If the PC/PMMA phase diagram were a true LCST system, on the basis of thermodynamic consideration, one would expect to observe the reappearance of the single phase upon cooling below the LCST. However, the DSC re-runs in Figure 1 reveal dual T_gs which are seemingly inconsistent with the above expectation. One plausible reconciliation, although by no means conclusive, is that the biphase structure may be frozen-in when cooling rapidly below the T_gs of the components.

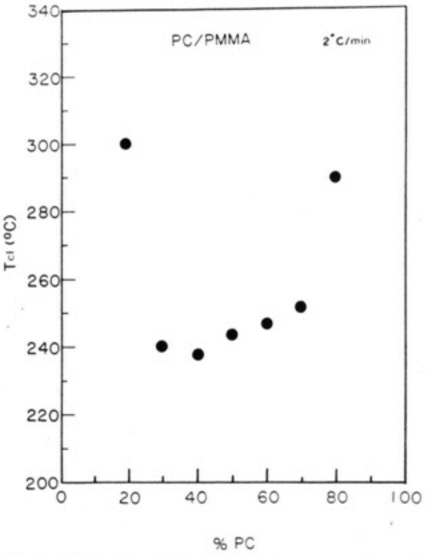

Figure 3. Plot of cloud point temperatures as a function of blend compositions at a heating rate of 2 °C/min.

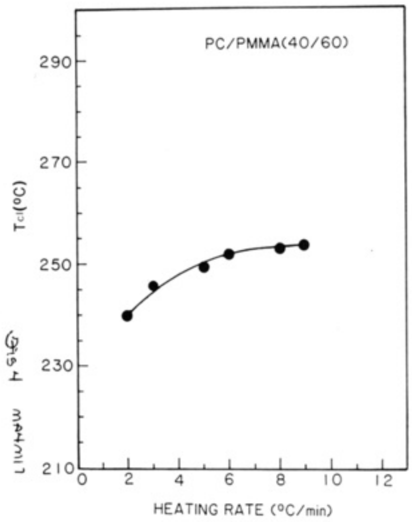

Figure 4. Variation of cloud point temperature as a function of heating rate.

In order to examine the reversibility of phase separation, the PC/PMMA (40/60) blend was cooled to 200 °C from the biphase region (256 °C) and kept isothermally for 4 h. The system does not completely return to a single phase; hence, we were unable to confirm the reversibility of this PC/PMMA blend from turbidity measurements. However, in a low molecular weight PC/PMMA (50/50) system, we observe both isothermal phase separation and

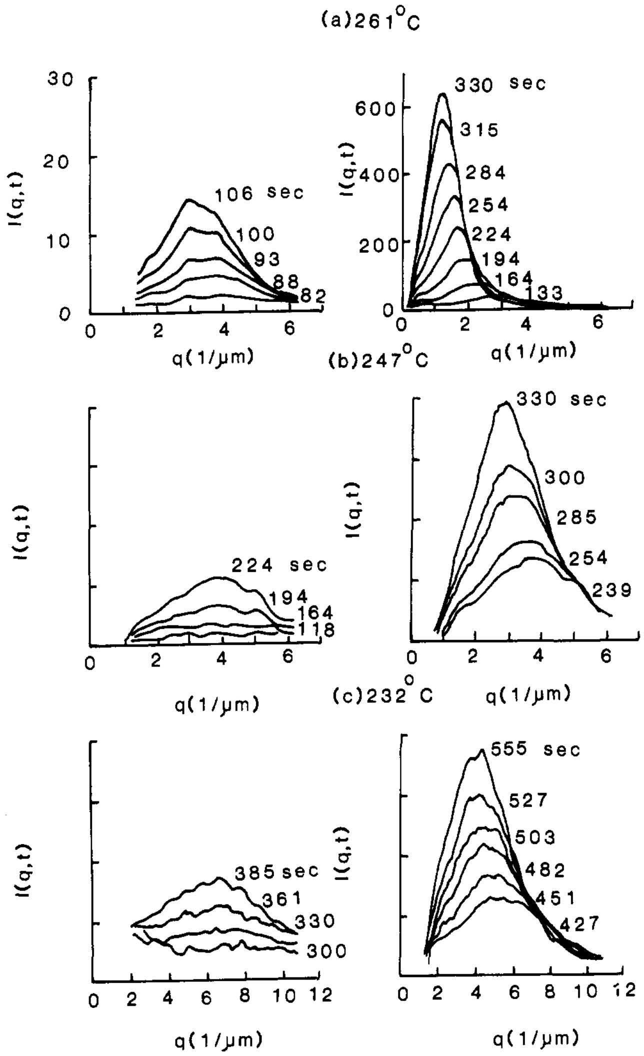

Figure 5. Time evolution of scattering profiles at various temperature jumps (ΔT) for the 40/60 (PC/PMMA) composition. The early and late periods are displayed separately.

phase dissolution at 210 °C.[39] The phase separation process is completed within 30 min while the phase dissolution process takes about 4 h for the system to completely return to a transparent single phase. It appears that the affect of molecular weight and its distribution might play an important role because of their intimate relation with the viscosity and the diffusivity. Visually, the annealed film is completely transparent without any traces of bubbles or any change of color. However, the effect of PMMA degradation cannot be ignored; in particular it may be severe in prolong experiments at elevated temperature above 200 °C. This will be the subject of a future paper.[39]

Next, we seek to understand the kinetic aspects of phase separation in the PC/PMMA (40/60) composition. A number of temperature jump (ΔT) experiments were carried out with this 40/60 blend. Two heating cells were employed; one was used to preheat the samples at about 200 °C for 1 min, and then the specimens were quickly transferred to the cell controlled at an experimental temperature. The time required to equilibrate at experimental temperatures varies from 10 to 40 s depending on ΔT. This time for equilibration is generally shorter than the actual phase separation time which is approximately over 120 s.

Some typical time evolution of scattering curves for the PC/PMMA (40/60) composition is depicted in Figure 5a–c for various temperature jumps. When the blend undergoes phase separation, a clear scattering maximum develops at a particular angle. As phase separation proceeds, this scattering maximum moves to lower scattering angles associated with phase growth, while the scattered intensity increases immensely with phase separation time. This scenario is most accentuated at the highest temperature jump to 261 °C, but the movement is less distinct with lower T jumps. Although the general trend of phase separation in this PC/PMMA system appears to be a nonequilibrium and nonlinear phenomenon, there is an appreciable time interval at which the peak position virtually remains stationary, but the intensity increases immensely. In this regime, phase-separated domains do not grow appreciably, but the concentration gradient at the interface merely increases. The length of time where the peak remains at a constant position becomes shorter with higher T jumps.

This kind of linear behavior was not experimentally observed in many binary systems, including metal alloys, ceramic glasses, solution mixtures, and polymer blends. Hashimoto et al.[23] were the first to report the existence of a linear regime in the SD of PS/PVME blends; however, it was not confirmed by others.[24] Very recently, Han et al.[40] have shown the virtual invariance of the scattering peak in the early stages of SD in the same PS/PVME blend. The present system, although predominated by the nonlinear behavior of phase growth, shows a possibility that a linear regime might persist in the early stages of spinodal decomposition. It proves worthy of testing with the so-called linearized Cahn–Hilliard theory in which the scattered intensity is predicted to increase exponentially, i.e.

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

where t is the phase separation time and q is the wavenumber being equal to $4\pi/\lambda \sin(\theta/2)$. Here, λ and θ are respectively the wavelength of light and the scattering angle measured in the medium. The amplification factor $R(q)$ which characterizes the growth behavior is further related by

$$R(q) = -Mq^2\{\Delta^2 f/\Delta c^2 + 2\kappa q^2\} \quad (2)$$

where f is the local free energy, c the concentration, κ the coefficient of composition gradient, and M the mobility. $R(q)$ is a quantity that may be determined experimentally by using time-resolved light scattering. The amplitude of fluctuation has a maximum value at $q = q_m$, where

$$q_m^2 = -(\partial^2 f/\partial c^2)/4\kappa \quad (3)$$

and $R(q)$ is zero at $q = q_c$, where

$$q_c^2 = -(\partial^2 f/\partial c^2)/2\kappa \quad (4)$$

or

$$q_m^2 = q_c^2/2 \quad (5)$$

The inadequacy of the Cahn–Hilliard theory was first pointed out by Cook who modified the linear theory by taking into account the effect of thermal fluctuation of the stable solution. The modified Cahn–Hilliard–Cook theory is presented as

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

where $I_s(q)$ is the scattering from the stable system. The results were further analyzed according to eq 1 by plotting logarithmic intensity versus phase separation time for all T jumps. Figure 6 shows a typical plot for the 40/60 jumped to 261 °C. In conformity with the prediction of the linear theory, the intensity increases exponentially for some initial periods and then deviates significantly. The departure from the exponential growth may be associated

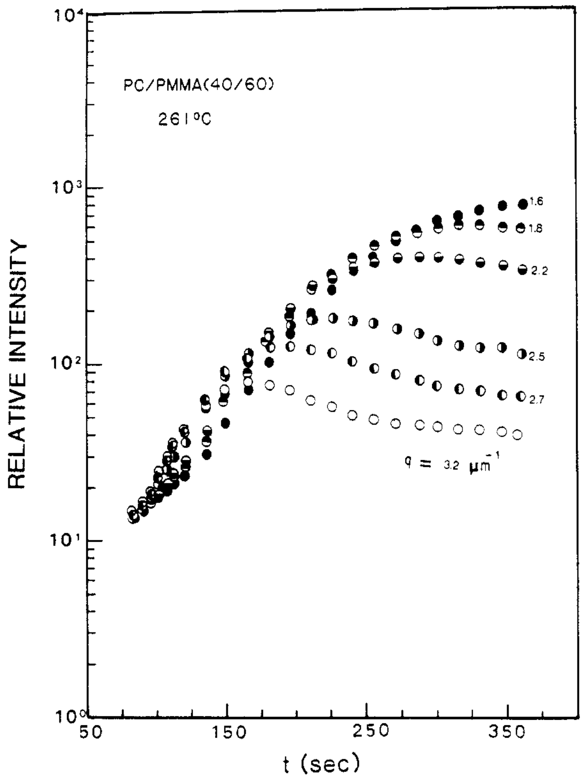

Figure 6. Plots of logarithmic intensity against phase separation time for the (40/60) composition at a T jump to 261 °C.

with additional processes occurring at the late stages of spinodal decomposition. From the slopes of the log I versus t plots, the amplification factors $R(q)$ for various q were determined. Then in accordance with eq 2, $R(q)/q^2$ were plotted against q^2 in Figure 7, parts a and b. At low T jumps in Figure 7a, the plot of $R(q)/q^2$ versus q^2 can reasonably be approximated by a single straight line, suggesting the virtual validity of the Cahn–Hilliard–Cook theory of spinodal decomposition.[4] At high T jumps in Figure 7b the data deviates appreciably exhibiting nonlinear character, thereby implying the inadequacy of the linear theory. If one draws a linear slope using the data at high q region in conjunction with the relation of q_m and q_c in eq 5, the diffusivities D_{app} may be determined from the intercepts from Figure 7. Figure 8 exhibits a plot of diffusivities as a function of temperature, in which the data appear as a curve; hence the spinodal point is not precisely determined. This behavior is in line with the previous observation in Figure 3 in which the equilibrium phase diagram could not be established.

As pointed out previously, the prevalent mechanism in the late stages is the nonlinear phase growth which causes the scattering halo to collapse to a smaller diameter. In this case, it is customary to focus on the time evolution of the ring diameter [or $q_m(t)$] and the ring intensity

$$I_m = I(q_m,t) \propto S(q_m,t) \qquad (7)$$

where $S(q_m,t)$ is the structure function. Contrary to the Cahn–Hilliard theory, there is no appreciable period in which $S(q,t)$ increases at an exponential rate but rather varies according to a power law scheme,[7] i.e.

$$q_m(t) \propto t^{-\alpha} \qquad (8)$$

or

$$I_m(t) \propto t^{\beta} \qquad (9)$$

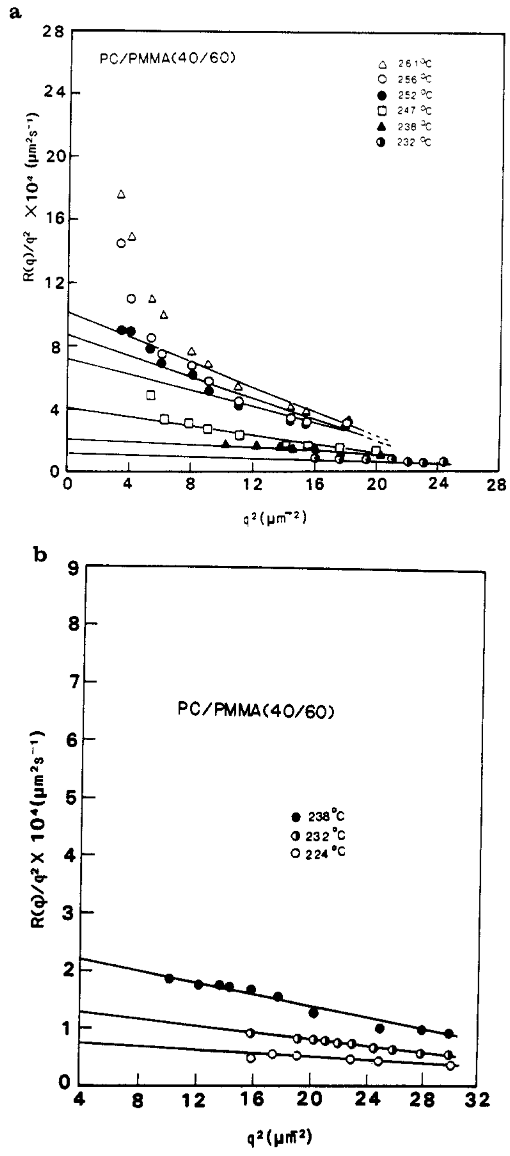

Figure 7. Linearized Cahn–Hilliard's plots in which $R(q)/q^2$ is plotted against q^2 for (a) all T jumps and (b) for low T jumps at an enlarged scale.

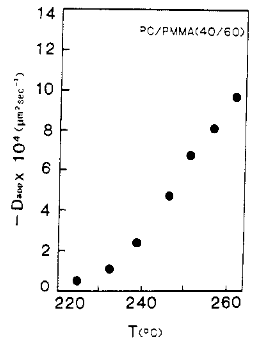

Figure 8. Variation of diffusion coefficient as a function of temperature jumps.

where α and β are the exponents. On the basis of the nonlinear statistical consideration, a theory has been put forward by Langer, Baron, and Miller (LBM)[a] who predicted that α is equal to 0.21. Another notable theory is the cluster dynamics of Binder and Stauffer (BS),[9] in that the clusters aggregate and coalesce into larger domains. The BS theory predicts that $\alpha = {}^1/_3$ and $\beta = 1$ with $3\alpha = \beta$. Recently, the values of $\alpha = 1$ and $\beta = 3$ have been proposed by Siggia[13] for the late stage of spinodal who considered that the coarsening occurs through the percolation process in that the materials diffuse via intercon-

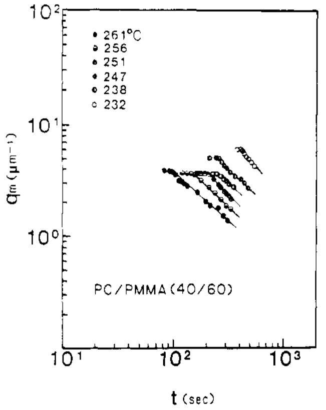

Figure 9. log–log plots of maximum wavenumber (q_m) as a function of phase separation time (t) for various temperature jumps.

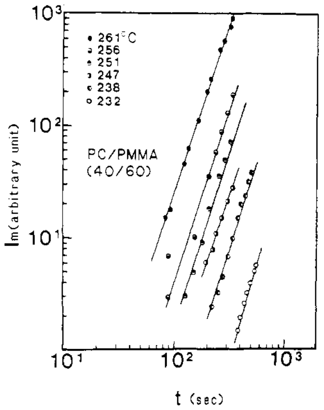

Figure 10. log–log plots of maximum scattered intensity (I_m) as a function of phase separation time (t) for various temperature jumps.

nected channels driven by surface tension.

The time evolution data of Figure 5 are reanalyzed according to eq 8 and 9 by plotting in log–log scale as shown in Figures 9 and 10, respectively, for q_m and I_m versus t. The q_m appears to be constant initially but decreases subsequently at a later time with the slope of −1. The corresponding plot of log I_m versus log t gives a slope of 3 for all temperature jumps. These values are exactly the values predicted by Siggia[13] for the late stages of spinodal decomposition in liquid mixtures, in which the mechanism has been identified to be a coarsening process driven by surface tension. Similar observations have been recently made by Han et al.[38] and Voigt-Martin et al.[30] for PS/PVME systems. The linear growth with time was first obtained by MacMaster[25] for SAN/PMMA and later by Gilmer et al.[26] for PS/poly(o-chlorostyrene) blends. This kind of fast diffusion has been attributed to the percolation process and has been commonly observed in critical mixtures and in some off-critical compositions with deep quench depths (or large T jumps in LCST).

Since there is an appreciable period at which q_m appears constant, the correlation length (ξ) in the single phase may be approximated as the initial fluctuation size of spinodal at the zero-phase separation time

$$\xi = 1/q_m(t = 0) \qquad (10)$$

The scaling analysis may be undertaken with reduced variables

$$Q = \xi q = q/q_m \qquad (11)$$

and

$$\tau = D\xi^{-2}t \qquad (12)$$

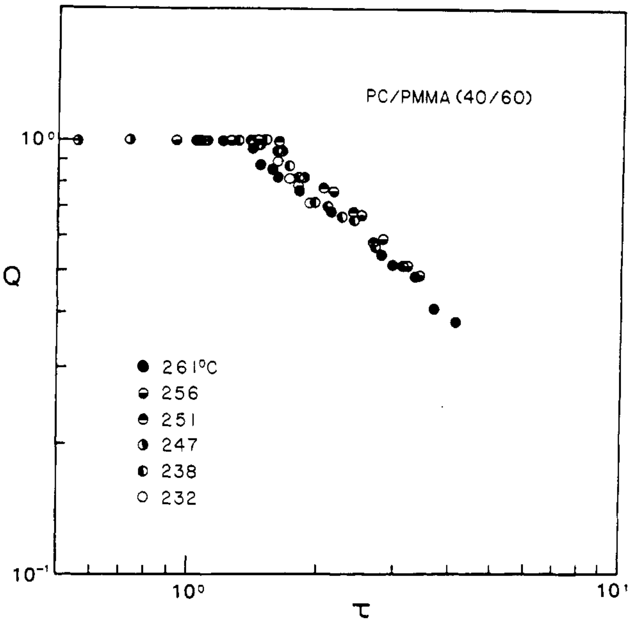

Figure 11. Reduced plot of Q versus τ for PC/PMMA (40/60) blends.

Experimentally, rigorous determination of ξ and D seems generally difficult because of the rapid evolution of the spinodal process. The reduced variable τ is 2 orders of magnitude smaller than the theoretical[8,9,11-13] and experimental[27,41] universal curves obtained for the critical mixtures, suggesting that the SD process in this 40/60 blend is at variance with the behavior of a critical mixture. Nevertheless, the reduced plot of Q versus τ in Figure 11 shows the general trend, indicating qualitatively that the time evolution of the fluctuation at different temperatures occurs according to a common mechanism.

According to the recent studies of Han et al.[40] and Hashimoto et al.[41] on the PS/PVME system, the universal curve comprises the crossover of various processes such as Cahn's linear region, Binder and Stauffer's cluster regime, and Siggia's percolation regime. In the present case the cluster regime ($\alpha = {}^1/_3$) is unable to be identified partly due to the rapid evolution of the SD process and uncertainty involved in the determination of the peak maximum especially at early times. It seems that the percolation regime predominates the phase separation in this PC/PMMA system. Because of the large T jumps, it is unclear whether the SD in the 40/60 blend follows a critical or off-critical behavior. This aspect is worthy of exploration by testing with the new scaling law of Furukawa[12] for the shape of the structure function. The scaling analysis on the late stages of spinodal decomposition in the PC/PMMA blends will be reported in a separate paper.[42]

Conclusion

We found a new miscible polymer pair, i.e. the blend of PC and PMMA, which was originally thought to be immiscible by others. The system reveals a miscibility window reminiscent of an LCST. The general trend of phase separation in this PC/PMMA is basically a nonlinear spinodal prevailed by the percolation regime in which the coarsening takes place due to surface tension. However, it should be pointed out that there is an appreciable period at which the peak maximum remains virtually invariant as predicted by the linear theory of Cahn–Hilliard.

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Registry No. PMMA, 9011-14-7; PC (copolymer), 25037-45-0; PC (SRU), 24936-68-3.

References and Notes

(1) Paul, D. R.; Newman, S. Eds. *Polymer Blends*; Academic: New York, 1978; Vols. 1 and 2.
(2) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*, Academic: New York, 1979.
(3) Gunton, J. D.; San Miguel, M.; Sahni, P. S. In *Phase Transitions and Critical Phenomena*; Domb, C., Lebowitz, J. L., Eds.; Academic: New York, 1983; Vol. 8.
(4) Cahn, J. W. *J. Chem. Phys.* **1965**, *42*, 93; *Trans, Metall. Soc. AIME* **1968**, *242*, 166.
(5) Hilliard, J. E. In *Phase Transformations*, ASME, Oct 1968, p 497.
(6) Cook, H. E. *Acta Metall.* **1970**, *18*, 297.
(7) Langer, J. S. *Acta Metall.* **1973**, *21*, 1649.
(8) Langer, J. S.; Baron, M.; Miller, H. S. *Phys. Rev. A* **1975**, *11*, 1417.
(9) Binder, K.; Stauffer, D. *Phys. Rev. Lett.* **1973**, *33*, 1006.
(10) Marro, J.; Bortz, A. B.; Kalos, M. H.; Lebowitz, J. L. *Phys. Rev. B: Solid State* **1975**, *12*, 2000.
(11) Kawasaki, K.; Ohta, T. *Prog. Theor. Phys.* **1978**, *59*, 362.
(12) Furukawa, H. *Physica A (Amsterdam)* **1984**, *123*A, 497.
(13) Siggia, E. D. *Phys. Rev. A* **1979**, *20*, 595.
(14) Wong, N. C.; Knobler, C. M. *J. Chem. Phys.* **1978**, *69*, 725; *Phys. Rev. A* **1979**, *43*, 1733.
(15) Chou, Y. C.; Goldburg, W. I. *Phys. Rev. A* **1981**, *23*, 858.
(16) Snyder, H. L.; Meakin, P. *J. Chem. Phys.* **1983**, *79*, 5588.
(17) Van Aartsen, J. J. *Eur. Polym. J.* **1970**, *6*, 919.
(18) Van Aartsen, J. J.; Smolders, C. A. *Eur. Polym. J.* **1970**, *6*, 1105.
(19) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1955.
(20) de Gennes, P.-G. *J. Chem. Phys.* **1980**, *72*, 4756.
(21) Pincus, P. *J. Chem. Phys.* **1981**, *75*, 1996.
(22) Nishi, T.; Wang, T. T.; Kwei, T. K. *Macromolecules* **1975**, *8*, 227.
(23) Hashimoto, T.; Kumaki, J.; Kawai, H. *Macromolecules* **1983**, *16*, 641.
(24) Snyder, H. L.; Meakin, P.; Reich, S. *Macromolecules* **1983**, *16*, 757.
(25) MacMaster, L. P. *Adv. Chem. Ser.* **1975**, *No. 142*, 43.
(26) Gilmer, J.; Goldstein, N.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2219.
(27) Nojima, S.; Nose, T. *Polym. J.* **1982**, *14*, 269; *Polym. J.* **1982**, *14*, 907.
(28) Russell, T. P.; Hadziioannou, G.; Warburton, W. K. *Macromolecules* **1985**, *18*, 78.
(29) Hill, R. G.; Tomlins, P. E.; Higgins, J. S. *Macromolecules* **1985**, *18*, 2555.
(30) Voigt-Martin, I. G.; Leister, K. H.; Rosenau, R.; Koningveld, R. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 723.
(31) Yang, H. J.; Shibayama, S.; Stein, R. S.; Han, C. C. *Polym. Bull.* **1984**, *12*, 7.
(32) Herkt-Maetzky, C.; Schelten, J. *Phys. Rev. Lett.* **1983**, *51*, 896.
(33) Kyu, T.; Saldanha, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 33.
(34) Gardlund, Z. G. In *Polymer Blends and Composites in Multiphase Systems*, Han, C. D., Ed., Advances in Chemistry 206; American Chemical Society: Washington, DC, 1984, Chapter 9, p 129.
(35) Koo, K. K.; Inoue, T.; Miyasaka, K. *Polym. Eng. Sci.* **1985**, *27*, 741.
(36) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *2*(2), 123.
(37) Chiou, J. S.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1459.
(38) Kambour, R. P.; Gundlach, P. E.; Wang, I. C. W.; White, D. M.; Yeager, G. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Sci.)* **1987**, *28-2*, 140.
(39) Kyu, T.; Lim, D. S. *J. Polym. Sci., Polym. Lett. Ed.*, submitted for publication.
(40) Han, C. C.; Sato, T.; Okada, M.; Wu, C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Sci.)* **1987**, *28*, 358. Okada, M.; Han, C. C. *J. Chem. Phys.* **1986**, *85*, 5317.
(41) Hashimoto, T.; Itakura, M.; Hasegawa, H. *J. Chem. Phys.* **1986**, *85*(10), 6118. Hashimoto, T.; Itakura, M.; Shimadzu, N. *J. Chem. Phys.* **1986**, *85*(11), 6773.
(42) Kyu, T.; Saldanha, J. M, Lim, D. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Sci.)*, in press.

Phase Separation of Oligomeric Polystyrene–Polybutadiene Blends As Studied by Excimer Fluorescence

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ABSTRACT: The binodal curve and phase separation behavior of 826 MW polystyrene (PS)/2500 MW polybutadiene (PB) blends have been studied by optical density measurements and fluorescence spectroscopy, respectively. The equilibrium compositions from the binodal curve and the Gelles–Frank two-phase model, which relates the composition of phases generated during spinodal decomposition to the ratio of excimer to monomer fluorescence intensity, I_E/I_M, were used to follow the time-dependent compositions of the phases during phase separations as well as the kinetics of phase separation. For 30 wt % and 60 wt % PS blends quenched at 32 °C, the change in I_E/I_M during phase separation was quite small, less than 10%, but nevertheless large enough to yield precise information. Cahn's theory of spinodal decomposition apparently describes adequately at least the first 3 min of phase separation, and the Gelles–Frank two-phase model predicts quantitatively I_E/I_M at equilibrium. Fluorescence results for the 30 wt % blend indicate that equilibrium is achieved in about 60 min; on the basis of the composition of the PS-rich phase the phase separation is about 90% complete in the first 13 min. From the measured growth rate of decomposition, the Cahn–Hilliard diffusion coefficient is estimated to be of the order -10^{-12} cm^2/s for both the 30 and 60 wt % PS/PB blends.

Introduction

Over the past couple of decades, an increasing number of studies have been reported on phase separation phenomena in polymer solutions and blends.[2-30] A number of studies[2-15] were reported on cloud point measurements for several binary high-polymer mixtures; all of these systems exhibited lower critical solution temperature (LCST) behavior. In contrast, upper critical solution temperature (UCST) behavior has been obtained by cloud point measurements on oligomeric or relatively low molecular weight polymeric blends;[16-25] some of these studies have revealed asymmetry and bimodality of the phase diagrams.

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