Macromolecules 1984, *17*, 1505–1512

Polystyrene–Methylcyclohexane Solutions Undergoing Phase Separation: A Study by Fluorescence Spectroscopy

John M. Torkelson*,† **and Matthew Tirrell**

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

Curtis W. Frank

Department of Chemical Engineering, Stanford University, Stanford, California 94305.
Received December 28, 1982

ABSTRACT: The phase separation of 17 500 molecular weight polystyrene (PS)/methylcyclohexane solutions has been studied by fluorescence spectroscopy. In contrast to a previous report, the sensitivity to phase separation of the ratio of excimer to monomer fluorescence intensity, I_E/I_M, was small, with a decrease observed in those regions occupied by the PS-lean phase after macroscopic phase layering and an increase observed in those regions occupied by the PS-rich phase after macroscopic phase layering. A polychromator was used to continuously monitor I_E and I_M during phase separation. The magnitude of the changes with time in I_E/I_M compares favorably with those predicted by the two-phase model developed for PS/poly(vinyl methyl ether) phase separation by Gelles and Frank. For samples of critical composition, I_E/I_M changed about 10–15% during phase separation for quenches of less than 0.7 K below the critical temperature, increasing steadily at long times in rich-phase regions while decreasing steadily at long times in lean-phase regions. At short times, I_E/I_M variously increased and decreased, and the overall fluorescence intensity varied widely, depending upon the region of the sample cell being monitored. A sharp increase in I_E/I_M with increasing PS content for PS volume fractions <0.04 was observed in miscible solutions near the critical temperature and may be due to coil contraction caused by the trend toward segregation or to increasing intermolecular interactions.

Introduction

There has been considerable interest in using fluorescence spectroscopy to examine polymers both in solution and in the solid state. Recent studies have included molecular weight and solvent effects,[1,2] interpenetration of polymers in solution,[3] cyclization dynamics,[4] sensitivity of fluorescence to polymerization phenomena,[5] segmental motion near T_g,[6] polymer blend morphology,[7,8] and the use of polymers in solar energy harvesting.[9]

Polymer solution behavior during phase separation is another topic of much current study. A number of studies have been performed with light scattering[10–15] and optical microscopy[11,16–18] in order to follow this separation as a function of time. Depending upon the composition, quench temperature, and rate of cooling, there are two mechanisms by which this phase separation may occur: nucleation and growth[19] or spinodal decomposition.[20] In the case of nucleation and growth, the separation is initiated in small regions, the nuclei, which proceed to grow in extent. The structure is clearly two phase, and except for regions near an interface, there is no variation in composition within a phase. In the case of spinodal decomposition, the composition departs slowly from the average, and, at least at small times, the entire composition range between the composition extremes exists within the sample.[20]

Many of the recent papers have concentrated on phase separation by spinodal decomposition; this is accomplished by quenching the solution near the critical composition. These studies have attempted to determine the characteristic dimensions of the spinodal decomposition pattern,[10,11,16] the effective growth rate of the critical fluctuations,[13–15] and values of the negative composition diffusivity.[14,15] These are rather difficult quantities to measure and, moreover, since most of the available measurement techniques are somewhat indirect, it will take some time to establish a high degree of confidence in the reported values. There has also been a significant amount of work to obtain very exactly the equilibrium thermodynamic properties of phase separation in polymer solutions. Critical points and full coexistence curves of polystyrene in solvents such as cyclohexane,[21–27] methyl acetate,[28] or methylcyclohexane[29,30] have been determined.

Recently, Chu and Kubota[31] suggested that excimer fluorescence could be used as a probe of spinodal decomposition during phase separation of polymer solutions. In their study the change in the fluorescence spectrum of polystyrene in methyl acetate occurring a number of minutes after quenching below the coexistence curve was determined. It was reported that phase separation was accompanied by a dramatic rise in excimer fluorescence. An analogous experiment has been carried out by Gelles and Frank[32] for a polystyrene–poly(vinyl methyl ether) blend. They were able to follow the time dependence of the rich- and lean-phase compositions during phase separation and found that Cahn's theory[20] of spinodal decomposition adequately described the early stages of phase separation.

The intent of this paper is to extend the study of phase separation behavior via fluorescence spectroscopy. In particular, we wish to comment on the experimental results of Chu and Kubota[31] and on the applicability to polymer solutions of the analytical model originally developed by Gelles and Frank[32] for solid polymer blends. The polystyrene–methylcyclohexane system was selected for this study because the coexistence curve has been determined[29] with a high degree of precision and because polystyrene samples of low polydispersity and with molecular weights matching those of the coexistence curve study are readily available.

Experimental Section

Spectroscopic-quality methylcyclohexane was used without further purification. The polystyrene samples were standard polystyrene (Pressure Chemical Co.) of nominal molecular weight 17 500 and with a polydispersity of 1.04. The polystyrene was purified by precipitation from toluene with methanol and was dried in a vacuum oven for 3 days at approximately 370 K.

Solutions were prepared by weighing polystyrene into 5-, 10-, and 25-mL volumetric flasks and diluting with solvent. Sufficient

---

† Present address: Departments of Chemical Engineering and Materials Science, Northwestern University, Evanston, IL 60201.

0024-9297/84/2217-1505$01.50/0

Table I
Critical Points of Polystyrene in Methylcyclohexane

MW	T_c, K	ϕ_c	$\bar{M}_w/\bar{M}_n$
17 300[30]	296.13	0.1669	<1.06
17 500[29]	296.32	0.169	<1.06

time (>24 h) was allowed for dissolution. With samples of high concentration, gentle heating (<323 K) was used to facilitate dissolution. Volume fractions were calculated by using 0.9240[21,33] as the specific volume of polystyrene.

The sample cell was a water-jacketed, 1-cm path length Suprasil cell. Water was heated or cooled by a water bath–refrigeration system. The sample temperature was 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 solution. Temperature measurements were taken immediately before and after sample runs. Temperature variations were within 0.05 and 0.1 K during a run. Samples were nitrogenated immediately prior to use by bubbling N_2 through the cell for about 5 min.

The spectrofluorimeter used for the steady-state measurements has been described earlier.[34] Front-face optical excitation was employed to minimize self-absorption; the excitation wavelength was 255 nm. Fluorescence intensities were measured at several wavelengths: 335 nm (excimer) and 283 nm (monomer) or 332 nm (excimer) and 280 nm (monomer). At $\lambda = 332$ or 335 nm the emission is essentially of pure excimer origin. At $\lambda = 280$ or 283 nm there is a slight overlap of excimer and monomer bands with the excimer band probably contributing to several percent of the emission;[35] the contribution at 280 nm is smaller than at 283 nm. No attempt was made to correct for the slight contamination of the monomer by the excimer band.

Continuous measurements of the fluorescence intensities at 280 and 332 nm during phase separation of polystyrene–methylcyclohexane solutions were made with a Spex 1802 polychromatic spectrophotometer that had the capability of monitoring four wavelengths simultaneously. Two Keithley 244 high-voltage supplies (providing 1100 V each), two Keithley 414S picoammeters, a filter, and a Fisher Recordall Series 5000 chart recorder were used in conjunction with the Spex polychromator.

Results

The coexistence curve for the system used in this study was determined by Dobashi, Nakata, and Kaneko.[29] They obtained the coexistence curve of 17 300 molecular weight polystyrene in methylcyclohexane by measuring the refractive index difference between pure methylcyclohexane and the two coexisting phases. Their results, given in Figure 1, were determined with a precision of ±0.03% in the volume fraction.

The sample used in the present study was 17 500 molecular weight polystyrene. Shinozaki et al.[30] have determined the critical temperature and composition of 17 500 molecular weight polystyrene in methylcyclohexane; a comparison between their results and the critical point determined by Dobashi et al.[29] for 17 300 molecular weight polystyrene is given in Table I. Clearly, there is little difference in the critical points of these two samples. For convenience we have assumed that the shape of the coexistence curve for our sample is identical with the curve given in Figure 1, but we have taken as the critical temperature the value by Shinozaki et al.,[30] $T_c = 296.32$ K.

The dependence of I_E/I_M on polymer volume fraction is given in Figure 2. These results were obtained at 297.6 K or 1.3 K above the upper critical solution temperature. Values of I_E/I_M are plotted for several wavelengths. In one case, I_E/I_M is obtained by measuring the intensities at 335 nm (excimer) and 283 nm (monomer); these are the same wavelengths used in our previous study[35] on the fluorescence of dilute and semidilute solutions of polystyrene in dichloroethane or cyclohexane. In the other case, I_E/I_M is obtained by measuring the intensities at 332 nm (excimer) and 280 nm (monomer); these are the same wavelengths whose intensities were monitored continuously by the polychromator in our measurements of the fluorescence during phase separation.

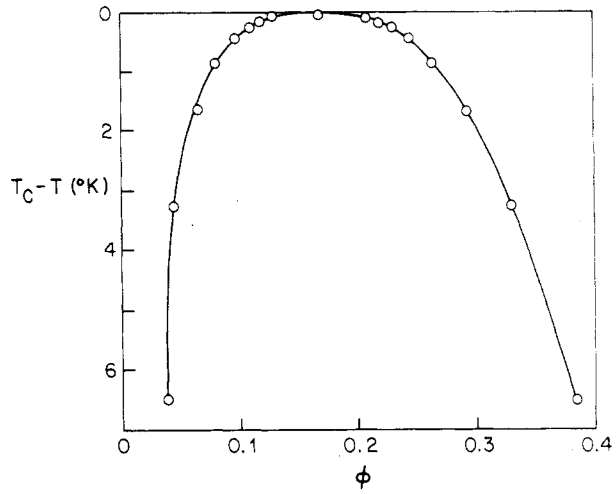

Figure 1. Coexistence curve of polystyrene–methylcyclohexane with molecular weight $\bar{M}_w = 17\,300$. ϕ is the volume fraction of polystyrene. Data are from ref 29.

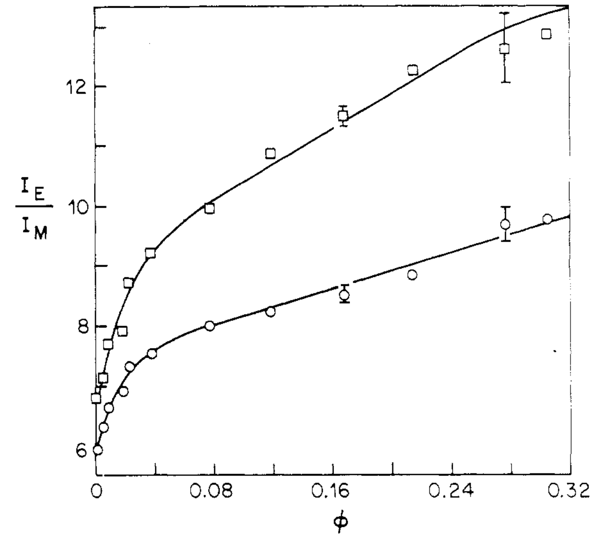

Figure 2. Variation of I_E/I_M with volume fraction of 17 500 molecular weight polystyrene, ϕ, in methylcyclohexane. (The error in measurement for $\phi < 0.12$ is the size of the symbols or smaller. The increasingly larger error in measurement at higher concentrations is due mainly to the difficulty in reproducibly nitrogenating very concentrated solutions.) (□) I_{332}/I_{280}; (○) I_{335}/I_{283}. $T = 297.6$ K.

Experimental results from the polychromator are given in Figure 3. The changes in I_{332}/I_{280} are shown as a function of time. (As the sample was within approximately 0.1 K of its final temperature at 30 s after initial quenching, this time was taken as $t = 0$ for the purposes of Figure 3a.)

Our experimental data show some very interesting effects of spatial inhomogeneity. The results in Figure 3a are for a sample with a quench depth of $T_c - T = 0.63 \pm 0.05$ K positioned such that the fluorescence is monitored from the bottom of the cell. This region is occupied by the rich phase after macroscopic phase layering occurs, which is manifested in the increase in I_E/I_M at long times. However, at shorter times there was a significant decline in I_E/I_M; this was before macroscopic phase layering. This suggests that there was either a depletion of polymer in the bottom of the cell or a large increase in the overall coil dimensions of the polymer.

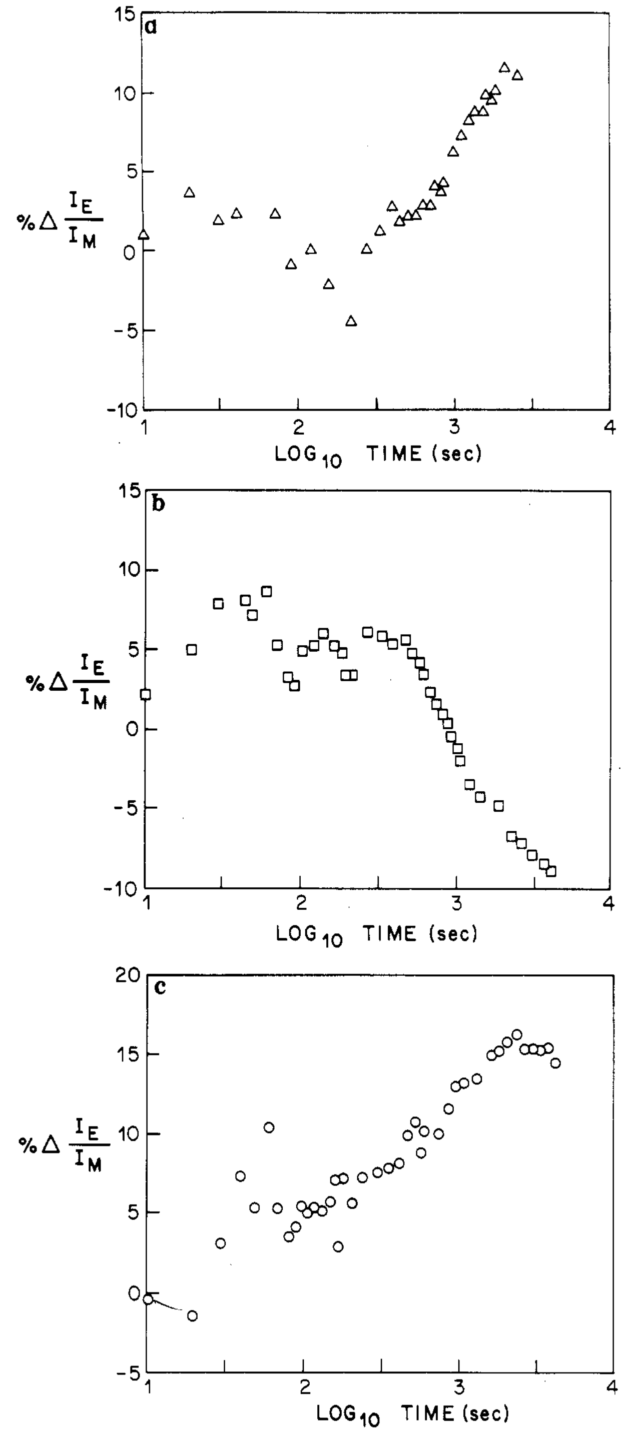

Figure 3. (a) Percentage change in I_{332}/I_{280} during phase separation as monitored by the polychromator. Fluorescence was monitored from the bottom of cell (rich phase after macroscopic phase layering occurs). $T_c - T = 0.63 \pm 0.05$ K. (b) Percentage change in I_{332}/I_{280} during phase separation as monitored by the polychromator. Fluorescence was monitored from slightly above where the interface forms upon macroscopic phase layering (lean phase near the interface). $T_c - T = 0.12 \pm 0.03$ K. (c) Percentage change in I_{332}/I_{280} during phase separation as monitored by the polychromator. Fluorescence was monitored near the region where the interface forms upon macroscopic phase layering (combination of rich and lean phase, more rich than lean, after macroscopic phase layering occurs). $T_c - T = 0.22 \pm 0.03$ K.

The results in Figure 3b are for a sample with a quench depth of $T_c - T = 0.12 \pm 0.03$ K which is positioned such that the fluorescence is monitored at a position slightly above where the interface forms upon macroscopic phase layering, i.e., in the lean phase near the interface. At long times a steady decrease in I_E/I_M is manifested. However, at short times several hills and valleys in I_E/I_M are observed, suggesting alternate depletion and enrichment of polymer or changes in overall coil size in the region being monitored. Similar phenomena for a quench depth of 0.22 ± 0.03 K are observed in Figure 3c, for which the fluorescence is monitored from a region near the middle of the sample cell, and as such the region consists of both lean and rich phases (more rich than lean) once macroscopic phase layering occurs.

While the overall sensitivity of fluorescence spectroscopy to phase separation of polystyrene solutions appears to be small, in fact it is very sensitive in determining when macroscopic phase separation becomes more significant than microscopic phase separation. Macroscopic phase separation may be observed visually by the development of an interface between rich and lean phases; in the particular studies done here, the interfaces formed between 1000 and 1500 s into the phase separation. However, fluorescence spectroscopy indicates that the macroscopic phase separation begins to dominate approximately 300 s into phase separation as evidenced by the monotonic nature of the change in I_E/I_M at long times.

Besides I_E/I_M, the fluorescence of the polystyrene in a sample undergoing phase separation also yields another type of information; this is the overall fluorescence intensity, $I_E + I_M$. In all three sample runs, there were significant changes in $I_E + I_M$ during the first minute of phase separation. Upon quenching the sample there may be expected to be a small increase in $I_E + I_M$ due to the slight decline in temperature (from just above to just below the coexistence curve). However, temperature studies on dilute solutions of polystyrene over the same temperature intervals indicate that the overall fluorescence intensity increases by less than 10% upon cooling.[36]

The most dramatic change in $I_E + I_M$ occurred for the run which monitored the lean-phase fluorescence upon macroscopic phase layering (Figure 3b). At 60 s after the cooling began, $I_E + I_M$ was 60% higher than before the cooling was started. At 120 s after initial quenching, $I_E + I_M$ was only 40% higher than before cooling began. For times greater than 300 s into the quench, there was a monotonic decline in $I_E + I_M$, and the overall fluorescence intensity approached its original value at long times.

Smaller changes in $I_E + I_M$ were observed in the other two runs. In the run where the fluorescence was monitored from the bottom of the cell (Figure 3a), $I_E + I_M$ decreased by about 25% in the first 4 min and increased nearly monotonically for times exceeding 13 min. In the run where the fluorescence was monitored near the middle of the cell (Figure 3c), there was a 38% increase in $I_E + I_M$ in the first 50 s followed by a slow decline. In contrast to the results obtained in the two other cases, there was no monotonic behavior in $I_E + I_M$ at longer times. This may be due to the fact that there was a combination of rich and lean phases being monitored in this case. Our results may indicate depletion of polymer near the bottom of the cell and enrichment of polymer higher in the cell during initial stages of phase separation.

Figure 4 shows the complete fluorescence spectrum of an air-equilibrated sample of critical composition before phase separation as well as the fluorescence of the rich phase and the lean phase at 45 and 50 min after quenching below the coexistence curve, respectively. Macroscopic phase layering had occurred a little more than 15 min into the quench as evidenced by the formation of an interface between the rich and lean phases. These results clearly show a small decrease in the lean-phase fluorescence intensity and an increase in the rich-phase fluorescence in-

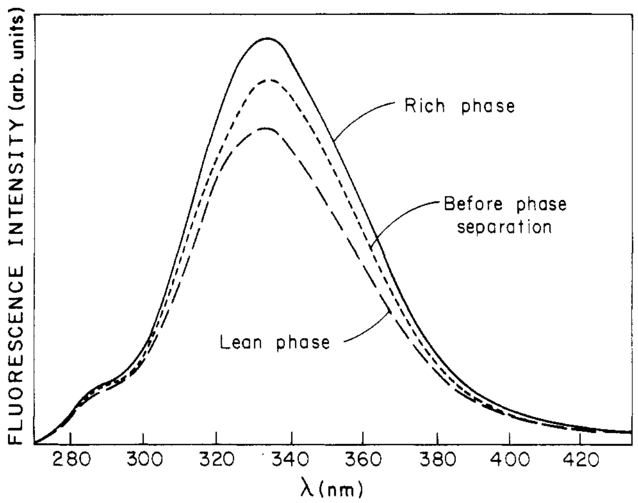

Figure 4. Fluorescence spectra of an air-equilibrated 17 500 molecular weight polystyrene/methylcyclohexane sample of critical composition: (- - -) sample before phase separation with $T - T_c = 1.0$ K; (—) rich phase 45 min after initial phase separation with $T_c - T = 0.4$ K; (— — —) lean phase 50 min after initial phase separation with $T_c - T = 0.4$ K. The width of the curves representing the spectra in the figure exceeds the noise of the measured fluorescence signal.

tensity. Furthermore, there is a slight decline in I_E/I_M for the lean phase while there is a slight increase in I_E/I_M for the rich phase.

As is clear from results presented earlier in this paper, there is only a relatively small overall sensitivity of fluorescence to phase separation in polystyrene solutions. However, Figure 4 provides a good comparison with the results recently published by Chu and Kubota.[31] They showed several spectra in support of the idea of using fluorescence as a molecular probe of spinodal decomposition in polymer solutions. Specifically, they studied polystyrene in methyl acetate. Their conclusion was that there was a very dramatic increase in excimer emission upon phase separation. They suggested that if the concentration dependence of this emission could be determined, it would be possible to obtain the concentrations of the rich- and lean-phase droplets. In view of our results, the spectra by Chu and Kubota[31] are anomalous. There is not a dramatic increase in excimer emission upon phase separation, and at best it would be difficult to determine accurately the rich- and lean-phase compositions from the changes in I_E/I_M that we have found.

There are several possible reasons for the spectra obtained by Chu and Kubota. First of all the solvent, methyl acetate, absorbs the excitation light and even absorbs some of the monomer emission. When phase separation occurs, the generation of alternating rich and lean phases results in a time-dependent penetration depth of the exciting radiation, and the absorbance of the exciting radiation by the solvent only further complicates the problem.

Secondly and more importantly, the geometry chosen, right-angle excitation, results in severe self-absorption of the monomer fluorescence and these effects would also be time dependent in a solution undergoing phase separation. We have shown in a recent study[35] of polystyrene in dilute and semidilute solutions in dichloroethane and cyclohexane that I_E/I_M is not very sensitive to concentration, in contrast to work by others.[37,38] It is possible that results of these earlier studies[37,38] had been adversely affected by self-absorption of fluorescence which led to an apparent increase in I_E/I_M. When such effects are accounted for, there is at most only a slow and smooth increase in I_E/I_M at higher concentrations. This relative insensitivity of I_E/I_M to polystyrene concentration suggests that Chu and Kubota's[31] spectra, in which there were dramatic increases in excimer fluorescence during phase separation, could have been affected by experimental artifacts such as self-absorption.

Thus, it may appear that I_E/I_M increases sharply during phase separation when in fact the monomer fluorescence is merely undergoing self-absorption by the polymer. We have repeated Chu and Kubota's use of the right-angle geometry with samples differing in concentration and, in agreement with our previous work,[35] have found increasing self-absorption of the monomer fluorescence with increasing polymer concentration.

Chu and Kubota[31] also observed a high level of fluorescence at ~450 nm which is absent in our results given in Figure 4. We have no explanation for their observation.

Discussion

A. Miscible Solution Behavior. In order to interpret the phase separation results, it is first necessary to characterize the dependence of the fluorescence upon polystyrene concentration for a miscible solution. Figure 2, which shows I_E/I_M as a function of polystyrene volume fraction in a solution at ~1.3 K above the upper critical solution temperature, leads to a very interesting comparison with previous results[35] on the fluorescence of polystyrene in dilute and semidilute solutions of cyclohexane and 1,2-dichloroethane. For $\phi > 0.04$, the present results agree well with those of the previous study. There is a slow and smooth increase in I_E/I_M with increasing polystyrene composition. In the earlier study, this increase was attributed to a possible combination of intermolecular excimer formation, and enhanced vicinal excimer formation as well as enhanced intramolecular and intermolecular energy migration with increasing concentration. These effects may also exist in the present system.

However, for $\phi < 0.04$, and especially for $\phi < 0.02$, the results in this study are in stark contrast with the previous work. In cyclohexane or dichloroethane, I_E/I_M was approximately constant at low polystyrene concentrations. In the present system of polystyrene–methylcyclohexane, there is a sharp decline in I_E/I_M with decreasing polystyrene content. This trend was the same in air-equilibrated and nitrogenated solutions and was observed to compositions as low as $\phi = 2.8 \times 10^{-4}$ (0.30 g/L). This effect may be caused by the fact that methylcyclohexane is a very poor solvent for polystyrene. The Θ-temperature of polystyrene in methylcyclohexane has been variously quoted as 340.3,[39] 341.1,[40] 343.1,[41] and 343.6 K[42,43] while in cyclohexane and dichloroethane the Θ-temperatures are 307.6[44] and 190 K,[45] respectively.

The very poor thermodynamic solvent quality of methylcyclohexane means that the polymer coils are contracted to an average size smaller than at the Θ-temperature. A study by small-angle neutron scattering[46] on a dilute solution of 29 000 molecular weight polystyrene in cyclohexane has found that in the Θ-regime the radius of gyration, R, is approximately constant whereas in the sub-Θ-regime ($T < 292$ K or $M^{1/2}(\Theta - T)/T \gtrsim 9$) $R \sim |(T - \Theta)/\Theta|^{-0.32\pm0.05}$. Below the Θ-regime the coils contract with decreasing temperature due to the trend toward segregation and the approach of phase separation at the coexistence curve.[47] Light scattering studies[48,49] have indicated that Θ-behavior is observed for $0 \leq M^{1/2}|(\Theta - T)/T| \lesssim 10$; for values > 10 there is a contraction of the coils but the asymptotic collapsed regime for which $R \sim |(T - \Theta)/T|^{-1/3}$ is not reached until $M^{1/2}(\Theta - T)/T \gtrsim 35$. Although the small-angle neutron scattering results appear to disagree with the light scattering studies as to the point at which the asymptotic collapsed regime is reached, it is clear that in our study, in which $M^{1/2}(\Theta - T)/T \geq 20$, the 17 500 molecular weight polystyrene coils are smaller than their Θ-dimensions. What happens at constant T in the sub-Θ-regime as concentration is increased is not certain at this time. The closer approach to incipient phase separation may cause a sharp increase in I_E/I_M due either to further coil contraction or to intermolecular interactions.

If in our system there is a decrease in the overall coil dimensions with increasing polymer concentration, there may be an accompanying increase in vicinal excimer formation as well as an increased efficiency in energy migration to excimer-forming sites. This more efficient energy migration is due to the looping of the contracted coil back on itself; under this condition energy may migrate not only between phenyl groups adjacent on the chain backbone but also across loops in the polymer (between phenyl groups on different portions of the chain). Energy migration down the backbone of the chain has been termed strictly one-dimensional while energy migration in a contracted coil with transfer across loops may be called nearly one-dimensional or quasi-one-dimensional.[50,51] The energy migration across loops would result in a significant increase in the number of distinct chromophores sampled; the number of sites sampled in n hops goes as $n^{1/2}$ for a strictly one-dimensional process while it goes as n for the first few steps after a hop between nonadjacent chromophores.

We note the strong similarity between the results in Figure 2 and the results of Gashgari and Frank[8,52] in their study of the dependence of I_E/I_M on the concentration of poly(2-vinylnaphthalene) (P2VN) guest polymer in poly(methyl methacrylate), poly(ethyl methacrylate), and poly(n-butyl methacrylate). They found that I_E/I_M increased in a slow, approximately linear manner for P2VN concentrations between 0.1 and 8.0 wt %. However, there was an abrupt rise in excimer fluorescence between 0 and 0.1 wt %. For all three polymer blends, there is a trend to thermodynamic segregation and incompatibility with increasing concentration. They postulated that the abrupt rise of I_E/I_M at low concentration was due to incipient phase separation leading to aggregation of guest polymer chains. With the results obtained in the present work, it seems that another possible explanation of the blend behavior might be a decrease in guest polymer coil size with increasing concentration because of the trend toward segregation. This explanation is also supported by temperature studies in miscible polystyrene/poly(vinyl methyl ether) blends;[53] it was postulated that there was a decrease in polystyrene coil dimensions with increasing temperature due to adverse thermodynamic interactions with the poly(vinyl methyl ether) host.

Although the possibility of using this fluorescence method for the study of coil contraction problems is intriguing, it is not necessary to have a quantitative understanding of the chain conformational behavior in order to study phase separation. The dependence of excimer fluorescence on concentration for a miscible solution may be used as a calibration curve for interpretation of the two-phase behavior. The appropriate modeling for the miscible system was done by Fitzgibbon and Frank,[54] who showed that the ratio of excimer-to-monomer fluorescence intensities may be given by

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

Q_E/Q_M is the ratio of excimer-to-monomer intrinsic fluorescence quantum yields, M is the overall probability

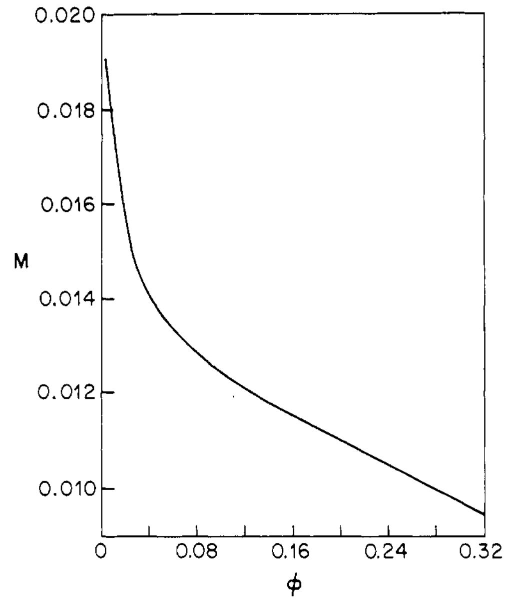

Figure 5. Dependence of the overall probability of radiative and nonradiative emission of monomer, M, on the volume fraction of 17 500 molecular weight polystyrene, ϕ, in methylcyclohexane. T = 297.6 K.

of radiative and nonradiative emission of monomer, and $1 - M$ is the overall probability that an absorbed photon results in radiative or nonradiative emission of excimer. D is the probability that an excimer state results in radiative or nonradiative emission from the excimer. In the case of polystyrene, where it has been shown that the dissociation from excimer to excited monomer is negligible,[55,56] $D = 1$ and eq 1 simplifies to

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

Several approaches are available for determining Q_E/Q_M. If Q_S and Q_L are the probabilities per photon absorbed by the system for monomer and excimer emission, respectively, then Q_S/Q_M (or Q_L/Q_E) is the probability that the excited monomer (or excimer) is responsible for loss of the photon from the system due to either a radiative or nonradiative process.[57] Because the absorbed photon must escape the system, it follows that[57]

$$\frac{Q_S}{Q_M} + \frac{Q_L}{Q_E} = 1 \tag{3}$$

Equation 3 is valid if excited monomer and excimer are the only two excited species that are interconvertible. Q_E and Q_M may be calculated as the intercepts of a plot of Q_L vs. Q_S.

A second approach has been given by Fitzgibbon and Frank.[54] In this case

$$\frac{Q_E}{Q_M} = \frac{\phi_E}{Q_0 - \phi_M} \tag{4}$$

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 may be determined from the fluorescence quantum yield of a monomeric model compound of the polymer.

Figure 5 shows the variation in the overall probability of monomer emission, M, with the polymer volume fraction, ϕ. M was calculated by using eq 2, the results given in Figure 2 (I_{332}/I_{280}), and the ratio of intrinsic quantum yields for excimer and monomer, Q_E/Q_M. For this system, we found $Q_E/Q_M = 0.134$ using eq 4. This result was determined from envelope intensities which were uncorrected for spectral response and which may not reflect true quantum yield ratios; i.e., ϕ_E and ϕ_M are represented by I_{332} and I_{280} of the polystyrene solution while Q_0 is represented by I_{280} of a corresponding ethylbenzene solution.

Figure 5 indicates that over our region of interest, i.e., $0.05 < \phi < 0.30$, M is essentially linear and varies over a small range from 0.095 to 0.135. As will be clear shortly, the linearity in M, when coupled with the small magnitude of change in its value with changes in ϕ, results in only a small sensitivity to phase separation of I_E/I_M.

B. Phase Separation Behavior. In their study of phase separation of polystyrene/poly(vinyl methyl ether) blends, Gelles and Frank[32] developed a simple model that relates the observed I_E/I_M to the compositions of the two phases. Since one of the objectives of the present study was to evaluate the effectiveness of this model for polymer solutions, we outline the essential features of the treatment.

In this model, it is assumed that energy migration does not occur between the two phases and that the composition within a phase is uniform. As a result, I_E/I_M may be described by a summation of the fluorescence from both phases:

$$\frac{I_E}{I_M} = \frac{Q_E}{Q_M}\left[\frac{X_R(1 - M_R) + (1 + X_R)(1 - M_L)}{X_R M_R + (1 - X_R)M_L}\right] \quad (5)$$

where X_R is the fraction of chromophores in the polymer-rich phase, and M_R and M_L are the probabilities of radiative or nonradiative monomer emission from an absorbed photon in the polymer-rich and -lean phases, respectively. M_R and M_L are obtained from a plot of M vs. polymer volume fraction; X_R is given by

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

where ϕ_R and ϕ_L are the rich- and lean-phase polymer volume fractions, respectively, and V_R is the volume fraction of the rich phase. In turn, V_R is given by

$$V_R = (\phi_B - \phi_L)/(\phi_R - \phi_L) \quad (7)$$

where ϕ_B is the bulk polymer volume fraction. If the phase separation is initiated by spinodal decomposition rather than nucleation, V_R will be constant and equal to its equilibrium value. Thus, V_R may be calculated if ϕ_B and the coexistence curve giving ϕ_L and ϕ_R are known.

This model may be used to predict I_E/I_M as a function of ϕ_R in the following manner. For a known ϕ_B and quench depth, V_R may be calculated from eq 7 and X_R from eq 6. With prior measurements of I_E/I_M as a function of ϕ at a temperature slightly above the critical temperature, a plot of M as a function of ϕ may be obtained from eq 2. This plot yields the values of M_R and M_L which, along with X_R, are substituted into eq 5. From this, predicted values of I_E/I_M as a function of ϕ_R are obtained. Comparisons between predicted and experimental values of I_E/I_M for phase separation allow one to calculate the composition of the phases as a function of time. The importance of this calculation is evident as Cahn[20] stated that to establish that the composition of the phases change continuously during phase separation is proof that the spinodal mechanism has occurred.

Figure 6 gives the trends in I_{332}/I_{280} during phase separation as predicted from the model. These trends were calculated by using eq 5 and are for samples that are originally of approximately critical composition, i.e., ϕ = 0.1667–0.169. Predictions are shown for a number of different quench depths; the quench depth strongly affects the equilibrium ϕ_L and ϕ_R. The model predicts only small and smooth increases in I_{332}/I_{280} for samples undergoing phase separation.

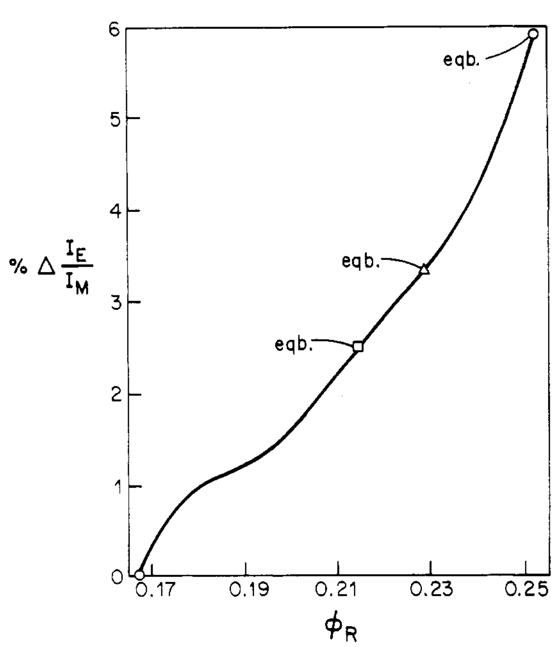

Figure 6. Changes in I_{332}/I_{280} predicted from the two-phase model. Values marked "eqb" are the equilibrium values for each quench depth and thus denote the maximum change in I_E/I_M that may be expected at those temperatures. (□) $T_c - T = 0.12$ K; (△) $T_c - T = 0.22$ K; (○) $T_c - T = 0.63$ K.

The magnitude of the predicted change in I_E/I_M is qualitatively consistent with what is observed. The fact, however, is that the changes in I_E/I_M predicted by the fluorescence model are much smaller for the polystyrene/methylcyclohexane solutions of this work than compared to the polystyrene/poly(vinyl methyl ether) blends. In the polymer blend study by Gelles and Frank,[32] I_E/I_M values were predicted to change from approximately 1 to 4.5, a 350% increase. Indeed, the experimental results showed a change in I_E/I_M from 1 to 3.5. Such gross changes allowed Gelles and Frank[32] to follow the change in composition of the phases during phase separation and further to determine the time frame over which Cahn's spinodal decomposition theory[20] was valid.

By contrast, with changes as small as shown in Figure 6, it is obvious that while it might be possible to follow changes in composition of the phases during liquid–liquid phase separation, it would be extremely difficult to determine the time frame over which spinodal decomposition is occurring. One positive point concerning the use of this model for following the phase separation in polymer solutions is that, even while the sensitivity is greatly reduced in comparison to blends, the solution fluorescence is much more reproducible than the blend fluorescence. Under proper circumstances, it may be possible to obtain quantitative information about phase separation in polymer solutions by using this model.

It appears that full utility of the two-phase model in studying phase separation in polystyrene systems may be limited to cases in which there is a substantial change in polymer composition of the phases during phase separation. Polystyrene–solvent systems exhibit a small sensitivity of fluorescence to phase separation because vicinal excimers are the dominant contributor to excimer fluorescence in polystyrene solutions with low polymer volume fractions ($\phi < 0.3$).[35] As vicinal excimers are very local in nature, longer range interactions such as the overlap or the entanglement present for $\phi < 0.3$ make at most only small contributions to changes in I_E/I_M with changing concentration. Consequently, in polystyrene–solvent phase separation in which $\phi_R - \phi_L < 0.20$–0.25 and $\phi_R \leq 0.3$, relatively small changes in I_E/I_M during phase separation would be expected. In contrast to the study by Chu and Kubota,[31] the present study confirms the small magnitude of changes in I_E/I_M during polystyrene–solvent phase separation. It would be desirable to have a system in which I_E/I_M (or M) changes greatly and in a nonlinear manner over the ϕ of interest. These conditions were met in the study of polystyrene/poly(vinyl methyl ether) phase separation by Gelles and Frank in which $\phi_R - \phi_L$ was as high as 0.75.[32] Even in their study, however, there were limitations. If the blends had undergone phase separation at a different temperature so that the equilibrium ϕ_R was less than 0.6, it would have been difficult to get the quantitative data on phase compositions that were obtained in their study. This is simply because I_E/I_M was not very sensitive to ϕ_R until $\phi_R > 0.6$.

The model itself is also somewhat restrictive in its assumptions that each phase is of distinct uniform composition and that energy migration does not occur between phases. While these assumptions make the model very attractive in its simplicity, they are not strictly correct on physical grounds. As for the assumption concerning phase composition, at the early stages of phase separation the entire composition range between the composition extremes exists within the sample, and the spread in composition increases with time.[20] The assumption concerning energy migration between phases implies that either sharp interfaces exist or energy migration is negligible. In fact, no details are known about the structure of the interface between the lean and rich phases, but there is much evidence to suggest that it is diffuse.[46] Consequently, quantitative results concerning phase composition during phase separation, even when easily calculable, should be considered as approximations.

It is obvious from Figure 3 that while the two-phase model developed for polymer blends is correct in predicting the magnitude of the changes in I_E/I_M during phase separation of polymer solutions, the model ignores the effects of macroscopic phase layering as well as the inhomogeneity of the phases once layering has occurred. In our case, with the onset of macroscopic phase layering, the polystyrene-rich phase lies under the lean phase. Even after a distinct interface has formed between the two layers, there is some preferential exchange of polymer between the phases, with the rich phase gaining polymer from the lean phase. Visual inspection of the sample cell also shows uneven levels of cloudiness within a phase, indicating that the concentration of polymer within a phase is a function of position.

Although the polystyrene–methylcyclohexane system yields only a relatively small overall sensitivity of fluorescence during phase separation and thereby severely limits the utility of the two-phase model by Gelles and Frank,[32] this small sensitivity of fluorescence may not be general to all polymer–solvent systems. In particular, poly(benzyl methacrylate) is a polymer that exhibits little excimer fluorescence in dilute solution but has an increasingly prominent excimer emission as concentration is increased.[3] Much of this concentration dependence is likely due to remote excimer formation; thus, poly(benzyl methacrylate) is one of a number of polymers that breaks Hirayama's "$n = 3$" rule.[58] Once the coexistence curve for a well-characterized sample of the polymer is obtained, it may be possible that its fluorescence would be fairly sensitive to phase separation.

Another possibility is the use of an "antenna"[9] polymer in which a small percentage of a fluorescence trap is copolymerized with another fluorescence species. Energy can migrate from the main type of chromophore to the trap, and the ratio of trap fluorescence to main chromophore fluorescence is highly dependent on the dimensionality of the energy migration. This leads to a fluorescence spectrum that is sensitive to concentration and consequently to phase separation.

Finally, due to the broad integration of the fluorescence signal, we are limited in our ability to study quantitatively the effects of position within the sample cell on I_E/I_M and $I_E + I_M$. However, it might be possible to obtain very interesting results if lasers were used as the excitation source. The source could be focused on a very small specific position in the cell, and such things as wall effects, the development of the macroscopic interface between phases, and the effect of height within the cell could be more carefully determined.

Summary

In contrast to the report by Chu and Kubota,[31] the sensitivity of fluorescence to the phase separation of polystyrene solutions is relatively small. Nevertheless, their work was very provocative and stimulating since we have shown here, by continuous monitoring of I_E and I_M, that macroscopic changes during phase separation may be followed by fluorescence spectroscopy. There is a steady increase in I_E/I_M at long times during development of the rich phase as well as an analogous decline in I_E/I_M at long times during development of the lean phase. The two-phase model developed for polymer blend phase separation by Gelles and Frank[32] correctly predicts the magnitude of the changes in I_E/I_M but does not account for such details as macroscopic phase layering and phase inhomogeneity present in polymer solution phase separation, which is the point of interest in this study. Fluorescence spectroscopy is also sensitive to miscible solution behavior near the coexistence curve; the dramatic increase in I_E/I_M with increasing polystyrene content at low polystyrene volume fractions may be attributed to the contraction of the polymer coils or increasing intermolecular interactions with increasing concentration.

Acknowledgment. We gratefully acknowledge partial support of this work by each of several programs: the Army Research Office (Contract DAAG 29-82-K-0019) (C.W.F.), the Research Corp. (C.W.F. and M.T.), the Alfred P. Sloan Foundation (M.T.), the Camille and Henry Dreyfus Foundation (M.T.), and the Graduate School of the University of Minnesota (J.M.T.). We also acknowledge valuable advice and assistance of Richard Gelles and William Tao and valuable discussions with Professor Sanford Lipsky. Finally, we express our sincere appreciation to Professor Ben Chu, who refereed the manuscript in an exceptionally thorough and fair fashion. His extensive remarks forced us to examine and strengthen the paper, for which he deserves credit and our thanks.

Registry No. Methylcyclohexane, 108-87-2; polystyrene (homopolymer), 9003-53-6.

References and Notes

(1) Ishii, T.; Handa, T.; Matsunaga, S. *Macromolecules* **1978**, *11*, 40.
(2) Torkelson, J. M.; Lipsky, S.; Tirrell, M. *Macromolecules* **1981**, *14*, 1601.
(3) Jachowicz, J.; Morawetz, H. *Macromolecules* **1982**, *15*, 828.
(4) Winnik, M. A.; Redpath, T.; Richards, D. H. *Macromolecules* **1980**, *13*, 328.
(5) Loutfy, R. O. *Macromolecules* **1981**, *14*, 270.
(6) Frank, C. W. *Macromolecules* **1975**, *8*, 305.

(7) Semerak, S. N.; Frank, C. W. *Macromolecules* **1981**, *14*, 443.
(8) Gashgari, M. A.; Frank, C. W. *Macromolecules* **1981**, *14*, 1558.
(9) Holden, D. A.; Rendall, W. A.; Guillet, J. E. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 11.
(10) van Aartsen, J. J.; Smolders, C. A. *Eur. Polym. J.* **1970**, *6*, 1105.
(11) Smolders, C. A.; van Aartsen, J. J.; Steinbergen, A. *Kolloid-Z. Z. Polym.* **1971**, *243*, 14.
(12) van Emmerik, P. T.; Smolders, C. A. *J. Polym. Sci., Part A-2* **1972**, *39*, 311.
(13) Feke, G. T.; Prins, W. *Macromolecules* **1974**, *7*, 527.
(14) Andreyeva, V. M.; Tager, A. A.; Tyukova, I. S.; Golenkova, L. F. *Polym. Sci. USSR (Engl. Transl.)* **1978**, *19*, 3005.
(15) Keuvahara, N.; Tachikawa, M.; Hamano, K.; Kenmochi, Y. *Phys. Rev. A* **1982**, *25*, 3449.
(16) van Aartsen, J. J. *Eur. Polym. J.* **1970**, *6*, 919.
(17) van Emmerik, P. T.; Smolders, C. A.; Geymeyer, W. *Eur. Polym. J.* **1973**, *9*, 309.
(18) Nojima, S.; Shiroshita, K.; Nose, T. *Polym. J.* **1982**, *14*, 289.
(19) Lauritzen, J. I.; Hoffman, J. D. *J. Res. Natl. Bur. Stand. Sect. A* **1960**, *64A*, 73.
(20) Cahn, J. W. *J. Chem. Phys.* **1965**, *42*, 118.
(21) Shultz, A. R.; Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 4760.
(22) Debye, P.; Coll, H.; Woermann, D. *J. Chem. Phys.* **1960**, *32*, 939.
(23) Debye, P.; Chu, B.; Woermann, D. *J. Chem. Phys.* **1962**, *36*, 1803.
(24) Scholte, Th. G. *J. Polym. Sci., Part A-2* **1971**, *9*, 1553.
(25) Kuwahara, N.; Nakata, M.; Kaneko, M. *Polymer* **1973**, *14*, 415.
(26) Nakata, M.; Kuwahara, N.; Kaneko, M. *J. Chem. Phys.* **1975**, *62*, 4278.
(27) Nakata, M.; Dobashi, T.; Kuwahara, N.; Kaneko, M.; Chu, B. *Phys. Rev. A* **1978**, *18*, 2683.
(28) Saeki, S.; Konno, S.; Kuwahara, N.; Nakata, M.; Kaneko, M. *Macromolecules* **1974**, *7*, 521.
(29) Dobashi, T.; Nakata, M.; Kaneko, M. *J. Chem. Phys.* **1980**, *72*, 6685.
(30) Shinozaki, K.; van Tan, T.; Saito, Y.; Nose, T. *Polymer* **1982**, *23*, 728.
(31) Chu, B.; Kubota, K. *Macromolecules* **1981**, *14*, 1837.
(32) Gelles, R.; Frank, C. W. *Macromolecules* **1982**, *15*, 1486.
(33) Fox, T. G., Jr.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.
(34) Frank, C. W.; Gashgari, M. A. *Macromolecules* **1979**, *12*, 163.
(35) Torkelson, J. M.; Lipsky, S.; Tirrell, M.; Tirrell, D. A. *Macromolecules* **1983**, *16*, 326.
(36) Torkelson, J. M., unpublished results.
(37) Nishihara, T.; Kaneko, M. *Makromol. Chem.* **1969**, *124*, 84.
(38) Roots, J.; Nyström, B. *Eur. Polym. J.* **1979**, *15*, 1127.
(39) Blandamer, M. J.; Fox, M. F.; Powell, E.; Stafford, J. W. *Makromol. Chem.* **1969**, *124*, 222.
(40) Blackmore, W. R.; Alexander, W. *Can. J. Chem.* **1961**, *39*, 1888.
(41) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953; p 615.
(42) Billmeyer, F. W.; Stockmayer, W. H. *J. Polym. Sci.* **1950**, *5*, 121.
(43) Altares, T.; Wyman, D. P.; Allen, V. R. *J. Polym. Sci., Part A-1* **1966**, *2*, 4533.
(44) Cragg, L. H.; Dimitru, T. E.; Simkens, J. E. *J. Am. Chem. Soc.* **1952**, *74*, 1977.
(45) Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook"; Wiley: New York, 1975.
(46) Nierlich, M.; Cotton, J. P.; Farnoux, B. *J. Chem. Phys.* **1978**, *69*, 1379.
(47) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(48) Perzynski, R.; Adam, M.; Delsanti, M. *J. Phys. (Paris)* **1982**, *43*, 129.
(49) Sun, S.-T.; Izumi, N.; Swislow, G.; Tanaka, T. *J. Chem. Phys.* **1980**, *73*, 5971.
(50) Wieting, R. D.; Fayer, M. D.; Dlott, D. D. *J. Chem. Phys.* **1978**, *69*, 1996.
(51) Dlott, D. D.; Fayer, M. D.; Wieting, R. D. *J. Chem. Phys.* **1978**, *69*, 2752.
(52) Frank, C. W.; Gashgari, M. A. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 387.
(53) Gelles, R.; Frank, C. W. *Macromolecules* **1982**, *15*, 741.
(54) Fitzgibbon, P. D.; Frank, C. W. *Macromolecules* **1982**, *15*, 733.
(55) Vala, M. T.; Haebig, J.; Rice, S. A. *J. Chem. Phys.* **1965**, *43*, 886.
(56) Ghiggino, K. P.; Wright, R. D.; Phillips, D. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1499.
(57) Hirayama, F.; Lipsky, S. *J. Chem. Phys.* **1969**, *51*, 1939.
(58) Hirayama, F. *J. Chem. Phys.* **1965**, *42*, 3163.

Optical Properties of (Hydroxypropyl)cellulose Liquid Crystals. Cholesteric Pitch and Polymer Concentration

Rita S. Werbowyj and Derek G. Gray*

Pulp and Paper Research Institute of Canada and Department of Chemistry,
McGill University, Montreal, Quebec, Canada H3A 2A7.

Received October 5, 1983

ABSTRACT: Liquid crystalline solutions of (2-hydroxypropyl)cellulose (HPC) in water, acetic acid, and methanol were examined by optical microscopy, refractometry, optical rotatory dispersion, and optical diffraction. Light transmission through thin and thick layers of the liquid crystalline phase was measured spectrophotometrically. The apparent absorption of light by thick layers and the angular variation in reflected wavelength were in accord with a polydomain structure. The cholesteric pitch was determined as a function of HPC concentration from measurement of the reflection band wavelength and the average refractive index for short-pitch samples and by optical microscopy or laser diffraction for long-pitch samples. The reciprocal pitch varied as the third power of the HPC concentration. The data also followed the concentration dependence predicted in a recent theory (H. Kimura, M. Hosino, and H. Nakano, *J. Phys. Soc. Jpn.*, **51**, 1584 (1982)).

A large number of cellulose derivatives form lyotropic and thermotropic liquid crystalline phases.[1] The polymeric component of these phases consists of a linear chain of β-(1–4)-linked anhydroglucose units with a wide variety of *nonmesogenic* substituents on the hydroxyl groups. The cellulose backbone is optically active and cellulosic mesophases show cholesteric properties. Lyotropic systems often reflect visible light,[2,3] indicating that the cholesteric pitch is of the magnitude of the wavelength of light, but much larger pitch values ($P \sim 1$–$10\ \mu\text{m}$) have been observed for some solutions of cellulose derivatives.[4,5] Cholesteric reflection has also been observed for solvent-free thermotropic cellulose derivatives at elevated[6] and room temperatures.[7]

In this paper, the relationships between the cholesteric pitch and some optical properties are summarized. The experimental variation in pitch with solvent concentration for (2-hydroxypropyl)cellulose (HPC) is presented. The results are compared with those for other cholesteric liquid crystalline materials and with theory.

Discussion of optical properties of cholesterics[8] is based on the theory of de Vries;[9] the interpretation of the fin-

0024-9297/84/2217-1512$01.50/0