Phase Separation in Polystyrene/Poly(vinyl methyl ether) Blends As Studied by Excimer Fluorescence

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ABSTRACT: Excimer fluorescence has been used to study spinodal decomposition in a polystyrene (PS)/poly(vinyl methyl ether) (PVME) blend phase separated by thermal means. From the measurement of the ratio of excimer-to-monomer fluorescence emission intensities, the time dependence of the rich- and lean-phase compositions during phase separation has been determined. Cahn's theory of spinodal decomposition appears to describe adequately the early stages of phase separation. Fluorescence results indicate, however, that equilibrium is not reached during this time period. From the measured growth rate of decomposition, the macroscopic diffusion coefficient for a 10% PS/PVME blend annealed at 423 K is calculated to be of the order -10^{-11} cm^2/s.

Introduction

Polymer–polymer blends typically show a decrease in miscibility with increasing temperature. McMaster used a modified Flory equation of state thermodynamic model to show that the existence of a lower critical solution temperature (LCST) is caused mainly by differences in the pure-component thermal expansion coefficients.[1] The LCST behavior is illustrated by the schematic polymer–polymer phase diagram in Figure 1. The binodal, defined as the locus of points for which the chemical potentials of each component are equal in both phases, separates the stable one-phase region from the region in which two phases coexist at equilibrium. The spinodal, the locus of points for which the second derivative of the Gibbs free energy of mixing F equals zero, divides the two-phase region into metastable and unstable portions.

The mechanism of phase separation is expected to depend upon whether the single phase is metastable or unstable. In the metastable region $\partial^2F/\partial\phi^2 > 0$ and small fluctuations in volume fraction ϕ decay with time. For phase separation to take place, a large composition fluctuation is required. For example, for a blend with a composition close to the left ascending branch of the binodal, a concentration fluctuation, or nucleus, is stable only for compositions close to the other branch of the binodal. Once such a nucleus is formed, it can grow by normal diffusion. During this nucleation and growth process, the composition of the growing phase remains constant. Although no kinetic model of nucleation and growth for polymeric systems exists, the phenomenon has been observed for polymer blends by both optical[2] and transmission electron microscopy.[3] Within the unstable region inside the spinodal $\partial^2F/\partial\phi^2 < 0$ and there is no thermodynamic barrier to phase separation. As a result, small concentration fluctuations can grow with time by a mechanism termed spinodal decomposition. A kinetic treatment of the early stages of the process has been developed by Cahn.[4]

Experimental verification of the spinodal decomposition mechanism has been obtained for a number of polymeric systems. The characteristic interconnected phase morphology has been observed for both polymer–polymer blends[2,3] and polymer solutions.[5,6] Van Aartsen[5] successfully predicted the magnitude of the phase spacing for spinodal decomposition in polymer–solvent mixtures using Cahn's theory together with a Flory–Huggins expression for the free energy of mixing. Finally, Nishi, Wang, and Kwei[2] have analyzed phase separation in polystyrene (PS)/poly(vinyl methyl ether) (PVME) blends using pulsed NMR. Their results gave direct evidence of the spinodal mechanism: the concentrations of the two phases changed exponentially with time at short times while only slight changes in the volume fractions of the phases were observed.

The purpose of this work is to study the kinetics of phase separation in PS/PVME blends by means of excimer fluorescence. Miscible blends exhibiting LCST behavior can be prepared by film casting from toluene.[1,2,7–10] In an earlier study on such miscible blends at low PS concentration, excimer fluorescence was demonstrated to be sensitive to the size of the PS coil.[11] When the blend was heated, it appeared that the PS coil dimensions decreased as the LCST was approached. In a second study a two-phase model was developed to treat quantitatively the fluorescence of phase-separated systems.[12] This was applied to the photostationary fluorescence results for immiscible PS/PVME blends cast from tetrahydrofuran. In the present work the two-phase model will be used to analyze the fluorescence of PS/PVME blends phase separated by thermal means.

Experimental Section

PS/PVME blends, at a concentration of 10% PS, were prepared by film casting from toluene onto sapphire disks at room temperature. The PS, obtained from Pressure Chemical Co., was monodisperse with a molecular weight of 100 000. The PVME, supplied by GAF, was polydisperse with an average molecular weight of 44 600 as determined from its intrinsic viscosity in benzene at 303 K. Purification techniques have been described elsewhere.[11]

The solid films, 10 μm thick, were dried under vacuum at 323 K for at least 4 days to remove the casting solvent. No evidence of residual solvent was found in the fluorescence spectra of pure PVME films prepared under identical conditions. To ensure good contact between the film and the cover disk, two of the supported films were pressed together and annealed at 323 K for 2 more days. This was found to remove all air spaces in the sample.

Thermal treatment was carried out in an oil bath whose temperature was controlled to within ±0.1 K. (In order to prevent oil contamination of the samples, they were enclosed in packets formed from the heat-sealable polymer film used in the Dazy Seal-A-Meal cooking pouches.) After the sample was held in the bath for the desired annealing time, it was rapidly quenched in an ice–water mixture.

Fluorescence spectra were taken in air at room temperature both before and after thermal treatment. The spectrofluorimeter has been described earlier.[13] Front-face optical excitation was used to minimize self-absorption; excitation was at 260 nm. Simple fluorescence intensities were measured at 280 nm (monomer) and 332 nm (excimer), where there is no overlap of excimer and monomer bands.

It should be noted that the experiment could have been carried out in such a way as to measure continuously the fluorescence of a sample during the thermal treatment. It was not done in this study, however, for two reasons. First, films maintained at high temperatures were found to degrade when exposed to the

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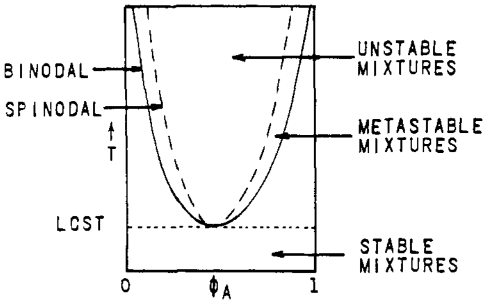

Figure 1. Schematic phase diagram of a polymer–polymer blend which exhibits a lower critical solution temperature (LCST).

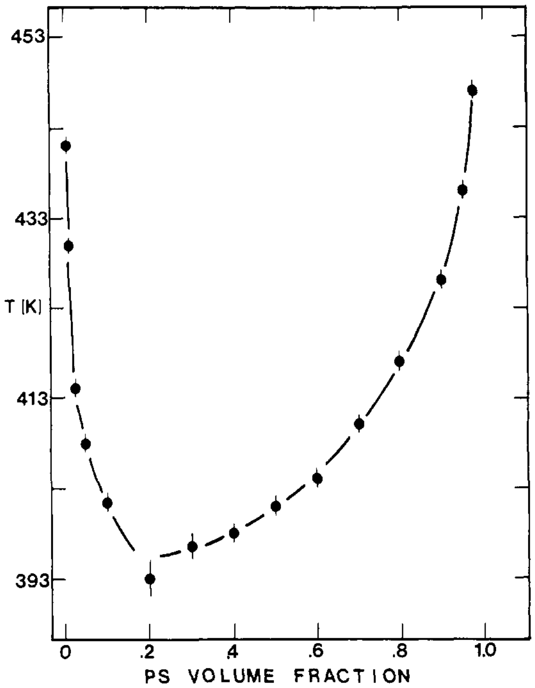

Figure 2. Experimental cloud point curve for the polystyrene (PS)/poly(vinyl methyl ether) (PVME) blend. The PS is monodisperse with $\bar{M}_n$ = 100 000 and the PVME is polydisperse with $\bar{M}_w$ = 44 600.

high-intensity xenon arc lamp light source. Second, the two-phase model requires fluorescence data for miscible blends taken at the same temperature as those for the phase-separated samples.

The cloud point measurements were carried out simply by determining the minimum temperature at which a given blend showed visual signs of phase separation after 15 min of annealing in the oil bath. In general, films turned milky within 1 or 2 min at the cloud point temperature.

Results

The cloud point curve for the PS/PVME blend is shown in Figure 2. The occurrence of the extremum temperature at a low PS volume fraction is a result of the higher molecular weight of this component.[1] In the following analysis it will be assumed for simplicity that the cloud point curve represents the true binodal of the system. In fact, this assumption should not be strictly valid due to the polydispersity of the PVME.[1,14,15] The absence of a "dimple" on the left ascending branch of the cloud point curve, however, indicates that the assumption may be a reasonable one.[1]

Typical uncorrected emission spectra of a 10% PS/PVME blend taken before and after annealing at 423 K are shown in Figure 3. The sensitivity of the fluorescence probe to phase separation in the PS/PVME blend is illustrated by the fact that films annealed at 423 K for less than 1.5 min showed no visual signs of opalescence while the emission spectra changed for all annealing times examined.

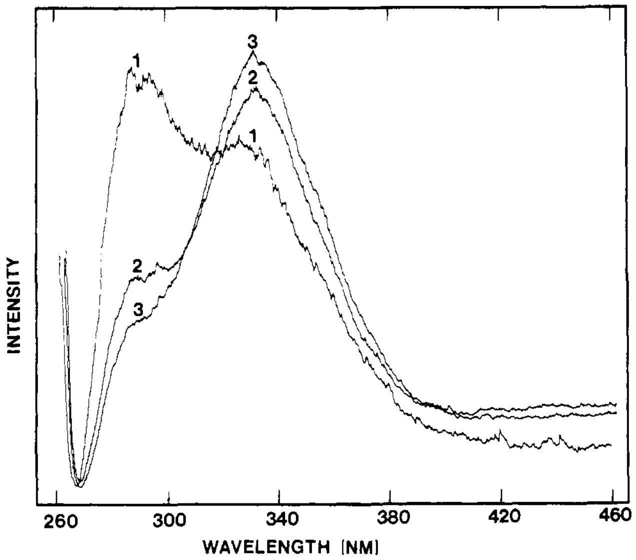

Figure 3. Comparison of typical uncorrected fluorescence spectra for 10% PS/PVME blends measured at room temperature both before and after thermal treatment: (1) no thermal treatment; (2) annealed for 5 min at 423 K; (3) annealed for 30 min at 423 K. The fluorescence intensity is given in arbitrary units.

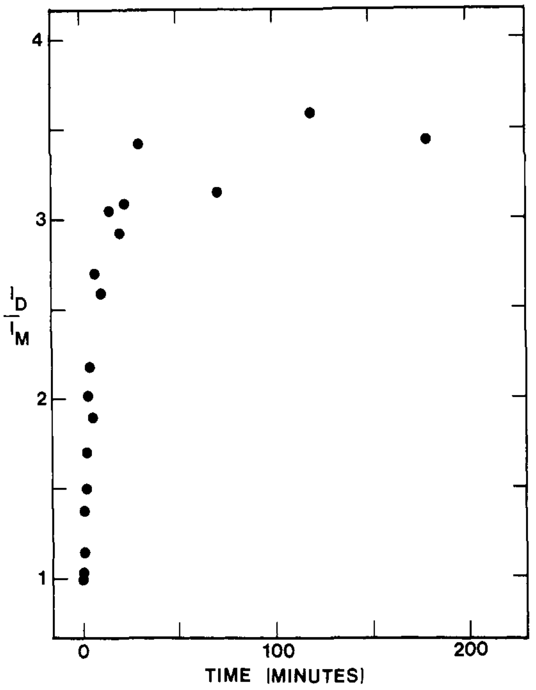

Figure 4. Effect of annealing time on the ratio of excimer-to-monomer fluorescence intensities, I_D/I_M, for a 10% PS/PVME blend at 423 K.

The dependence of the ratio of excimer-to-monomer fluorescence intensities, $R \equiv I_D/I_M$, on time of annealing at 423 K for 10% PS/PVME blends is shown in Figure 4. The points for times less than or equal to 30 min are averages of the values for three films while measurements at longer times were made only on single samples. The ratio at $t = 0$, corresponding to the average ratio of a film before thermal treatment, equals 0.99. Figure 4 shows that I_D/I_M increases rapidly with time at short times and much more slowly at longer times. After 30 min, the ratio is constant, within experimental error.

The results for the first 30 min are replotted in Figure 5 together with error bars representing a simple standard

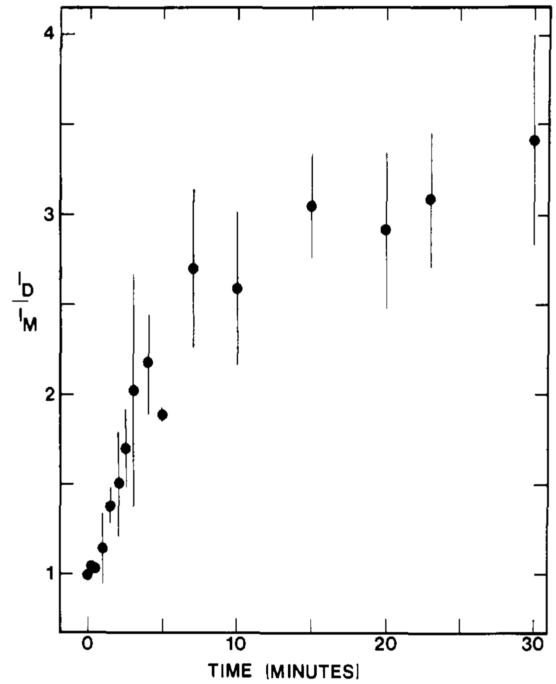

Figure 5. Effect of annealing time on the ratio of excimer-to-monomer fluorescence intensities at 423 K for the first 30 min. Error bars represent simple standard deviations for three measurements.

deviation of three measurements. Although the uncertainty level is relatively high, it appears that the majority of the change in R occurs in the first 6 min and that the ratio is still increasing, albeit rather slowly, at longer times. It is interesting to note that the magnitude of the ratio correlated qualitatively with the opaqueness of a film. No attempt was made to quantify this relationship for this study, however.

Discussion

In a series of recent papers, excimer fluorescence has been applied to the study of polymer blend miscibility. Experimental variables have included the solubility parameters of the fluorescent guest and nonfluorescent host polymers,[13] guest concentration,[16] guest and host molecular weight,[17] and film-casting temperature.[18] The objective in these studies was to demonstrate that this relatively new technique could monitor changes in segment density of the fluorescent guest polymer that were brought about by changes in the blend thermodynamics. No attempt was made, however, to determine the segment density quantitatively. Rather, the trends in I_D/I_M were correlated either with classical bulk measurements of optical clarity[17,18] or differential scanning calorimetry[19] or with calculations of equilibrium thermodynamics based on Flory–Huggins theory.[17,18]

A more sophisticated treatment of the photophysics has been followed in the recent work on PS/PVME blends.[11,12] Since the analysis of the kinetics of phase separation pursued in the present work depends upon knowledge of the previous analytical models, a brief review is warranted.

In the first paper of a series on energy migration in the aromatic vinyl polymers, Fitzgibbon[20] showed that the ratio of excimer-to-monomer fluorescence intensities is given by

$$R = \frac{Q_D}{Q_M}\left[\frac{D(1-M)}{1-D(1-M)}\right] \tag{1}$$

In eq 1 Q_D/Q_M is the ratio of intrinsic quantum yields for excimer and monomer fluorescence. M is the overall probability that a photon absorbed by a pendant aromatic ring will lead to radiative or nonradiative decay from the monomer state. Correspondingly, $1 - M$ is the probability that the absorbed photon will lead to decay from the excimer state. Finally, D is the probability that an excimer state, once formed, will lead to radiative or nonradiative decay from the excimer, rather than dissociate to excited monomer.

All information about the morphological and dynamic properties of the polymer are contained in M. Fitzgibbon has developed an analytical expression for M under conditions for which the polymer chain is isolated and the energy migration rate is much faster than the segmental rotation rate.[20] In such a case, electronic energy transport among the pendant aromatic rings may be treated as a one-dimensional (1-D) random walk along the chain. The model successfully explains the molecular weight dependence of intramolecular excimer fluorescence observed for poly(2-vinylnaphthalene) in 2-methyltetrahydrofuran: rapid increase in I_D/I_M at low molecular weight followed by a leveling at high molecular weight.

In the second paper of this energy migration series, the 1-D model was applied to analogous PS fluorescence results obtained for 5% PS/PVME blends.[11] Monodisperse PS samples of different molecular weights were examined in blends with PVME over a temperature range in which no thermal deactivation of the excimer to excited monomer takes place. For this situation, D will be unity and eq 1 reduces to

$$\frac{I_D}{I_M} = \frac{Q_D}{Q_M}\left[\frac{1-M}{M}\right] \tag{2}$$

Rotational isomeric state calculations were performed to determine the equilibrium population of excimer-forming conformation dyads. Use of these values and the experimentally observed dependence of I_D/I_M on PS molecular weight allowed determination of Q_D/Q_M.

Below 303 K, the observed molecular weight dependence of I_D/I_M for PS could be fit quite well with the 1-D model, yielding values of Q_D/Q_M ranging between 0.36 at 286 K and 0.49 at 303 K. A similar temperature dependence has been observed for benzene in solution.[21] The value of Q_D/Q_M found in this work falls within, but at the high end of, the range of literature results for related systems.[11] It contains an instrumental response factor, however, which is between 1 and 2. Fortunately, the ambiguity arising from this indeterminacy has no bearing on the results of the two-phase model, to be described shortly.

In the third paper of this series, the effect of PS concentration on I_D/I_M was studied for both miscible and immiscible PS/PVME blends.[12] For miscible toluene-cast PS/PVME blends, the ratio was constant at low concentrations, increased nearly linearly up to a PS volume fraction of 0.5, and then showed some curvature and a rapid increase at high PS concentrations. The major thrust of the analysis was to explain the high-concentration behavior in terms of a relatively simple three-dimensional (3-D) random walk model. The immiscible blends were prepared by using tetrahydrofuran as a casting solvent. The markedly different concentration dependence of the fluorescence ratio for phase-separated systems was explained quite well using a two-phase model. In the present work this two-phase model will be applied to the fluorescence results obtained for PS/PVME blends that were phase separated by thermal treatment.

In deriving an expression for the ratio of excimer-to-monomer fluorescence for a two-phase mixture, we have made a number of simplifying assumptions. The major one is that energy migration does not occur between the phases. This reduces an extremely complicated problem to two simpler ones: the first is to determine what fraction of photons is absorbed by each phase, and the second is to characterize what happens to a photon absorbed by a phase of a known composition. This assumption is a good one for both high and low phase concentrations.

A simple mass balance may be used to determine what fraction of photons is absorbed by aromatic rings in the rich phase. First, the volume fraction of the rich phase V_R is given by

$$V_R = (\phi_B - \phi_L)/(\phi_R - \phi_L) \tag{3}$$

where ϕ_B, ϕ_L, and ϕ_R are the bulk, lean-phase, and rich-phase polystyrene volume fractions, respectively. Then the fraction of rings in the rich phase, X_R, is given by

$$X_R = \frac{\phi_R V_R}{\phi_R V_R + \phi_L(1 - V_R)} \tag{4}$$

It is apparent that X_R also equals the probability that an absorbed photon starts in the rich phase. The result of the two-phase model is that for a phase-separated blend

$$\frac{I_D}{I_M} = \frac{Q_D}{Q_M}\left[\frac{X_R(1 - M_R) + (1 - X_R)(1 - M_L)}{X_R M_R + (1 - X_R)M_L}\right] \tag{5}$$

where M_R and M_L are the probabilities of eventual radiative or nonradiative monomer decay for an absorbed photon starting in the PS-rich and -lean phases, respectively.

In order to apply eq 5 it is necessary to know values for Q_D/Q_M and the dependence of M on PS concentration. Q_D/Q_M has been estimated to be equal to 0.42 at 295 K for 5% PS/PVME blends.[11] Although it was assumed that Q_D/Q_M does not depend on concentration, this assumption has not been justified experimentally. Q_D/Q_M can only be measured directly using model compounds for systems in which the aromatic ring concentration is low enough to preclude excimer formation, as shown by Fitzgibbon.[20] An attempt was made to evaluate Q_D/Q_M using cumene-doped PVME samples but the cumene readily evaporated from the films. In addition, the cumene photodegraded rapidly under ultraviolet illumination. Although efforts to measure Q_D/Q_M directly are continuing, the assumption that Q_D/Q_M is independent of concentration must be made in order to apply the current two-phase model. In fact, as will be shown, this seems to give reasonable results.

To characterize what happens to a photon absorbed by a phase of a specific composition, fluorescence measurements for miscible blends taken at 298 K were used along with eq 2 to determine the concentration dependence of M, the probability that an absorbed photon will lead to monomer decay. Although no correction for self-absorption was applied to the fluorescence results, the films were relatively thin (10 μm) and front-face excitation was employed to minimize reabsorption. That these precautions were largely successful has been demonstrated in the previous study in which PS/PVME blends were cast from tetrahydrofuran over the entire composition range.[12] The I_D/I_M ratios for the immiscible PS/PVME films cast from THF for PS volume fractions greater than 0.3 were equal to I_D/I_M for the pure PS film. If self-absorption had been a serious problem, one would expect it to be more significant for the neat PS film than for the phase-separated THF-cast blend and, hence, I_D/I_M should have been larger for neat PS. This was not the case. The major reason for the dramatic decrease in M with increasing PS concentration is the increase in dimensionality of the energy migration from one- to three-dimensional.[12]

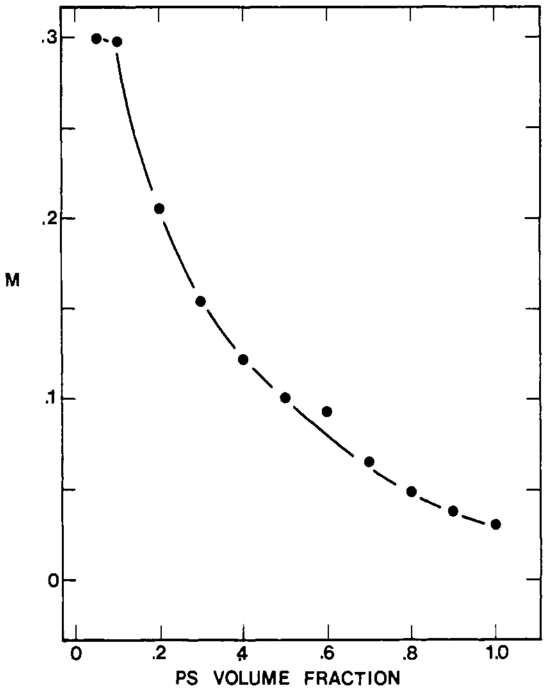

Figure 6. Dependence of M, the probability of eventual monomer emission by both radiative and nonradiative means, on polystyrene volume fraction for miscible blends. The solid line was obtained using eq 4 and experimental fluorescence data.

Because the films were annealed well above the cloud point temperature, the mechanism of phase separation is assumed to be spinodal decomposition. As such, the volume fraction of the rich phase should remain constant during phase separation. Since breakup of the spinodal structure and subsequent coalescence of the phases will not change the volume fractions of the two phases, the volume fraction of the rich phase will be equal to its equilibrium value. These concentrations are obtained from Figure 2 to be $\phi_R = 0.875$ and $\phi_L = 0.016$ at equilibrium. The volume fraction of the rich phase, V_R, calculated from eq 3, is then 0.0978.

Since the volume fraction of the rich phase is known, the ratio of excimer-to-monomer fluorescence is a unique function of the rich-phase polystyrene volume fraction, ϕ_R. This relationship is depicted in Figure 7, which has been constructed using eq 2–5 and Figure 6. Figure 7, together with eq 3, can be used to convert the raw fluorescence results into rich- and lean-phase compositions. The dependence of ϕ_R and ϕ_L with time is presented in Table I.

Application of the two-phase model leads to a predicted equilibrium ratio of 4.9, but the fluorescence data in Figure 4 show that the ratio levels off to about 3.5 at long times. Thus it might appear at first that the blend system is still far from equilibrium after 3 h of annealing. In fact, as can be seen from Figure 7, R increases rapidly at high-rich-phase PS volume fraction so that a ratio of 3.5 corresponds to a rich-phase composition of $\phi_R \simeq 0.79$, which is 90% of the equilibrium value.

In order to apply the two-phase model for excimer fluorescence to the study of the kinetics of phase separation, it is necessary to outline the major elements of Cahn's theory of spinodal decomposition. For the early stages of spinodal decomposition, Cahn obtained the diffusion equation

$$\frac{\partial \phi}{\partial t} = N\left[\frac{\partial^2 f}{\partial \phi^2}\nabla^2\phi - 2K\nabla^4\phi\right] \tag{6}$$

where K is the gradient energy coefficient, f is the free

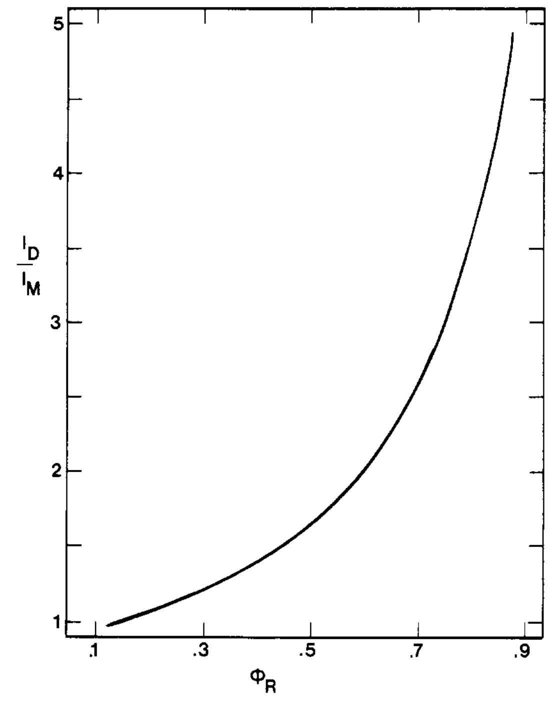

Figure 7. Dependence of the ratio of excimer-to-monomer fluorescence intensities on the rich-phase polystyrene volume fraction, ϕ_R, calculated from the two-phase model with the volume fraction of the rich phase set equal to 0.0978.

Table I
Rich- and Lean-Phase Compositions during Spinodal Composition

time, min	R_{exptl}	ϕ_{rich}	ϕ_{lean}	$\phi_R - \phi_B$
0.25	1.04 ± 0.03	0.173	0.092	0.073
0.50	1.03 ± 0.03	0.165	0.093	0.065
1.0	1.14 ± 0.20	0.255	0.083	0.155
1.5	1.38 ± 0.10	0.386	0.069	0.286
2.0	1.50 ± 0.29	0.440	0.063	0.340
2.5	1.70 ± 0.22	0.515	0.055	0.415
3	2.02 ± 0.65	0.601	0.046	0.501
4	2.18 ± 0.28	0.630	0.043	0.530
5	1.89 ± 0.03	0.566	0.049	0.466
7	2.70 ± 0.44	0.713	0.034	0.613
10	2.59 ± 0.43	0.699	0.035	0.599
15	3.05 ± 0.29	0.754	0.029	0.654
20	2.92 ± 0.44	0.740	0.031	0.640
23	3.09 ± 0.38	0.757	0.029	0.657
30	3.43 ± 0.59	0.785	0.026	0.685
71	3.15	0.762	0.028	0.662
120	3.59	0.798	0.024	0.698
180	3.44	0.786	0.026	0.686

energy of mixing per volume, and N is the Onsager coefficient, defined as the ratio of the diffusional flux to the chemical potential gradient. The solution to eq 6 was found to be

$$\phi - \phi_0 = \sum_{\text{all }\beta} \exp[R(|\beta|)t][A(\beta)\cos(\beta\cdot\mathbf{r}) + B(\beta)\sin(\beta\cdot\mathbf{r})] \quad (7)$$

where β is a wavevector, A and B are amplitudes, ϕ_0 is the initial composition, and $R(|\beta|)$ is a growth rate given by

$$R(|\beta|) = -N\beta^2[\partial^2 f/\partial\phi^2 + 2K\beta^2] \quad (8)$$

From eq 8, it is apparent that fluctuations will grow with time only for $\beta < \beta_c$, where

$$\beta_c = \left[-\frac{1}{2K}\frac{\partial^2 f}{\partial\phi^2}\right]^{1/2} \quad (9)$$

Cahn has also shown that phase separation is dominated

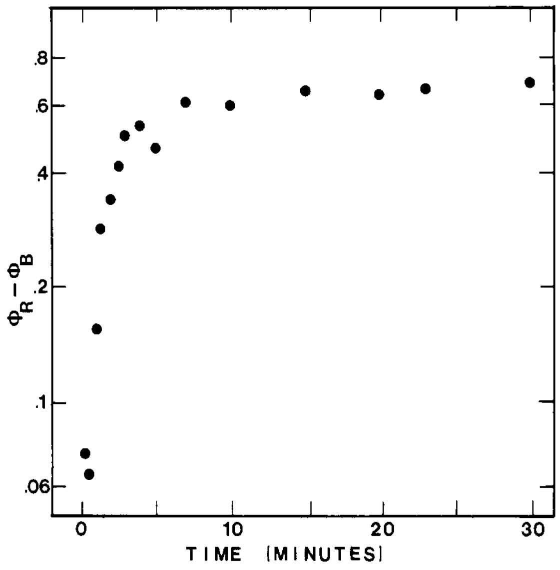

Figure 8. Dependence of the rich-phase polystyrene volume fraction on time of annealing at 423 K for a 10% PS/PVME blend.

by a fluctuation of wavenumber $\beta_{\max} = \beta_c/2^{1/2}$, which has a growth rate $R(\beta_{\max}) = -{}^1/_2 N(\partial^2 f/\partial\phi^2)\beta_m{}^2$. Since the coefficient of $\nabla^2\phi$ in eq 6 can be defined as a diffusion coefficient

$$R(\beta_{\max}) = -{}^1\!/_2 D\beta_m{}^2 \quad (10)$$

The model predicts that the volume fractions of the two phases remain constant with time while the compositions change gradually. From eq 7, it can be seen that at short times each phase is inhomogeneous in composition. Eventually, spinodal decomposition results in an interconnected morphology with a phase spacing equal to $2\pi/\beta_m$. This was demonstrated by Cahn to be true provided the volume fraction of the minor phase is at least 15%. Nishi et al.[2] have observed that the characteristic length of the spinodal morphology is much larger than the coil dimension.

At longer times, higher order terms ignored by Cahn are expected to distort the composition profile so that the two phases will be homogeneous except near the vicinity of the interface.[4] Also, as a result of surface tension, the interconnected structure is expected to break up into droplets which then grow by Ostwald ripening.

The two-phase model makes no allowances for phases which are inhomogeneous in composition. To use eq 7, it will be assumed that the fluorescence of a phase-separated film is sensitive to the average compositions of the two phases. It will be further assumed that the concentration profile within each phase is spherically symmetric and that only the dominant fluctuation need be considered. Thus

$$\phi_R - \phi_B = A(\beta_m)e^{R(\beta_m)t}\cos(\beta_m r) \quad (11)$$

and

$$\langle\phi_R - \phi_B\rangle = \int_0^{\pi/2\beta_m}(\phi_R - \phi_B)4\pi r^2\,dr \Big/ \int_0^{\pi/2\beta_m} 4\pi r^2\,dr = 0.36A(\beta_m)e^{R(\beta_m)t} \quad (12)$$

Hence a plot of ln $(\phi_R - \phi_B)$ vs. time should be linear and have a slope $R(\beta_m)$.

Figure 8 presents a semilogarithmic plot of the values of $\phi_R - \phi_B$ obtained from Table I vs. time. It is apparent that the spinodal decomposition model only holds for very short times. The results for the first 7 min of annealing are replotted in Figure 9. From Figure 9, it appears that the relationship given in eq 12 holds for the first 3 min of phase separation at the most, and perhaps only for the first

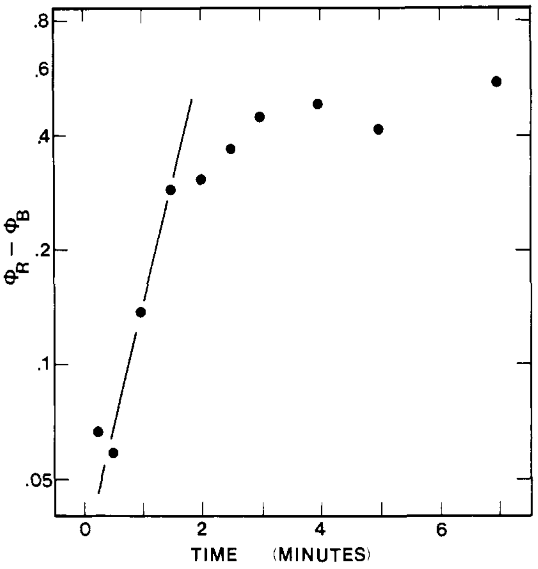

Figure 9. Short-time dependence of the rich-phase polystyrene volume fraction with time of annealing at 423 K.

1.5 min. Nishi et al. obtained a similar result.[2]

As can be seen in Figure 7, a large change in concentration at very short times does not lead to a large change in the ratio of excimer-to-monomer fluorescence. As a result of this reduced sensitivity, the value of the dominant growth rate $R(\beta_m)$ may be determined only to within a factor of 2. From the slope of the line drawn through the short-time data in Figure 9, $R(\beta_m) = 0.9 \pm 0.3$ min^{-1}. Nishi et al. obtained a growth rate for a 50:50 blend with higher molecular weight components annealed at 403 K which was an order of magnitude slower.

The diffusion coefficient describing the decomposition process can be calculated provided the wavelength of the dominant concentration fluctuation is known. From optical microscopy, this wavelength has been determined to be of the order of 1 μm.[2] From eq 9, the diffusion coefficient is then found to be of the order of -10^{-11} cm^2/s.

Finally, the fluorescence results show that phase growth is still taking place at long times where Cahn's model does not hold. From Table I, it appears that the growth rate at long times is several orders of magnitude slower than the rate during the early stages of decomposition.

Conclusions

The technique of excimer fluorescence can be used to study quantitatively the kinetics of phase separation in polymer blends. For a 10% PS/PVME blend annealed at 423 K, Cahn's model for spinodal decomposition adequately describes the process at short times, although the fluorescence results indicate that equilibrium is not reached during this period. The growth rate appears to be several orders of magnitude larger at short times than during the later stages of decomposition.

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Calculation of Liquid–Liquid Phase Separation in a Ternary System of a Polymer in a Mixture of a Solvent and a Nonsolvent

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ABSTRACT: A numerical method for the calculation of the binodal of liquid–liquid phase separation in a ternary system is described. The Flory–Huggins theory for three-component systems is used. Binodals are calculated for polymer/solvent/nonsolvent systems which are used in the preparation of asymmetric ultrafiltration or reverse osmosis membranes: cellulose acetate/solvent/water and polysulfone/solvent/water. The values for the binary interaction parameters are taken from literature sources. The effect of a concentration-dependent solvent/nonsolvent interaction parameter is discussed. Although knowledge of the interaction parameters for all compositions in the ternary system is rather poor, fairly good agreement has been found between calculated and experimentally found miscibility gaps when the solvent/nonsolvent parameter is taken to be concentration dependent and the other parameters, the polymer/solvent and the polymer/nonsolvent interaction parameter, are kept constant.

Introduction

The equilibrium thermodynamic properties of the system polymer/solvent/nonsolvent play an important role in the description of the formation process of an asymmetric reverse osmosis or ultrafiltration membrane. Such membranes are usually prepared by casting a concentrated polymer solution in a thin film on a supporting surface and immersing this film in a nonsolvent bath. Depending on

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