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

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

Fu-Jya Tsai[1a] and John M. Torkelson*[1a,b]

Department of Chemical Engineering and Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208.

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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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* Author to whom correspondence should be addressed.

A number of analytical methods have been developed to determine accurately the binodal curves for polymer solutions and melts. These include low-speed centrifugation,[19] light scattering[14,15,20] and pulse-induced critical scattering,[31] fluorescence quenching techniques,[10,13] and optical density measurements.[21] The latter technique is particularly attractive for studies on oligomeric blends due to the very small sample requirements and modest cost of absorbance spectroscopy equipment.

Excimer fluorescence techniques have recently been employed to try to gain insight into the mechanism associated with phase separation in polymeric systems. Gelles and Frank[8,9] used excimer fluorescenct to study spinodal decomposition[33] in polystyrene–poly(vinyl methyl ether) blends. They developed a two-phase model[8] to describe the relationship between the ratio of excimer and monomer fluorescence intensity, I_E/I_M, and the compositions of the PS-rich and PS-lean phases. They also showed that the early stages of phase separation of their blend were consistent with Cahn's[33] spinodal decomposition theory. Later, Torkelson et al.[27] used excimer fluorescence to study phase separation in PS–methylcyclohexane systems. While their study showed that the Gelles–Frank model correctly predicted the magnitude of changes in the I_E/I_M during phases, complications due to convective flow in the cell and macroscopic separation of the phases precluded a quantitative comparison of experimental results to spinodal decomposition behavior.

In the present study, phase separation of oligomeric polystyrene/polybutadiene (PB) blends is studied with optical density methods and fluorescence spectroscopy. The Gelles–Frank two-phase model is applied to obtain quantitative descriptions of the time-dependent compositions of PS-rich and PS-lean phases and to test whether the phase separation achieved is consistent with spinodal decomposition. The oligomeric PS/PB blends are particularly good candidates for this type of investigation, as previous studies by Hill et al.[20] and Russell et al.[21] on similar blends have shown the presence of UCST behavior at slightly above room temperature. Those previous studies[20,21] gave strong but incomplete evidence that spinodal decomposition occurs upon phase separation of these blends. By providing evidence that the compositions of the PS-rich and PS-lean phases formed during phase separation change continuously with time, the present study will be able to make significant comment on the presence of spinodal decomposition in oligomeric mixtures of PS/PB.

Experimental Section

Polystyrene (PS) (MW 826, $\bar{M}_w/\bar{M}_n = 1.14$) and polybutadiene (PB) (MW 2500, $\bar{M}_w/\bar{M}_n = 1.13$) were purchased from Pressure Chemical Co. The polybutadiene sample was cleaned by dissolution in spectrophotometric quality cyclohexane, precipitation with reagent grade methanol, and drying under vacuum at room temperature for at least 4 days. (The dissolution and precipitation procedures were repeated severl times.) The polystyrene sample was used without further purification.

Polymer–polymer solutions were prepared by adding the desired weight of PB to a preweighed amount of PS in a fluorescence sample cell. A homogeneous solution was produced by stirring the mixed blend with a 2- × 2-mm magnetic stirring bar inside the sample cell; the blend was stirred at 90 °C for about 6 h. One run of the 60 wt % PS sample was stirred at 90 °C for about 16 h. The sample cell was a water-jacketed, 1-cm path length Uvonic cell with a water jacket which was connected to a temperature-controlled water bath. Sample temperatures were monitored by placing a copper–constantan thermocouple inside a water-jacketed cell (containing water in the sample compartment) identical with the cell containing the polymer blends. Temperature measurements were taken immediately before and after each sample run. Temperature variations during a run were within 0.5 °C.

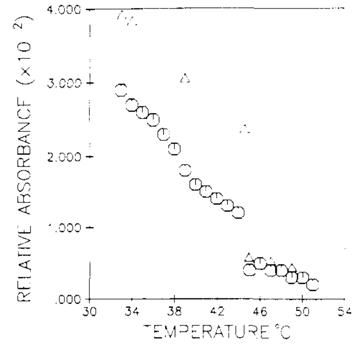

Figure 1. Variation of the relative optical density at 390 nm during cooling of a 60 wt % PS/PB blend: (○) as the temperature is swept down from 51 °C at approximately 0.29 °C min^{-1}; (△) by annealing at given temperatures for 2 h.

Cloud point measurements were made by taking homogeneous polymer blend samples in water-jacketed cells to temperatures about 15 °C above the expected cloud points. Sample cells were then cooled slowly until a sharp increase in optical density was observed. A cloud point was taken to be the temperature at which the optical density begins to increase sharply on a plot of optical density as a function of temperature. Two wavelengths (390 and 450 nm) were used for monitoring optical density.

Phase separation as a function of time monitored for 30 wt % and 60 wt % PS samples was performed by setting the temperatures of the water-jacketed cell at 40 and 47 °C, respectively, which are well above the cloud point temperatures based on the binodal curves obtained by optical density measurements. The 30 and 60 wt % PS samples were then quenched rapidly to 32 and 42 °C, respectively, which are well below the binodal curves (and may be below the spinodal curves). We estimate that approximate thermal equilibrium at the lower temperature was achieved about 10 s or slightly longer after the start of the quench. A second 60 wt % PS sample stirred at 90 °C for about 16 h was quenched rapidly from 47 to 32 °C. During phase separation, fluorescence intensities were monitored as a function of time. A Spex DM1B spectrofluorimeter with a single emission monochromator was used to monitor fluorescence. As this instrument is unable to measure simultaneously monomer (280 nm) and excimer intensities (332 nm), these intensities were monitored alternately at 30-s intervals. No attempt was made to correct for the slight contamination of the intensity at 280 nm by the excimer band. The excitation wavelength was 253.7 nm. Front-face optical excitation was employed to minimize self-absorption.

Results and Discussion

A. Cloud Point Measurement. An optical density method discussed by Vidakovic and Rondelez[32] was employed to obtain the phase diagram measurements for this study. The absorbances of PS/PB samples with 82, 70, 60, 45, 35, 20, and 10 wt % PS content were monitored at either 390 or 450 nm while the temperature of the originally miscible samples was continuously decreased. No evidence of significant absorption from either PS or PB was found at either 390 or 450 nm. Thus, as the cloud point temperature is approached from above, a sharp increase in absorbance can be observed, which is associated with the fact that the incident light gets scattered due to the phase separation.

Figure 1 shows a relative absorbance against temperature plot for a 60 wt % PS/PB blend sample. In order to study whether the cooling rate affects the optical density change and cloud point temperature, two cooling methods were used for this study. The first method consisted of controlling the cooling rate to about 0.29 °C min^{-1}. The second method was carried out by subsequently cooling the sample to given temperatures: 49, 47, 45, 44, 40, 34.8, and 33.5 °C. For each temperature, the sample was annealed for about 2 h and the absorbance measurements

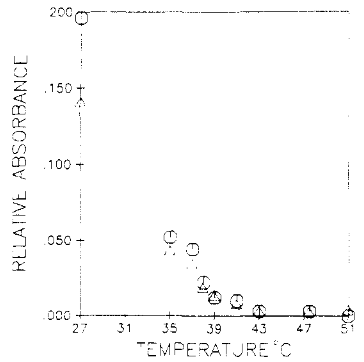

Figure 2. Variation of the relative optical density at 390 nm (○) and 450 nm (△) during cooling of a 45 wt % PS/PB blend as the temperature is swept down from 51 °C at approximately 0.29 °C min^{-1}.

were taken at the end of the 2-h period. The results in Figure 1 indicate that the coexistence curve temperature was independent of the cooling method. Both measurements show dramatic increases in optical density at 44 °C. A much more significant increase in absorbance at the cloud point temperature was observed in the case of the 2-h annealing time study. It is clear that the degree of phase separation taking place increases significantly with annealing time. Similar sharp increases in optical density were observed for all samples tested except the 10 wt % PS/PB blend, which is apparently miscible down to room temperature.

Figure 2 shows a plot of relative absorbance as a function of temperature for a 45 wt % PS/PB blend sample. Temperature was swept from 51 °C down to 27 °C at a rate of approximately 0.29 °C min^{-1}. In order to examine the effect of wavelength on the cloud point measurements, two wavelengths, 390 and 450 nm, were chosen for this study. The results show that the 390-nm wavelength leads to slightly higher changes in absorbance in the two-phase region. At 27 °C, the absorbance difference between these two measurements at 390 and 450 nm wavelengths becomes even more significant. These results indicate that 390-nm wavelength is more sensitive than the 450-nm wavelength in determining the cloud point temperature. However, the cloud point temperature measurements were very consistent between these two monitoring wavelengths studies, with both measurements showing a dramatic increase in optical density at 41 °C.

The coexistence curve obtained by optical density measurements described above for the polystyrene (826 MW)-polybutadiene (2500 MW) blend is given in Figure 3. These results are consistent with the cloud point curve obtained by Hill et al.[20] (1460 MW PS/2660 MW PB), which shows a maximum in the binodal curve at about 60 wt % PS. The cloud point curve determined by light-scattering techniques in Hill et al.'s[20] study shows a relatively large experimental uncertainty (>±1 °C). It appears that, in terms of determining phase diagrams, our optical density and temperature control methods have better precision than the techniques employed by Hill et al.[20] Our results also appear to be consistent with coexistence curves obtained by Russell et al.[21] with optical density methods in similar though not identical systems (2000 MW PS/1000 MW PB).

B. Study of Spinodal Decomposition Kinetics. 1. Excimer Fluorescence Results. In order to interpret the phase separation results, it is first necessary to characterize the concentration dependence of polystyrene fluorescence for hypothetically miscible solutions. The temperature at which we were interested in investigating the phase separation phenomena for a 30 wt % PS sample was 32 °C. On the basis of the phase diagram obtained (Figure 3), at 32 °C both 10 and 80 wt % PS samples are miscible. Thus, I_E/I_M as a function of PS volume fraction for the 10 and 80 wt % PS samples in miscible solution can be obtained directly at 32 °C. However, at 32 °C, 30, 45, and 60 wt % samples are in the phase-separated region. In order to obtain the ratio of excimer to monomer intensities, I_E/I_M, as a function of PS volume fraction for those three samples at 32 °C in hypothetically miscible states, an extrapolating method was utilized. Values of I_E/I_M measured at three miscible solution temperatures, 50, 42.5, and 36.5 °C, for a 30 wt % sample are shown in Figure 4. Values of I_E/I_M at 32 °C for a hypothetical 30 wt % PS sample which has not undergone phase separation are then obtained by extrapolating to 32 °C from these values. Similar plots and extrapolations for the 45 wt % PS and 60 wt % PS samples are also shown in Figure 4.

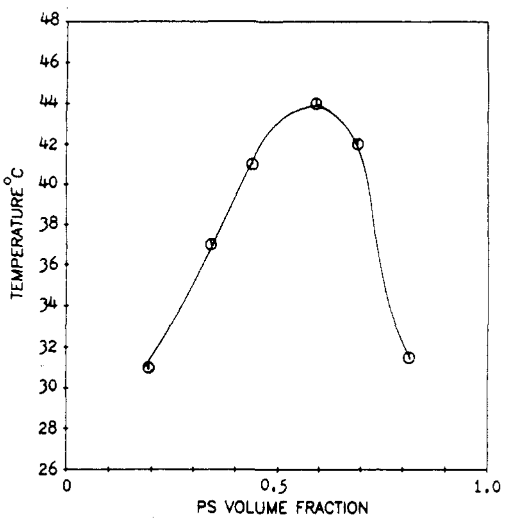

Figure 3. Experimental binodal curve for the 826 MW PS/2500 MW PB blend system obtained by optical density methods.

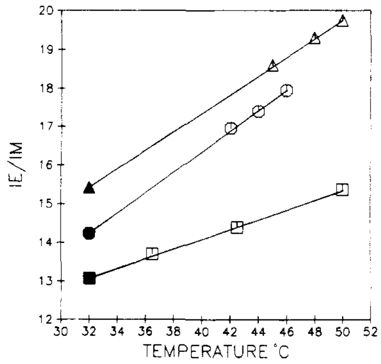

Figure 4. I_E/I_M as a function of temperature for PS/PB blends: (□) 30 wt % PS (miscible), (■) extrapolated to 32 °C; (○) 45 wt % PS (miscible), (●) extrapolated to 32 °C; (△) 60 wt % PS (miscible), (▲) extrapolated to 32 °C.

From the direct measurement of I_E/I_M at 32 °C for the 10 and 80 wt % PS samples and the values of I_E/I_M obtained by extrapolation as shown in Figure 4, the values of I_E/I_M as a function of PS volume fraction at 32 °C for hypothetical miscible samples were obtained and are given in Figure 5. These results show only a relatively small increase in I_E/I_M with increasing styrene content, less than a 60% increase in going from 10 to 80 wt % PS. This is consistent with previous studies[34,35] of the concentration dependence of I_E/I_M for polystyrene (from 800 to 1.8 × 10^6 MW) in solution.

Experimental results for the dependence of I_E/I_M on time of quenching at 32 °C for 30 wt % PS/PB blends are

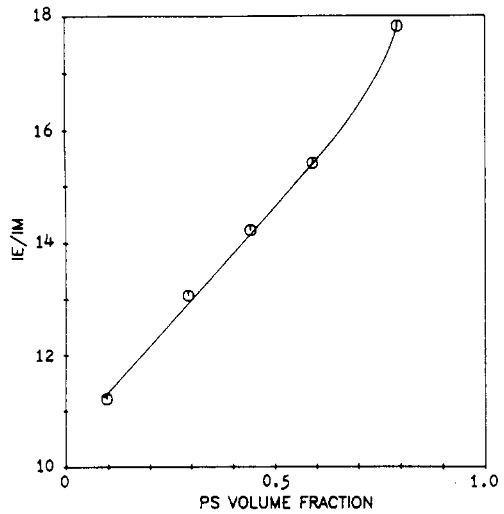

Figure 5. I_E/I_M as a function of PS volume fraction for hypothetical PS/PB miscible blends at 32 °C.

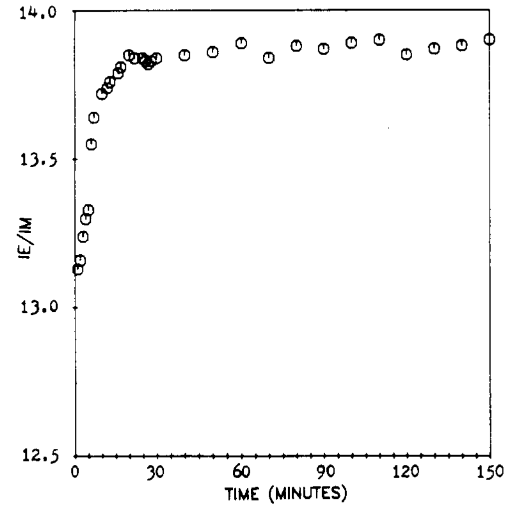

Figure 6. Effect of quenching time on I_E/I_M for a 30 wt % PS/PB blend at 32 °C. The quench temperature is 8 °C below the original temperature and about 2.5 °C below the coexistence curve.

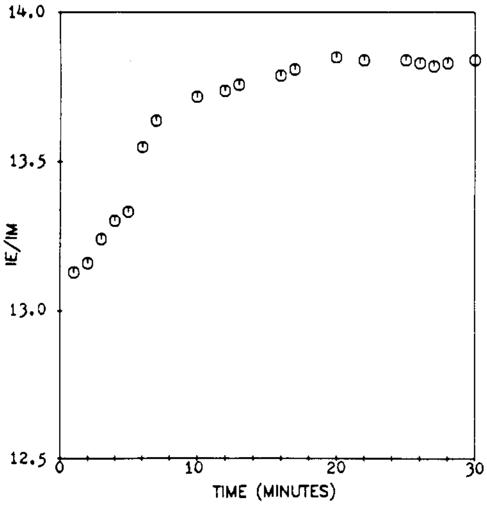

Figure 7. Effect of quenching time on I_E/I_M for a 30 wt % PS/PB blend at 32 °C during the first 30 min of quenching.

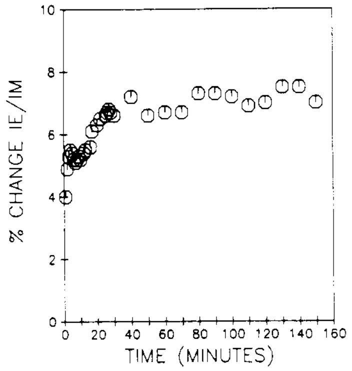

Figure 8. Effect of quenching time on I_E/I_M for a 60 wt % PS/PB blend at 42 °C. The quench temperature is 5 °C below the original temperature and about 1.5 °C below the coexistence curve. Note: this blend may have been less well mixed initially than the 30 wt % PS/PB blend, whose phase separation results are given in Figure 6.

given in Figure 6. The quenching depth is 8 °C below the original temperature (40 °C) and 2.5 °C below the coexistence curve. As the spectrofluorimeter was unable to monitor the monomer and excimer emission intensities simultaneously, the fluorescence intensities at 280 and 332 nm were monitored alternately during phase separation at 30-s intervals. The values of I_E/I_M in Figure 6 were obtained by interpolating the values of I_E and I_M from experimental data. The estimated error in I_E/I_M values in Figure 6 is represented by the size of the symbols.

I_E/I_M at $t = 0$ corresponds to I_E/I_M for a miscible 30 wt % PS/PB blend at 32 °C. From Figure 6, the value of this ratio is 13.07. Figure 6 shows that I_E/I_M increases rapidly over a short period of time and more slowly at longer times. After about 25 min, I_E/I_M is nearly constant within experimental error, and the system has reached equilibrium after about 60 min. Figure 7 shows the effect of quenching time on I_E/I_M for the 30 wt % PS/PB blend during the first 30 min of phase separation; it is clear that the major change in the I_E/I_M occurs in the first 10 min.

In Figure 8, we illustrate the effect of phase separation on I_E/I_M for a polymer blend sample which may not have been completely homogeneously mixed.

In this case, the sample was a 60 wt % 826 MW PS/40 wt % 2500 MW PB blend, and the quenching temperature was 42 °C. The quenching depth is 5 °C below the original temperature (47 °C) and about 1.5 °C below the coexistence curve. The results in Figure 8 indicate that the system came to equilibrium after about 30 min of quenching. However, at short times a small valley following a peak in percentage change of I_E/I_M is observed. This is possibly due to alternate depletion and enrichment of polystyrene in the region being measured or to thermal fluctuations. It may also be possible that the sample at $t = 0$ was slightly inhomogeneously mixed, which could result in the observed phase separation behavior. (In the study of the 60 wt % PS sample stirred at 90 °C for about 16 h, the resulting plot of I_E/I_M as a function of phase separation time is shaped similarly to the results for the 30 wt % PS sample; i.e., no peaks and valleys are evident. This indicates that our hypothesis of the effects of incomplete mixing on phase separation measurements is correct.) The homogeneous mixing of these viscous blends is a nontrivial and important requirement for studying phase separation by excimer fluorescence or other techniques. It should be noted that unlike the earlier phase separation studies on polystyrene solution systems[27] in which macroscopic phase separation occurred and precluded attempts to study spinodal decomposition, throughout the phase separation period investigated, there was no visual evidence for macroscopic phase separation taking place in either the 30 wt % PS blend or the 60 wt % PS blend.

It should also be noted that, contrary to the results of the studies[27] of phase separation in the polystyrene/methylcyclohexane system, the percentage changes of $I_E + I_M$ during phase separation are insignificant for our system. A slight monotonic increase in $I_E + I_M$ was observed for the 30 wt % PS sample. A small, fluctuating, but generally increasing trend in $I_E + I_M$ was observed over time for the 60% sample. This is in stark contrast with the results observed in the polystyrene/methylcyclohexane system[17] in which very large increases in overall intensity (60–100% increase) were observed during the first minute of phase separation.

2. Miscible Blend Behavior. In order to interpret the phase separation results, the two-phase model by Gelles and Frank,[8] which they applied to interpret I_E/I_M data for a high-polymer PS/PVME blend, was chosen for this study. This model makes use of information on miscible blends given by Fitzgibbon and Frank,[36] who showed that I_E/I_M may be represented by

$$I_E/I_M = (Q_E/Q_M)[D(1-M)/(1-D(1-M))] \tag{1}$$

where Q_E/Q_M is the ratio of intrinsic quantum yields for excimer and monomer fluorescence, M is the overall probability of radiative and nonradiative emission from the monomer state, $1 - M$ is the overall probability that an observed photon will lead to radiative or nonradiative emission from the excimer state, and D is the probability that an excimer state will lead to radiative or nonradiative emission from the excimer state instead of dissociating to excited monomer. It has been shown that the dissociation from excimer to excited monomer is negligibly small in polystyrene systems.[37,38] Thus, to a good approximation $D = 1$ in our case, and eq 1 can be simplified to

$$I_E/I_M = (Q_E/Q_M)[(1-M)/M] \tag{2}$$

Several approaches are available for determining Q_E/Q_M, and the one given by Fitzgibbon and Frank[36] was chosen for this study:

$$Q_E/Q_M = \phi_E(Q_0 - \phi_M) \tag{3}$$

where ϕ_E and ϕ_M are the excimer and monomer quantum yields, respectively, and Q_0 is the monomer quantum yield in the absence of excimer emission. Q_0 can be determined from the fluorescence quantum yield of a monomeric model compound of the polymer. In this study, ϕ_E and ϕ_M were obtained from the fluorescence intensities at 332 and 280 nm of the PS/PB blends while Q_0 was obtained from the fluorescence intensity at 280 nm of a corresponding ethylbenzene solution. By using eq 3, we found $Q_E/Q_M = 0.410 \pm 0.005$ for our system. It should be noted that this result was determined from intensities and not acutal quantum yields. Thus, this result may not reflect true quantum yield ratios.

Figure 9 shows the dependence of M on PS volume fraction for (hypothetical) miscible blends at 32 °C. In this study M was calculated by rearranging eq 2 to

$$M = ((I_E/I_M)(Q_M/Q_E) + 1)^{-1} \tag{4}$$

where experimental I_E/I_M values are obtained from Figure 6. Figure 9 shows that M varies only slightly nonlinearly with PS volume fraction from PS volume fraction = 0.1∼0.27 and varies nearly linearly with PS volume fraction at higher polystyrene content. This trend is similar to the results reported in previous studies of polystyrene solutions[27] or blends.[8] The decrease in M with increasing PS content may be due to increasing intermolecular interactions between polystyrene molecules, resulting in interpolymer energy migration and/or excimer formation.

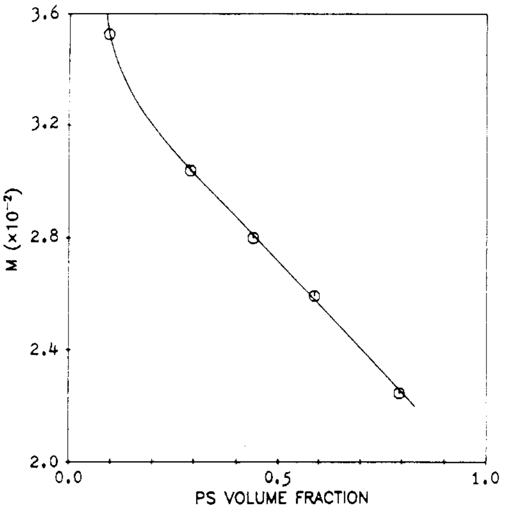

Figure 9. Dependence of M on PS volume fraction for (hypothetical) miscible blends at 32 °C.

3. Phase Separation Behavior. The two-phase model by Gelles and Frank[8] relates the experimental values of I_E/I_M obtained during phase separation to the composition of the PS-rich and PS-lean phases when a blend is undergoing spinodal decomposition. In order to comment on the applicability of the two-phase model to liquid polymer blends, a brief review of the model is necessary. In this two-phase model, two assumptions are made for simplifying the complex fluorescence phenomena associated with polymer blends undergoing phase separation. First, Gelles and Frank assumed that no energy migration occurs between the PS-rich and PS-lean phases. Second, they assumed that the composition within a phase is uniform (or equivalently that its fluorescence characteristics are the same as those of the average composition within a phase). With these two assumptions, the complicated two-phase system can be treated simply given that one can estimate the fraction of photons absorbed by each phase and understands how the photons absorbed in each phase undergo fluorescence.

In order to determine the fraction of photons absorbed by each phase, first the volume fraction of each phase must be known. The volume fraction of the PS-rich phase, V_R, is given by

$$V_R = (\phi_B - \phi_L)/(\phi_R - \phi_L) \tag{5}$$

where ϕ_B, ϕ_L, and ϕ_R are the polystyrene volume fractions in the bulk state prior to phase separation, in the PS-lean phase, and the PS-rich phase, respectively. The fraction of photons absorbed by PS chromophores in the rich phase, X_R, can then be given by

$$X_R = \frac{\phi_R V_R}{\phi_R V_R + \phi_L(1 - V_R)} \tag{6}$$

In the case of phase separation by a spinodal decomposition mechanism, V_R will remain constant. Therefore, if the phase diagram and the values of both ϕ_R and ϕ_L at equilibrium are known, then V_R and X_R can be obtained easily by using eq 2 and 3. When this information is applied to the simple two-phase model description by Gelles and Frank,[8] I_E/I_M for a phase-separated blend can be described by a ratio of the summation of excimer fluorescence from both phases to the summation of monomer fluorescence from both phases:

$$\frac{I_E}{I_M} = \frac{Q_E}{Q_M}\left[\frac{X_R(1 - M_R) + (1 - X_R)(1 - M_L)}{X_R M_R + (1 - X_R)M_L}\right] \tag{7}$$

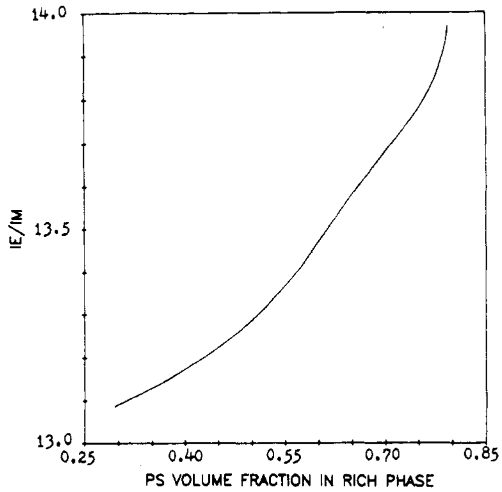

Figure 10. Dependence of I_E/I_M on the PS-rich phase volume fraction, ϕ_R, calculated from the two-phase model with $\phi_R = 0.291_3$.

where M_R and M_L are the values of M for the PS-rich and PS-lean phases, respectively.

Thus, for phase separation by spinodal decomposition (and using the fact that V_R is constant during spinodal decomposition), the two-phase model can be used to predict values of I_E/I_M as a function of ϕ_R. With that predication and the measured values of I_E/I_M obtained during phase separation, one can determine the composition of the PS-rich and PS-lean phases as a function of phase separation time.

In our study, we have no a priori conclusive evidence that phase separation in our blends occurs primarily by spinodal decomposition and not by nucleation. However, as we did observe the most substantial changes in I_E/I_M at very short phase separation times, it is not unreasonable to attempt to use Gelles and Frank's model[8] to interpret our data. As will be discussed later, application of their model shows our results to be consistent with the spinodal decomposition mechanism, especially in the fact that compositions of the phases formed during phase separation change continuously with time.

Figure 10 shows the dependence of I_E/I_M on ϕ_R for phase separation of the 30 wt % PS blend at 32 °C as calculated from eq 7. From comparison of Figures 6 and 10, values of ϕ_R and ϕ_L as functions of phase separation time can be determined, as shown in Table I. The results shown in Table I are entirely consistent with the spinodal decomposition mechanism of phase separation in which the composition of the phases generated varies continuously with time. It is interesting to note that according to our experimental fluorescence measurements the equilibrium value of ϕ_R is 0.793. This is in excellent agreement with the equilibrium value of ϕ_R, 0.80, obtained from the phase diagram given in Figure 3. Similarly, we achieve excellent agreement between equilibrium values of ϕ_L determined from Figure 3 ($\phi_L = 0.22$) and from our fluorescence measurements ($\phi_L = 0.221$). In the study of the 60 wt % PS sample stirred at 90 °C for about 16 h, our results also show excellent agreement between predicted values (based on the two-phase model) and experimental values of I_E/I_M, ϕ_R, and ϕ_L at equilibrium. Table I also reveals that on the basis of phase compositions almost 80% of the phase separation taking place in this system occurs in the first 7 min of phase separation. Although in Gelles and Frank's study[8] of PS/PVME phase separation it was unclear whether equilibrium was acutally achieved, they found that almost 88% of the phase separation achieved in their system after 180 min occurred in the first 7 min of phase separation, which is strikingly similar to the result in our study.

Table I
Rich and Lean Phase Composition during Spinodal Decomposition

time, min	I_E/I_M	ϕ_{rich}	ϕ_{lean}	$\phi_{rich} - \phi_{bulk}$
1	13.13	0.350	0.283	0.058
2	13.16	0.387	0.278	0.096
3	13.24	0.466	0.267	0.174
4	13.30	0.509	0.261	0.218
5	13.33	0.534	0.257	0.243
6	13.55	0.637	0.243	0.346
7	13.64	0.681	0.237	0.390
10	13.72	0.730	0.230	0.439
12	13.74	0.740	0.228	0.449
13	13.76	0.747	0.227	0.456
16	13.79	0.760	0.226	0.469
17	13.81	0.761	0.225	0.470
20	13.85	0.778	0.223	0.487
25	13.84	0.776	0.223	0.485
27	13.82	0.772	0.224	0.481
30	13.84	0.776	0.223	0.485
40	13.85	0.778	0.223	0.487
60	13.89	0.790	0.221	0.499
110	13.90	0.793	0.221	0.502
150	13.90	0.793	0.221	0.502

In contrast to the results of Gelles and Frank[8,9] for high-polymer PS/PVME blends, the changes in I_E/I_M obtained during phase separation of the oligomeric PS/PB blends are quite small. However, because measurement precision was very good in this study and far better than that obtained by Gelles and Frank (their problem with precision was due to difficulties inherent in obtaining reproducible film fluorescence and not to any deficiency in their procedure), the phase separation process in our system can be adequately monitored with fluorescence techniques. Nevertheless, owing to the small increase in I_E/I_M with phase separation, we must clearly state that the experiment should be performed carefully in order to obtain quantitative results.

4. Phase Separation Kinetics. In order to apply our results to study the kinetics of phase separation in our oligomeric PS/PB blends, we have applied the approach first used by Gelles and Frank,[8] which is briefly reviewed below. For the early stages of spinodal decomposition, the following equation was derived by Cahn:[33]

$$\frac{\partial \phi}{\partial t} = m\frac{\partial^2 G}{\partial \phi^2}\nabla^2\phi - 2mk\nabla^4\phi \tag{8}$$

where G is the Gibbs free energy of mixing, ϕ is the volume fraction (of polystyrene in this case), m is the diffusional mobility, and K is the gradient energy parameter. The solution to eq 8 is

$$\phi - \phi_0 = \sum_{\beta}\exp[R(\beta)t][A(\beta)\cos(\beta r) + B(\beta)\sin(\beta r)] \tag{9}$$

where $\beta = 2\pi/\lambda$ and λ are the wavelength of a concentration fluctuation, A and B are the Fourier coefficients, ϕ_0 is the initial homogeneous phase concentration (0.291_3 in this study), and r is the position variable. $R(\beta)$ is the amplitude growth rate of β and is given by

$$R(\beta) = -m[\partial^2 G/\partial\phi^2]\beta^2 - 2mk\beta^4 \tag{10}$$

Cahn[33] has shown that the growth rate shows a sharp maximum at $\beta = \beta_{max}$ where

$$\beta_{max} = \frac{1}{2}\left[-\frac{1}{k}\frac{\partial^2 G}{\partial \phi^2}\right]^{1/2} \tag{11}$$

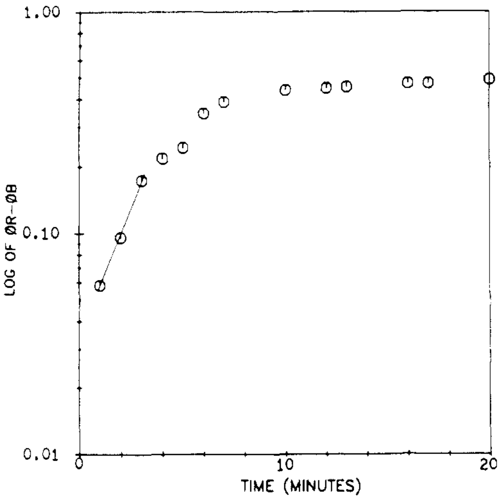

Figure 11. Short-time dependence of the PS-rich phase volume fraction with quenching time at 32 °C.

Generally, k is very small, and at very small values of β the second terms in eq 8 and 10 can be neglected. Thus, eq 8 can be written in a form analogous to a conventional diffusion expression:

$$d\phi/dt = D\nabla^2\phi \qquad (12)$$

where D is the Cahn–Hilliard diffusion coefficient, which equals $m\partial^2G/\partial\phi^2$. Further, D can be calculated from the growth rate at β_{max}, yielding

$$D = -2R(\beta_{max})/\beta_{max}{}^2 \qquad (13)$$

Gelles and Frank[8] made two assumptions to simplify eq 9 and obtain $R(\beta_{max})$ from ϕ_R. The first assumption is that the fluorescence of a phase-separated blend is sensitive to the average compositions of the two phases. The second assumption is that the concentration profile within each phase is spherically symmetric. With these assumptions, the second term in eq 9 vanishes and gives

$$\phi_R - \phi_B = A(\beta_{max})\exp[R(\beta_{max})t]\cos(\beta_{max}r) \qquad (14)$$

$\langle\phi_R - \phi_B\rangle$, $\phi_R - \phi_B$ averaged over the assumed spherical surface with radius $\pi/2\beta_{max}$, is given by

$$\langle\phi_R - \phi_B\rangle = \left[\int_0^{\pi/2\beta_{max}} (\phi_R - \phi_B)4\pi r^2\,dr\right] \Big/ \Big[\int_0^{\pi/2\beta_{max}} 4\pi r^2\,dr = 0.36A(\beta_{max})\exp[R(\beta_{max})t] \qquad (15)$$

Equation 15 indicates that if the phase separation kinetics are consistent with the early stages of spinodal decomposition then a plot of ln $(\phi_R - \phi_B)$ should be linear in time with the slope being equivalent to $R(\beta_{max})$.

Figure 11 is a plot of ln $(\phi_R - \phi_B)$ as a function of quenching time for the first 20 min of phase separation. It is clear that phase separation in this system is consistent with the spinodal decomposition model at short times, up to about 3 min and definitely no longer than 5 min. In our 60 wt % PS homogeneous blend, phase separation was observed to be consistent with the spinodal decomposition model for the first 3–4 minutes. These results compare favorably with data by Gelles and Frank[8] for high-polymer PS/PVME blends showing consistency of phase separation with the spinodal decomposition model during the first 2 min of phase separation.

The Cahn–Hilliard diffusion coefficient, D can be obtained by applying eq 11 and 13 to Figure 11 provided that λ_{max} is known. From the small-angle light-scattering study done by Hill et al.[20] on a similar PS/PB held system undergoing phase separation, λ_{max} has been determined to be of the order of 1 μm. From Figure 11, $R(\beta_{max}) = 0.238$ min^{-1}. D is then found to be of the order of 10^{-12} s^{-1} cm^2. With a similar analysis, D for the 60 wt % sample stirred at 90 °C for about 16 h was also found to be of the order of -10^{-12} s^{-1} cm^2. These results are in good agreement with the results of Hill et al.[20] on a similar PS/PB blend but is 1 order of magnitude smaller than that obtained by Gelles and Frank[8] for their high-polymer PS/PVME blends.

Summary

The binodal curve obtained by optical density methods was similar to those obtained by Hill et al.[20] and Russell et al.[21] for other oligomeric PS/PB blends. With the data from the binodal curves and estimation of the fluorescence characteritics of a "hypothetical blend" of the oligomeric PS and PB over the whole two-phase region, the Gelles–Frank model[8] was found to predict quantitatively I_E/I_M at equilibrium for blends which are "homogeneous" prior to phase separation. Furthermore, although the Gelles–Frank model apparently requires simultaneous monitoring of excimer and monomer fluorescence intensities, it was shown in this study that very good results may be obtained for certain systems even when the intensity at only one wavelength can be monitored at a given time. The continuous change in the composition of the phases generated during phase separation was consistent with the spinodal decomposition mechanism, and the kinetics of phase separation were observed to be consistent with Cahn's theory of spinodal decomposition[33] during early stages of phase separation. The Cahn–Hilliard diffusion coefficient, found to be of the order of -10^{-12} s^{-1} cm^2, was in good agreement with results obtained by Hill et al.[20] using light scattering for a similar PS/PB blend.

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Diffusion-Limited Phosphorescence Quenching Interactions in Polymer Solutions: Small Molecule–Small Molecule Interactions Interpreted by Free Volume Theory

Daniel H.-S. Yu[1a] and John M. Torkelson*[1a,b]

Department of Chemical Engineering and Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60201. *Received July 27, 1987; Revised Manuscript Received October 16, 1987*

ABSTRACT: Diffusion-limited interactions between benzil and anthracene were studied by phosphorescence quenching in polystyrene–cyclohexane, polystyrene–toluene, poly(methyl methacrylate)–toluene, and polybutadiene–cyclohexane solutions. Values of the bimolecular diffusion-limited quenching rate constant, k_q, were obtained by measuring benzil phosphorescence lifetime as a function of anthracene concentration and applying a Stern–Volmer analysis. Besides polymer species and solvent, k_q was measured as a function of polymer molecular weight and concentration, up to 560 g/L. k_q was found to be independent of polymer molecular weight in polystyrene–cyclohexane solutions and exhibited a slight molecular weight dependence in polystyrene–toluene solutions. The polymer concentration dependence of k_q in polystyrene–cyclohexane and polystyrene–toluene solutions was found to mimic the polymer concentration dependence of the solvent self-diffusion coefficient; this result is consistent with the notion that $k_q/k_{q0} \sim D_s/D_{s0}$ where D_s is the solvent self-diffusion coefficient and the subscript 0 indicates the value at zero polymer concentration. A very similar polymer concentration dependence of k_q was obtained in poly(methyl methacrylate)–toluene solutions. The Vrentas–Duda free volume theory for D_s was found to predict the polymer concentration dependence of k_q quantitatively for polystyrene–toluene and approximately for poly(methyl methacrylate)–toluene solutions; over the range of polymer concentrations studied in polystyrene–cyclohexane solutions, the agreement between the Vrentas–Duda theory and experimental measures of k_q appears to be less satisfactory. The Fujita–Doolittle theory can also be used to fit experimental measures of k_q in selected cases; however, it is possible to obtain unphysical results if the Fujita–Doolittle theory is applied over too wide a range in polymer concentration.

Introduction

Diffusion of solvent and probe molecules in polymer solutions is a subject which has received great study.[2-42] Several theories or models have been put forth to explain the polymer concentration dependence of small-molecule diffusional processes including those by Fujita,[2] Vrentas and Duda,[3-7,42] and others.[8] These theories or models relate the mobility of small molecules to the level of free volume present in the polymer system. Much effort has been expended by experimentalists over the last several decades to comment on the applicability of these free volume models; these studies have involved the use of a variety of techniques including forced Rayleigh scattering,[18-20] pulsed-gradient spin–echo NMR,[9-12,37,38,41] stress relaxation methods,[39,40] and "thin smear" methods.[28-30]

As yet there is not complete agreement on the applicability and utility of these theories or models to describe diffusional processes in polymer systems. Fujita[2] has indicated that the application of his theory should be limited to cases in which polymer volume fraction equals or exceeds 0.85. However, this has not precluded many investigators[11-13] from fitting their data to his theory even in dilute polymer solutions. The application and testing of Vrentas and Duda's theory has, by necessity, been limited due to the large number of parameters involved in their theory and the small number of systems[14,17] for which these parameters have been determined or estimated. Furthermore, the early form of their theory[3,4] basically restricted its use to temperatures exceeding the polymer's glass transition temperature, T_g (where T_g is for the solvent-free systems). A recent modification[14-16] allows application of this theory and associated parameters for room temperature studies of polystyrene–toluene, polystyrene–ethylbenzene, and poly(vinyl acetate)–methanol systems.

A process which is intimately related to the subject of small molecule diffusion in polymer solutions is diffusion-limited interactions or reactions of small molecules. Phosphorescence quenching is a particularly useful tool in obtaining information on diffusion-limited interactions in polymer solutions. Fluorescence quenching has been much more commonly investigated than phosphorescence

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* To whom correspondence should be addressed.

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