Time-resolved excimer fluorescence studies as a probe of the coil collapse transition and phase separation in isotactic polystyrene/benzyl alcohol gel

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Excimer fluorescence decays and time-resolved emission spectra are reported for isotactic polystyrene/benzyl alcohol (iPS/BA) gels stored at 283 K for extended periods of time. Characterization of the collapse of the coil structure is reported from macroscopic shrinkage measurements and microscopic observations of phase separation. A red-shifted band identified in the excimer emission spectrum is due to a long-lived (29 ns) excimer structure corresponding to a polymer-rich phase. Instability over an extended period of time of the long-lived component in the fluorescence decay of iPS gel is discussed.

(Keywords: Excimer fluorescence; fluorescence decay; phase separation; coil collapse transition; polystyrene gel)

INTRODUCTION

Excimer fluorescence studies have been widely used for the characterization of specific molecular interactions and more recently in the study of miscibility of polymer blends[1–10]. Investigations of heterogeneous aromatic vinyl polymer systems have indicated the sensitivity of the fluorescence method for the detection of phase changes[2,8–10]. Interpretation of the fluorescence studies on polymer blends is often complicated by the existence of a wide range of excimer structures, which leads to ambiguity over the mechanism of electronic excitation transport leading to excimer emission. Excimer fluorescence measurements on isotactic polystyrene gels have been explored over an extended period of time in an attempt to determine the influence of the chain movement on the excimer fluorescence and hence interpret the conformation of the gel.

The conformational changes associated with the long-term approach of an isotactic polystyrene gel to thermodynamic equilibrium have been investigated both theoretically and experimentally[11–16]. The process involves a transition from a swollen state to a collapsed state similar to that found in an isolated chain[11–13] and polymer gel networks[14–18]. The collapse process depends on the conditions used in the preparation of the gel. Starting with the swollen gel in a good solvent, lowering the temperature leads to a decrease in the quality of the solvent. If the quenching process of the pre-gelled solution is comparatively fast, of the order of minutes, the elimination of solvent cannot occur and the polymer is frozen in a thermodynamically non-equilibrium state. The rate at which the conformational transition occurs will depend on the conditions of the gel. In a previous study, a mixture of isotactic polystyrene (iPS) with benzyl alcohol (BA), heated at 443 K, was quenched rapidly to 273 K[19,20]. Time-dependent measurements and time-resolved spectroscopic studies of the fluorescence of the excimer state allowed the changes with time of the long-lived red-shifted excimer to be quantified. Moreover, the long-lived red-shifted component was shown to be associated with a polymer-rich phase, which is generated on phase separation. Macroscopic shrinkage measurements and microscopic observations of the phase separation have also been shown to correlate with the collapse process in the iPS gel. In this paper, these studies are extended to the investigation of the long-time dependence of the excimer states in the metastable gel state.

EXPERIMENTAL

Materials

Isotactic polystyrene (iPS) of molecular weight 9.1×10^5 was obtained from Shell Chemicals (batch 439/12), and low-molecular-weight additives were removed by treatment with decane for 3 h under nitrogen, then rinsed with

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methanol and dried in vacuum for 10 h. The tacticity of the polymer was investigated using ^{1}H n.m.r. and the structure shown to be 95% isotactic. Benzyl alcohol (BA), obtained from Aldrich Chemical Company, was used as the solvent for preparation of the gel. The purity of the solvent was checked using fluorescence spectroscopy. A 10% w/w iPS/BA gel was prepared by heating the mixture at 443 K under nitrogen until a completely transparent solution was obtained, which was then quenched to 273 K on precooled quartz plates. The clear gel obtained by this method was 40 μm thick.

In order to ensure that the long-term effects observed were due to true changes in the gel structure and not a consequence of solvent vaporization, the samples were stored at 283 K in an environment saturated with solvent. The storage temperature was chosen to be sufficiently far below the glass transition temperature, T_g, that the changes occurring in the system are sufficiently slow for fluorescence decay measurements to be performed in pseudo-equilibrium[17,18].

Fluorescence decay and time-resolved spectroscopy

In previous studies[19], the photophysics of the iPS gel has been discussed in detail. The excimer emission was shown not to be affected by solvent emission or absorption, indicated by the fact that no influence of concentration on the excimer emission band was observed in the concentration range 5–15 wt%. In this study fluorescence decay and time-resolved spectroscopic measurements were performed using a photon-counting fluorometer. An excitation wavelength of 257 nm was used with a slit width of 10 nm for both the excitation and analysis beams. In order that sufficient intensity can be obtained for the time-resolved measurements it was necessary to increase the slit width of the excitation beam to 20 nm. The problem of elimination of the possible effects of scattered light was overcome by the introduction of a polarizer into the emission beam at the magic angle. The gel films were mounted at 45° to the excitation beam and all measurements were performed at room temperature.

Photophysical parameters (*Table 1*) were obtained by reconvolution analysis, which includes the leading edge of the decay traces and uses a non-linear least-squares fitting of the data in which χ^2 is used as the criterion for the goodness of the fit.

RESULTS AND DISCUSSION

The excimer emission of the gel is characteristic of the distribution of conformations adopted by the iPS in the gel state. This distribution depends upon the thermal history of the sample and the conditions used in casting[2,8,9]. In the previous paper, the short-time evolution of the excimer spectra was examined; in this study, the analysis of data collected over a period of 1656 h will be discussed. The steady-state spectra of the iPS/BA gel annealed at 283 K was measured and exhibits marked changes in both intensity and position with time (*Figure 1*). The monomer emission shows a marked decrease and there is a corresponding increase in the excimer emission and also a shift towards the red after a period of about 200 h. To obtain further information on the excimer states present in the system, fluorescence decay measurements were performed at 330 and 350 nm corresponding to the wavelengths of the observed maxima. Examples of the fluorescence decays obtained

Table 1 Fluorescence decay data for iPS/BA gel obtained at 298 K using an excitation wavelength of 257 nm and a slit width of 10 nm

Storage time (h)	λ_{EM} (nm)	τ_1 (ns)	τ_2 (ns)	B_1 (%)	B_2 (%)	χ^2
1	310	5.1 ± 0.2	16.3 ± 0.4	76.6	23.4	1.14
	320	5.3 ± 0.2	17.2 ± 0.4	63.5	36.5	1.05
	330	5.2 ± 0.2	16.9 ± 0.4	61.6	48.4	1.07
24	310	5.4 ± 0.3	18.3 ± 0.2	31.6	68.4	1.17
	320	5.9 ± 0.5	18.5 ± 0.2	19.8	80.2	1.15
	330	11.6 ± 1.3	19.6 ± 0.5	18.4	81.6	1.19
48	310	6.4 ± 0.9	18.6 ± 0.9	58.5	41.5	0.81
	320	7.3 ± 0.3	19.7 ± 0.2	34.1	66.0	1.12
	330	12.4 ± 0.2	20.6 ± 0.4	45.3	54.2	1.15
74	310	5.3 ± 0.2	18.3 ± 0.2	49.3	50.7	1.00
	320	6.3 ± 0.6	19.5 ± 0.2	20.7	79.3	1.12
	330	14.7 ± 1.3	21.9 ± 0.5	39.7	60.3	1.09
240	310	7.8 ± 0.7	18.8 ± 0.5	49.2	50.8	1.22
	320	8.1 ± 0.6	20.7 ± 0.3	22.8	77.2	1.30
	330	14.9 ± 2.1	22.8 ± 0.5	38.8	61.2	1.05
336	310	5.3 ± 0.3	18.8 ± 0.3	47.5	52.5	1.10
	320	5.6 ± 0.4	19.9 ± 0.2	19.7	80.3	1.22
	330	11.4 ± 0.3	21.4 ± 0.4	25.8	74.2	1.18
432	310	5.4 ± 0.2	18.2 ± 0.2	44.7	55.3	1.12
	320	6.1 ± 0.4	19.7 ± 0.2	28.6	71.4	1.21
	330	8.2 ± 0.9	21.1 ± 0.2	23.6	76.4	1.26
	340	13.3 ± 1.5	23.2 ± 0.4	37.5	62.5	1.07
	350	17.5 ± 1.2	27.7 ± 0.2	27.7	72.3	1.15
528	330	7.4 ± 0.7	21.2 ± 0.8	17.7	82.3	1.22
	350	18.5 ± 0.3	29.4 ± 0.5	80.1	19.9	1.23
552	330	7.3 ± 0.6	21.1 ± 0.2	20.8	79.1	1.14
	350	13.4 ± 0.3	23.2 ± 0.8	32.1	67.9	1.09
652	330	6.6 ± 0.3	20.9 ± 0.3	19.1	80.9	1.28
	350	11.7 ± 0.3	22.8 ± 0.3	25.4	74.6	1.23
744	330	7.4 ± 0.6	21.1 ± 0.2	20.2	79.8	1.19
	350	11.2 ± 0.4	21.8 ± 0.3	17.2	82.8	1.18
816	330	6.6 ± 0.8	20.7 ± 0.3	17.6	82.4	1.05
	350	9.6 ± 0.6	21.5 ± 0.2	13.4	86.6	1.08
864	330	7.9 ± 0.3	19.6 ± 0.3	17.9	82.1	1.20
	350	9.4 ± 0.4	20.2 ± 0.3	14.3	87.6	1.14
1656	330	4.9 ± 0.3	19.0 ± 0.2	18.3	81.7	1.31
	350	6.8 ± 0.9	19.9 ± 0.2	15.2	84.8	1.18

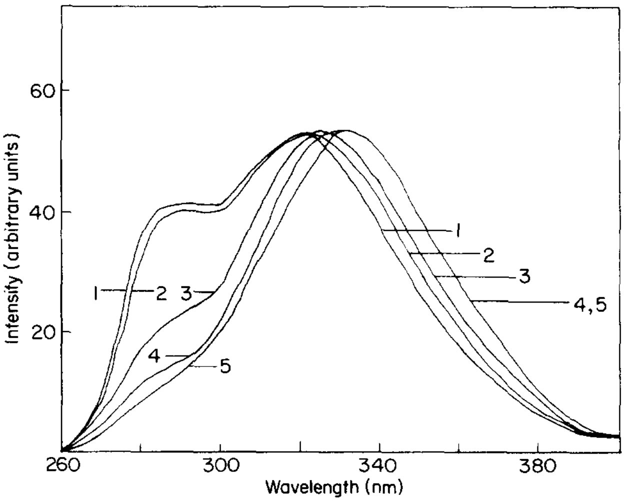

Figure 1 Steady-state fluorescence emission spectra of iPS/BA gel after storage for: (1) 1 h, (2) 240 h, (3) 432 h, (4) 744 h, (5) 864 h; χ_{EX} = 257 nm, slit width 5 nm

for 330 nm are presented in *Figure 2*. The decay curves for the fluorescence emission intensity $I(t)$ may be described in terms of two exponential functions by the equation:

$$I(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) \qquad (1)$$

where τ_1 and τ_2 are lifetimes of fluorescence emission of particular components, and B_1 and B_2 are the pre-exponential factors, corresponding to the separate components. Analysis of the data (*Figure 2*) yields decay parameters (*Table 1*); the values of B represent the percentage of each of the components contributing to the observed excimer emission. Initially the lifetime of the second component, the first component corresponding to monomer emission in the excimer region, is independent of wavelength, indicative of there being only one excimer structure present initially. The characteristic lifetime of 17 ns has a similar value to that reported in the literature for the excimer in high-molecular-weight polystyrene[21–25]. The precise value appears to depend on the solvent and probably reflects the effects of the local environment on the lifetime; values of 17 and 17.5 ns have been reported for dilute solutions in dichloroethane[22,24], in dichloromethane $\tau = 18.9$ ns[23], in toluene $\tau = 15.5$ ns[21] and in films $\tau = 22$ ns[25].

Changes in the lifetimes for the excimer emissions at 330 and 350 nm (*Figure 3*) and corresponding changes in the relative contributions indicated for the decay parameters (*Table 1*) are observed and are indicative of the collapse process[2,8,9]. After two or more days of storage the gel exhibits an emission spectrum that contains a quantifiable amount of a red-shifted excimer component with a longer lifetime. The presence of this component is reflected in an increase in the lifetime of the excimer emission at 350 nm. After storage for 432 h, approximately 30% of the excimer has changed into the long-lived component, and a separate emission band at 345 nm is detectable with a lifetime of between 27 and 29 ns after 528 h of storage. The lifetime of this component is very different from those reported previously for the excimer fluorescence in polystyrene[1,21–25]. From measurements of the time-resolved emission spectrum (*Figure 4*), it may be concluded that two phases exist in the system. The previous paper[20] has discussed the interpretation of the excimer fluorescence and suggests that the interfacial regions are responsible for the long-lived fluorescence emission.

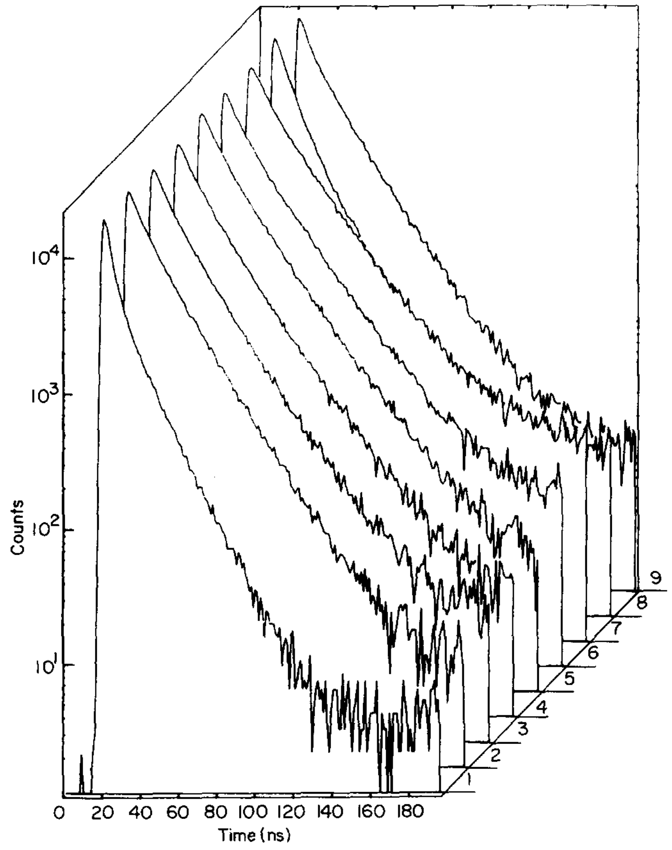

Figure 2 Fluorescence emission decays at 330 nm for iPS/BA gel after storage for: (1) 1 h, (2) 24 h, (3) 74 h, (4) 240 h, (5) 432 h, (6) 744 h (7) 816 h, (8) 846 h, (9) 1656 h

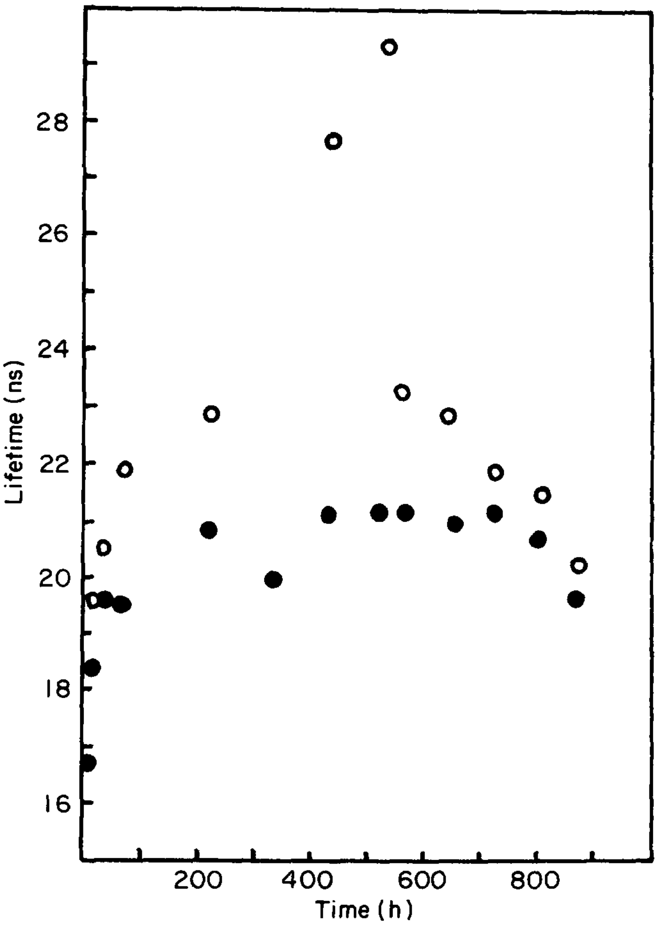

Figure 3 Dependence of lifetime of the excimer fluorescence emission at 330 nm (●) and at 350 nm (○) on storage time

A higher-energy excimer band with maximum at 325 nm was observed in the spectrum obtained with no delay and using a time interval of 9 ns (*Figure 4*, curve 1). The measurements were repeated using a time interval from 6 to 11 ns (*Figure 4*, curve 2) in order to differentiate it from monomer emission. The 'dotted' curve in *Figure 4* represents the steady-state fluorescence emission spectrum obtained from the gel immediately after it was formed. A close correspondence exists between this band and the short-lived component. The red-shifted excimer emission with maximum at about 345 nm is observed using a time window from 79 to 152 ns (curve 3). This excimer band can be ascribed to the long-lived component in the analysis of the fluorescence decay.

Time-resolved emission spectra observed after a period

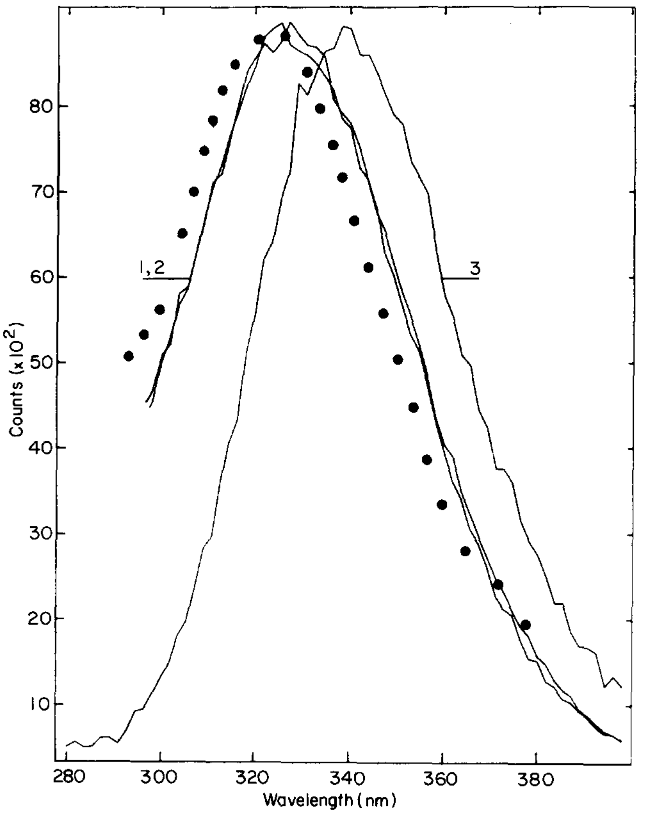

Figure 4 Time-resolved emission spectra for iPS/BA stored for 240 h, $\lambda_{EX} = 257$ nm, slit width 20 nm: (1) obtained with no delay following excitation with time interval 9 ns; (2) obtained with an interval from 6 to 11 ns; (3) obtained with an interval from 79 to 152 ns; 'dotted' curve is steady-state fluorescence emission spectrum for iPS/BA gel after preparation

of 744 h (*Figure 5*) indicate that the excimer emission obtained using a time interval of 8 ns is different from that observed in the initial gel (*Figure 4*, curves 1 and 2) and is shifted towards the red with a maximum at 330 nm. This spectral component (*Figure 5*, curves 1 and 2) agrees with the steady-state emission spectrum of the iPS gel stored for 1656 h, shown 'dotted'. The divergence of the spectrum observed at long wavelengths may be attributed to the low-energy component (*Figure 4*, curves 3 and 4). This band is in good agreement with the excimer emission band obtained from a 68% crystalline iPS gel sample and identified with excimer emission from the lamellae interfacial region[20]. The excimer component (*Figure 5*) obtained with a time interval 96 to 198 ns is in close agreement with the red-shifted excimer component with maximum emission at 345 nm, observed in the gel stored for 240 h (*Figure 4*). The excimer component observed previously with maxima at 325 nm (*Figure 4*, curves 1 and 2) is not observed in *Figure 5*, indicating that this excimer has been transformed into a new structure with emission at 345 and 330 nm as a result of the phase separation process. The excimer structure initially at 325 nm transforms at short time into an unstable excimer structure with emission at 345 nm; both are observed after 240 h of storage (*Figure 4*). At longer times, the red-shifted excimer at 345 nm is transformed into an excimer at 330 nm, leading to the spectrum of the gel after 1656 h corresponding to essentially a single-component spectrum. The excimer component having a maximum at 330 nm (*Figure 5*) is in good agreement with the steady-state emission spectrum of the sample having 68% crystallinity. Comparison of these observations with other data indicates that in the long-time limit the gel will achieve a stable helical structure to which the observed excimer emission at 330 nm may be ascribed.

The collapse transition of the polymer gel is accompanied by the generation of an excess of solvent. Measurements of the density of the gel after removal of the excess solvent which collects at its surface were performed. Using these data it was possible to calculate the relative concentration of the gel (*Figure 6*, curve a) and the number of solvent molecules per monomer unit (curve b).

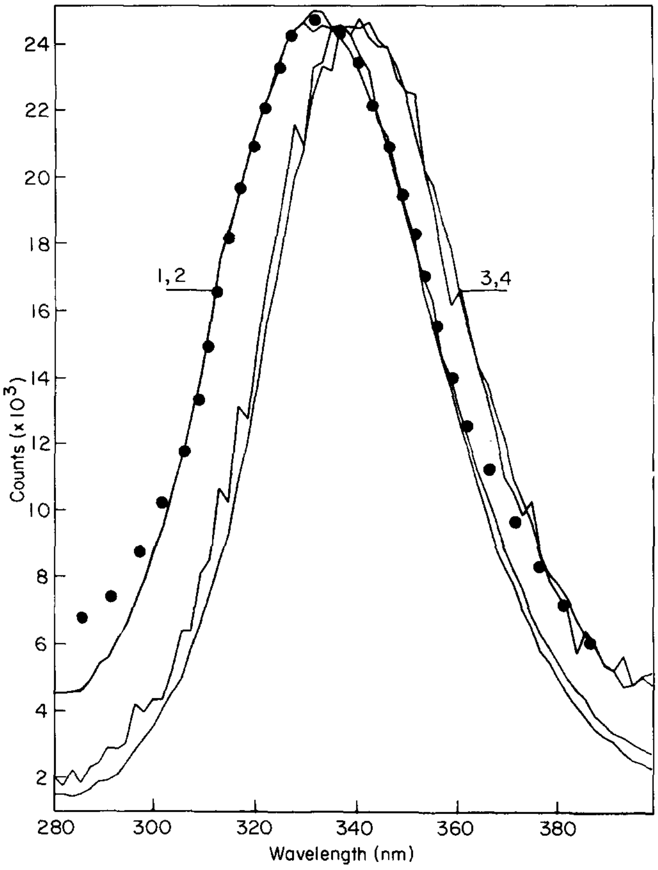

Figure 5 Time-resolved emission spectra for iPS/BA gel stored for 744 h: (1) with no delay following excitation and with time interval 8 ns; (2) with time interval 4 to 15 ns; (3) with time interval 79 to 101 ns; (4) time interval 96 to 198 ns; 'dotted' curve is steady-state fluorescence emission spectrum for iPS/BA stored for 1656 h

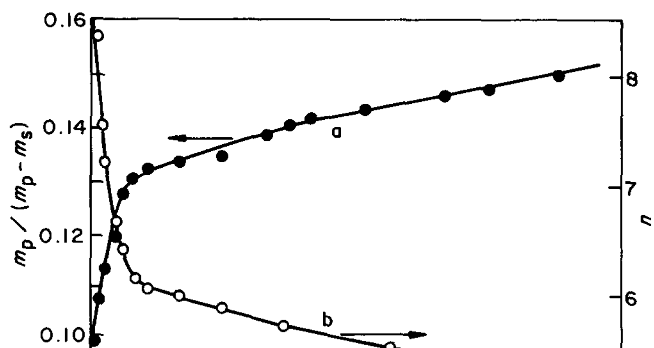

Figure 6 (a) Fraction of polymer in iPS/BA gel as a function of time of storage; (b) number of solvent molecules per monomer unit in the chain as a function of storage time

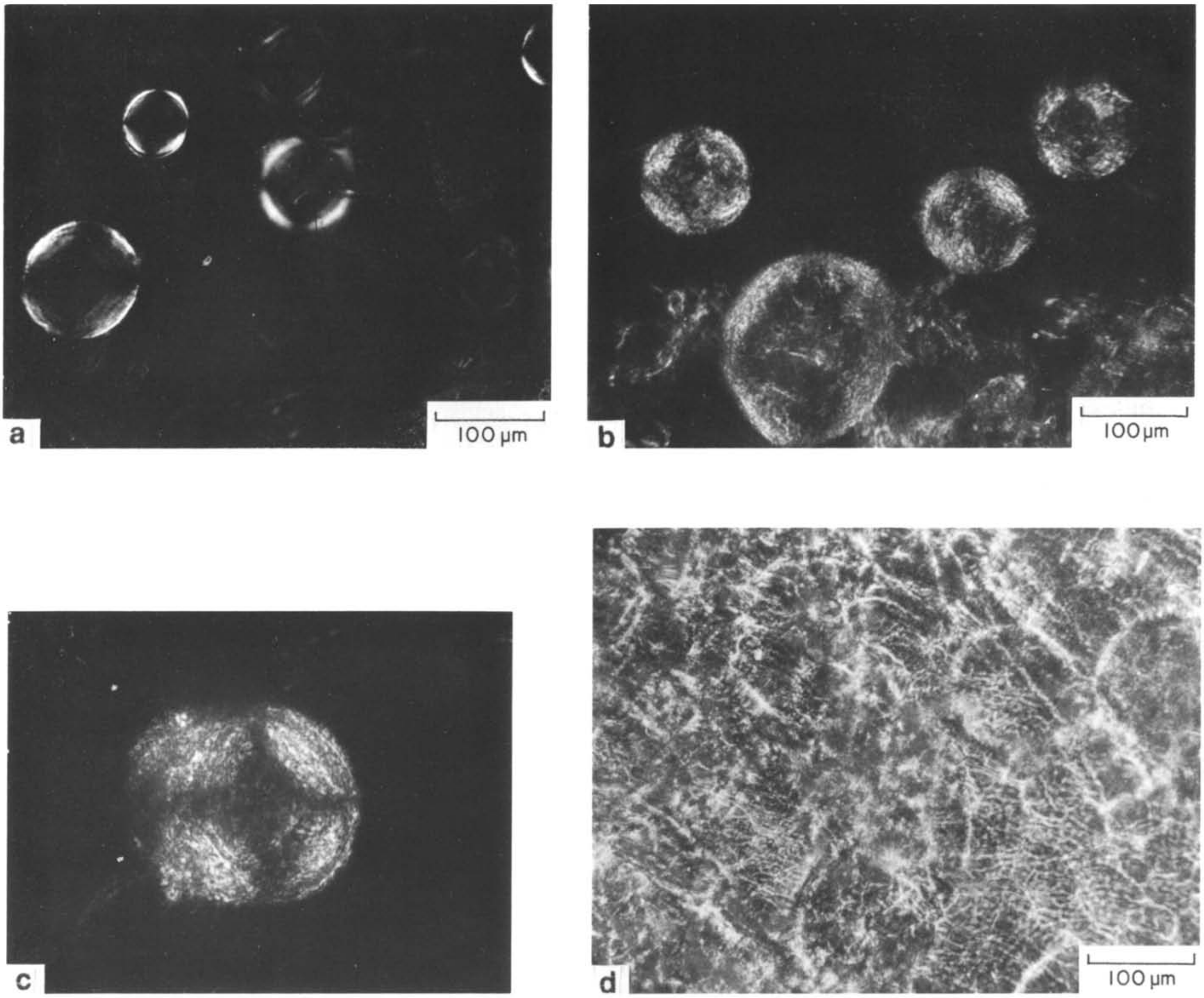

Figure 7 Microscopy of the phase-separated structures obtained at different storage times: (a) 240 h, (b) 744 h, (c) pin-cushion morphology, (d) sample (b) after solvent evaporation

Polarized microscopic observations were made of the structures observed after different periods of storage (*Figure 7*). After 240 h of storage, phase separation occurs leading to structures that have diameters ranging from 50 to 150 μm (*Figure 7a*). After periods of storage of longer than 744 h, a pin-cushion morphology is observed consistent with the generation of a crystalline phase (*Figures 7b* and *7c*). A sample, freeze dried to about 17% of solvent (*Figure 7d*) has a crystallinity of 7% as measured by differential scanning calorimetry, a value of 80.4 J g^{-1} being used for the enthalpy of fusion[26]. An endotherm peak was also observed at 494 K corresponding to melting of the crystalline three-fold helix conformation[17,20,27,28].

Transformation of the iPS gel from the extended to the three-fold helix conformation and correlation of the crystalline state with the emission at 330 nm with a lifetime of 21 ns has been discussed previously[19,20]. Analysis of the above data indicates that the intensity of the 330 nm excimer increases over the first 200 h of storage. The collapse process occurring during this period

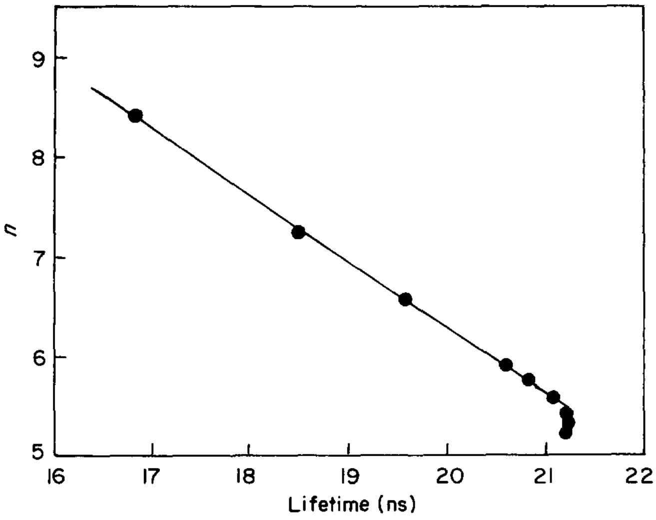

Figure 8 Correlation of the solvent elimination parameter, n (number of solvent molecules per monomer unit) with the excimer fluorescence lifetime as a function of storage time

is accompanied by the elimination of solvent from the gel (*Figure 6*). A correlation between the excimer fluorescence lifetime at 330 nm and the solvent expulsion parameter is observed (*Figure 8*). The observed increase in the lifetime of the excimer structure with the generation of the phase-separated structure supports the suggestion that the long-lived excimer emission is due to the interfacial region. For long periods of storage (*Figure 4*), the first excimer emission at 325 nm vanishes and a new excimer emission at 330 nm, corresponding to the crystalline component of iPS, is generated (*Figure 5*). The red-shifted fluorescence component at 345 nm is transformed into the excimer component associated with an interface formed between the original polymer-rich phase and some precrystallite structures of iPS, which has an emission at 330 nm.

CONCLUSIONS

The collapse transition in the iPS gel involves a loss of the initial excimer emission at 325 nm and the generation of an unstable excimer with emission at 345 nm, which finally transforms itself into an excimer with an emission at 330 nm. Confirmation of the existence of these three separate states and their interconversion was obtained by time-resolved analysis of the emission spectra. It should also be noted that no coarsening of the supermolecular structure was observed in the later stages of phase separation in these systems, which contain only 7% crystallinity. These results suggest that further growth of concentration fluctuations may be due to a micellar type of precrystallite formation in the polymer-rich phase. In order to understand correctly the densification process, it will be necessary to determine the phase separation diagram for these systems, and measurements are currently being carried out in this topic. Fluorescence measurements are able to provide further insight into the transformations occurring in the iPS gel and the nature of the conformations that are generated in the microstructures which occur at various times in the system.

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