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Photophysical Studies of Isotactic Polystyrene in Its Gel State

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ABSTRACT: Fluorescence emission spectra and decays are reported as a function of time and temperature for isotactic polystyrene in its gel state. A comparison of changes in the excimer spectra with variation of the conformational distribution based on Fourier transform infrared measurements indicates the existence of at least two different specific conformations in the gel state. The intensities of monomer and excimer emissions are time and temperature dependent and allow relaxation processes occurring within the gel matrix to be probed. Fluorescence decay and emission spectra investigated at various temperatures indicate that, below 310 K, the system is thermodynamically reversible, whereas above this temperature the system is irreversible. Three excimer structures were identified in the high-temperature spectra, and their time dependence is discussed in terms of changes in the polymer–solvent and conformational distribution of the gel structure. Time-resolved fluorescence spectra allow unambiguous identification of three separate excited-state complexes. Differences in the types of conformations that dominate in different conditions can be correlated with the form of the crystallites obtained from the gel. The time-dependent data are discussed in terms of a structured gel network capable of exhibiting conformational and reptational relaxation behavior.

Introduction

Quenching of a solution of isotactic polystyrene (iPS) in benzyl alcohol (BA) from a temperature of 443 to 273 K leads to the formation of a gel. X-ray diffraction, infrared spectroscopy, and electron and optical microscopy measurements[1-6] have been performed on the gel and indicate that the polymer chains exist in an extended conformation. The gel formed by cooling a solution of iPS in BA from a temperature of 403–343 K, at a maximum cooling rate of 25 K/min, leads to an unstable gel in which the chains adopt a 3-fold helical structure. A slow transformation is observed to occur to the more stable crystallizable lamellar form over a period of time. The gel structure can readily be converted into the closed helical form by heating to between 383 and 393 K; the rate at which this process occurs depends critically upon the solvent and precise conditions used.[3] The mechanisms whereby the interconversion process occurs are not fully understood and may either involve direct interconversion or, alternatively, a disruption of the extended helical structure prior to the formation of the closed helical form.

Conformational change in polystyrene has been studied by a wide range of techniques,[7-10] and measurements of the oligomers 2,4-diphenylpentane[8,9] and 2,4,6-triphenylheptane[8] have shown that, in the isotactic isomer, the tg and gt structures are more stable than the tt conformation, which has an energy 8 kJ/mol higher than the former and accounts for less than 5% of the molecules present. Barriers for conformational change of between 9 and 12 kJ/mol are observed for the oligomers. The most probable conformation in isotactic polystyrene has the tt and tg$^+$ or g$^-$t structures and leads to the generation of a helical form that favors the extended form. Ultrasonic measurements[7] on solutions of atactic polystyrene indicate that a helix–coil transition can be induced on heating above approximately 340 K, in agreement with earlier light-scattering measurements.[7]

This paper considers the photophysics of iPS/BA gels. The behavior of polystyrene[11-15] is dominated both in dilute solution and the solid state by inter- and intramolecular excimer formation. The latter is associated with the occurrence of a specific conformation of the polymer chain[16] in which two neighboring phenyl groups share the excited-state energy. Excimer formation has been investigated by a number of researchers interested in the conformational distribution, dynamics, and photodegradation of polystyrene[11-15] and can be explained in terms of a combination of local rotational isomeric and longer range diffusional motion of the whole chain.[18-20]

In the present study the iPS gel state has been investigated extensively in BA, which is not at first sight ideal for a photophysical study of iPS; however, it has the advantage of being both a good solvent for gel formation and transparent in the infrared regions where the characteristic absorptions of the helical conformation occur. Moreover, it has been found that BA plays an important role in determining the conformational structure of the gels.[1-6]

Experimental Section

Materials. Isotactic polystyrene (iPS) of molecular mass 9 $\times 10^6$ (M_w) and $M_w/M_n \sim 5.2$ was obtained from Shell Chemicals. The polymer was purified by refluxing in decane for 3 h under a blanket of nitrogen, then rinsed with methanol, and dried in vacuo for 10 h. This procedure removed low molecular mass fractions, stabilizer, and antioxidants that might interfere with interpretation of the fluorescence measurements. Absorption spectra were used to monitor the efficiency of this process. The tacticity was investigated by using a Bruker 270-MHz NMR, and the ^{1}H spectra indicated approximately 95% of the polymer has the isotactic structure. Gel liquid chromatographic grade benzyl alcohol obtained from the Aldrich Chemical Co. was used as the solvent; the purity was checked by using its absorption spectra.

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Table I
Fluorescence Decay Data for Benzyl Alcohol and Related Reference Systems, Measured with an Excitation Wavelength λ = 257 nm and a Band-pass of 20 nm

benzyl alcohol			benzyl alcohol (3×10^{-5} M) in hexane		
λ_{EM}/nm	τ/ns	χ^2	λ_{EM}/nm	τ/ns	χ^2
280	11.19 ± 0.06	1.09	285	6.68 ± 0.03	1.23
300	11.28 ± 0.05	1.19	300	6.60 ± 0.03	1.14
320	11.34 ± 0.05	1.05	320	6.62 ± 0.03	1.13
340	11.54 ± 0.05	1.24			
360	11.54 ± 0.05	1.24			

5% w/w Solution of Atactic Polystyrene in Benzyl Alcohol

λ_{EM}/nm	τ_1/ns	%	τ_2/ns	%	χ^2
280	5.31 ± 0.24	82.7	15.1 ± 1.2	17.3	1.26
300	5.78 ± 0.09	72.4	18.5 ± 0.3	27.6	1.03
320	5.89 ± 0.15	47.4	18.8 ± 0.2	52.6	1.02
340	6.81 ± 0.33	24.3	19.2 ± 0.2	75.7	1.07

Preparation of Solutions and Gels. Benzyl alcohol containing 5, 10, and 16% of iPS was heated to about 440 K under a blanket of nitrogen to exclude oxygen, and an optically clear solution was produced. Gel films were obtained by quenching a drop of the solution on precooled quartz plates held at 273 K. Optically clear films of 40 μm thickness, dry to touch, were obtained after equilibration for about 2 days at 273 K. This procedure was rigorously followed to ensure reproducibility of the data.

Steady-State Fluorescence Measurements. Fluorescence emission and excitation spectra of gels mounted on quartz plates were recorded by using a Shimadzu RF-540 spectra fluorometer. In all of the films studied, the emission spectra were invariant with excitation wavelength. An excitation wavelength of 257 nm and a slit width of 5 nm were used in all of the studies.

Fluorescence Decay and Time-Resolved Measurements. Fluorescence decay and time-resolved measurements were performed by using a single-photon timing technique already published.[21] A slit width of 10 nm for the excitation and analysis beams was used, and this was increased to 20 nm for the time-resolved excitation measurements. The problem of scattered light was minimized by introduction of a polarizer into the emission beam, and the films were mounted at 45° to the excitation beam. Measurements were performed at room temperature (298 K). Approximately 10^4 counts were required in order to obtain accurate lifetimes and intensities by reconvolution analysis and include data from the rising edge of the peak. Data analysis was performed by using the IBH software package incorporating nonlinear least squares on a PDP 11/73 microcomputer. The value of χ^2 was used as the test of the goodness of fit,[22] and values of 1.2 or lower were interpreted as indicating the appropriateness of the kinetic model.

Fourier Transform Infrared Measurements. A Nicolet FFT 60 spectrometer fitted with a thermostated cell, allowed investigation of the temperature and time dependence of the conformational structure of the iPS gel and involved subtraction of solvent from solution spectra.

Results and Discussion

Photophysics of Benzyl Alcohol. Benzyl alcohol is capable of absorbing light between 210 and 240 nm and fluorescing between 265 and 310 nm and therefore has the potential of transferring energy to polystyrene. Measurements of the fluorescence lifetime performed on BA and a solution in hexane (Table I) indicate a single-exponential decay invariant with wavelength. However, a small amount of solvent emission at 350 nm could interfere with the fluorescence of the iPS gel. A solution of atactic polystyrene was investigated to explore the possibility of interference effects, and it was found that the absorption and emission spectra and lifetimes were identical with those published previously[11-15] for solutions of nonabsorbing solvents (Table I).

Diluting BA with hexane lowers the viscosity and consequently the monomer lifetime. The solution of atactic polystyrene exhibits a two-component lifetime spectra, the shortest component being close to that for BA in hexane, and it is impossible to differentiate between solvent and polymer monomer emission. The second component has a lifetime comparable to that for excimer emission in polystyrene.[11-20]

Steady-State Fluorescence Emission of Benzyl Alcohol Solutions. Both solvent and polymer are capable of excimer formation, and this process can be described by the scheme due to Birks[11,23] for polystyrene

$$\begin{tikzcd} M^* + M \arrow[r, shift left, "k_{MD}"] \arrow[d] & (M + M)^* \arrow[l, shift left, "k_{DM}"] \arrow[d] \\ k_{FM} + k_{IM} & k_{FD} + k_{ID} \end{tikzcd}$$

where k_{FM} and k_{IM} are the rate constants of fluorescence emission and nonradiative energy decay of excited monomer chromophores and k_{FD} and k_{ID} are the rate constants for the fluorescence and nonradiative decay of the excimer. In the gel allowance must be made for the role of solvent and a more complex scheme is possible.

(i) Polymer

$$\begin{tikzcd} M^* + M \arrow[r, shift left, "k_{MD}"] \arrow[d] & (M + M)^* \arrow[l, shift left, "k_{DM}"] \arrow[d] \\ k_{FM} + k_{IM} & k_{FD} + k_{DI} \end{tikzcd}$$

(ii) Solvent

$$\begin{tikzcd} BA^* + BA \arrow[r, shift left, "k_{MD}"] \arrow[d] & (BA + BA)^* \arrow[l, shift left, "k_{DM}"] \arrow[d] \\ k_{FM} + k_{IM} & k_{FD} + k_{IM} \end{tikzcd}$$

(iii) Polymer–Solvent

$$\begin{tikzcd} M^* + BA \arrow[r, shift left, "k_{MD}"] \arrow[d] & (M + BA)^* \arrow[l, shift left, "k_{DM}"] \arrow[d] \\ k_{FM} + k_{IM} & k_{FD} + k_{IM} \end{tikzcd}$$

The excimer formed in i may be either an intra or inter excimer, and exiplex iii could involve a solvent molecule sandwiched between two monomer units. Observation of a single lifetime for the solvent (Table I) suggests that scheme ii can be neglected. The above scheme does, however, allow the excimer and exiplex emissions (i and iii) (J_E) to be related to the combined monomer (J_M) emission. In the iPS/BA gel there is a small overlap of the monomer and excimer bands requiring a correction of approximately 5% to the data. The effects of excimer on the monomer emission were modeled by using the fluorescence spectra of atactic polystyrene and ethylbenzene. Excimer fluorescence in polystyrene has been shown to reflect the conformational distribution of the system.[4-15]

The emission spectrum of the iPS gel varies reversibly with temperature in the region 273–306 K (Figure 1), the excimer emission intensity being constant while the monomer emission intensity increases with increasing temperature. Reversibility of the spectra indicates that the system is in thermodynamic equilibrium. X-ray, infrared, and optical studies of the morphology of the gel[1] indicate

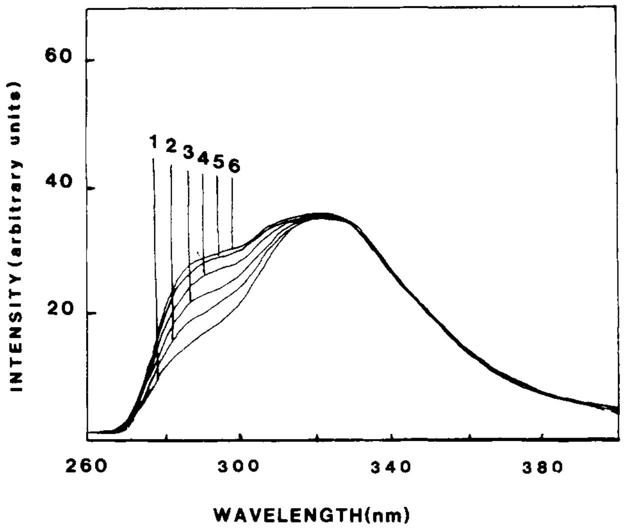

Figure 1. Fluorescence emission spectra of 5% w/w iPS/benzyl alcohol gel at 273, 277, 285, 289, 295, and 306 K (1–6, respectively).

that it is stable, consistent with reversibility of the emission spectra.

Above 306 K, the intensities of both the monomer (J_M = 285 nm) and excimer (J_E = 330 nm) emission are temperature dependent (Figure 2) and indicate that a nonradiative process is responsible for the changes of monomer emission intensity in the region 273–306 K. Above 306 K, there is a marked decrease in the monomer emission intensity and a corresponding increase in the excimer emission intensity (Figure 3), and the gel becomes unstable and can change its viscosity and crystallize. Oxygen diffusion and quenching cannot explain the initial increase in the monomer emission, and reversibility below 306 K may be attributed to changes in the conformational distribution in the gel. Optical density,[23] infrared, viscosity, and NMR measurements[24] indicate that above 313 K the iPS chains undergo conformational changes that are time dependent and irreversible, supporting the assumption that the effects are directly related to changes in the conformational distribution.

At low temperatures strong intramolecular interactions between neighboring phenyl rings lead to a high probability of excimer formation. Benzyl alcohol at low temperatures is a poor solvent for iPS, and, hence, phenyl–solvent interactions are unfavorable in comparison to intramolecular phenyl–phenyl interactions. Because of the irreversibility of the processes above 313 K, the measurements of the intensities were made at a heating rate of 0.4 K/min and are believed to involve both changes in the local conformation and long-range structure of the gel. The kinetic nature of the processes can be seen from changes in the spectra at 318 K over a period of 30 min (Figure 3). Variation in the rate of change, reflected in the ratio of J_E/J_M as a function of time and temperature (Figure 4), indicates that the process cannot be represented by a single rate equation and implies a possible diffusional character to the processes. A major part of the monomer emission will come from the solvent and, hence, reflects changes in the viscosity of the solvent. The fact that the ratio initially increases before decreasing indicates significant effect arising from polymer monomer emission. Above 318 K, a combination of local conformational changes perturbed by the effects of intermolecular interactions between neighboring polymer chains controls excimer formation. Below 318 K, chain diffusion appears to be inhibited, and conformational changes of the chains are reversible and

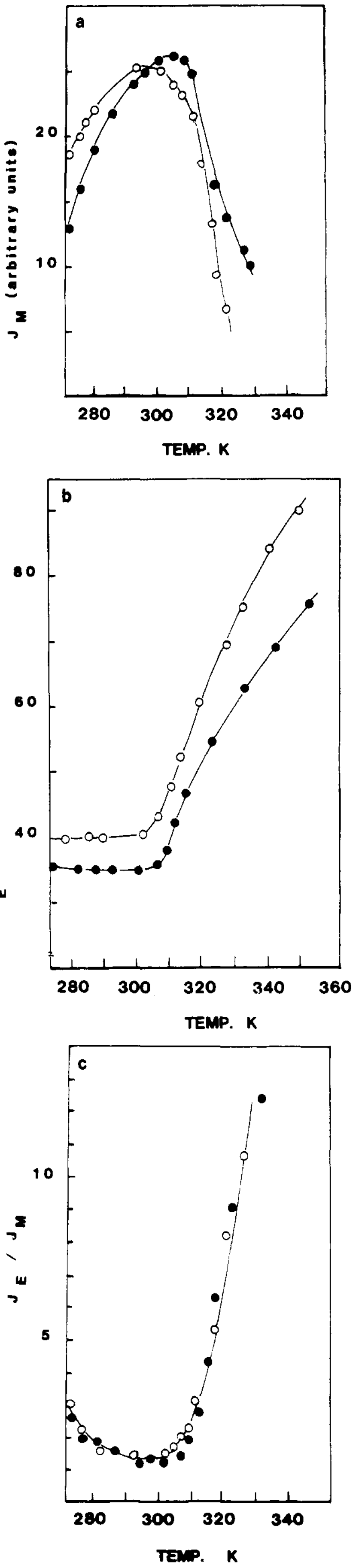

Figure 2. Dependence of monomer (a) and excimer emission (b) intensity (λ_{EM} = 285 and 330 nm) and the ratio (J_E/J_M) (c) on the temperature of a iPS gel of different concentrations: 5% w/w, 0–10% w/w (iPS/benzyl alcohol).

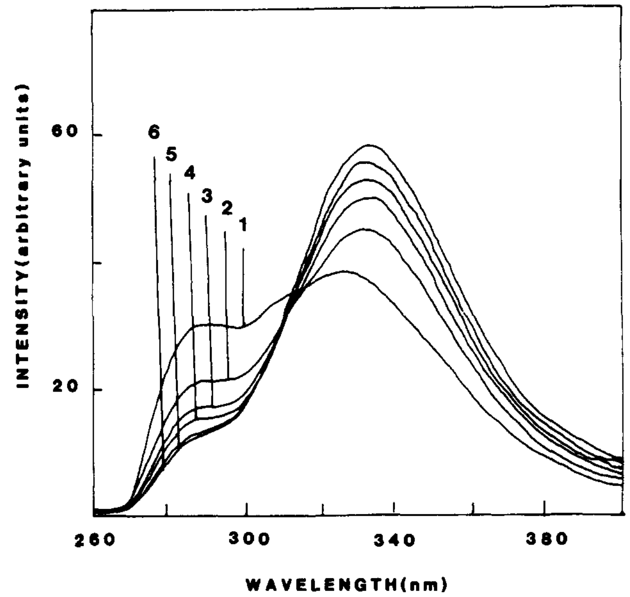

Figure 3. Changes of the fluorescence emission spectrum of a iPS gel (10% w/w) annealed at 318 K: (1) 0 min, (2) 4 min, (3) 9 min, (4) 14 min, (5) 20 min, (6) 30 min.

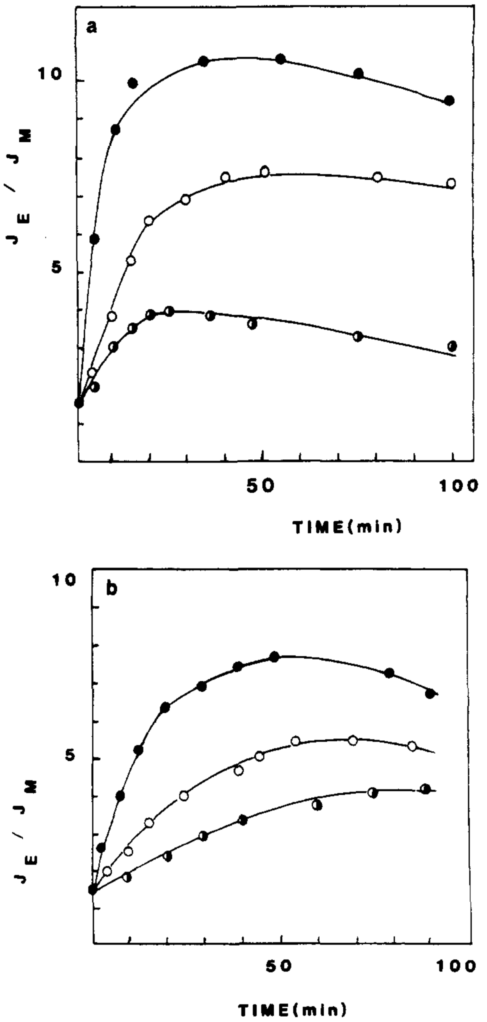

Figure 4. Kinetics of the ratio J_E/J_M during heating of a iPS gel (10% w/w) at (a) different temperatures, 0–318 K, 0–316 K, and 0–314 K, and at (b) different concentrations, 0–16%, 0–10%, and 0–5% w/w (iPS/benzyl alcohol), at 318 K.

the intermolecular interactions are constant.

The ratio of excimer to monomer emission intensity (J_E/J_M) was investigated for three concentrations of iPS in BA annealed at 318 K (Figure 4). Roots et al.[19,24] have observed that the ratio of J_E/J_M varies with concentration and is the result of intermolecular excimer formation. Close correspondence between the variation of J_E/J_M with time and concentration implies that the dominant process is intramolecular, the differences with concentration reflecting the intermolecular excimer. At 5% the polymer chains are just at the volume-filling limit, whereas at 16%, a stable gel will be formed. The variable helical structure in the gel[1] makes it impossible to calculate the number of contacts; however, the formation of a gel at 5% indicates that at least two contacts must exist per chain. The time dependence is a result of a combination of polymer diffusion and changes in solvent mobility.

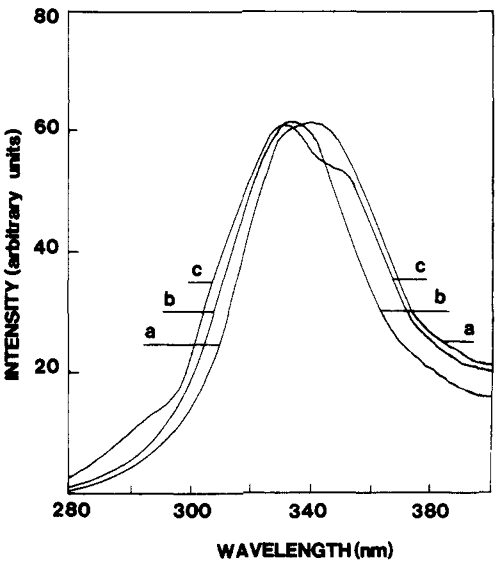

Figure 5. Fluorescence emission spectra of iPS gel (10% w/w) (λ_{EX} = 257 nm): (a) after annealing at 343 K for 3 h, (b) after annealing at 383 K for 3 h, (c) after annealing for 3 h at 353 K.

Annealing of the iPS gel between 313 and 353 K leads to a decrease in intensity of monomer emission, which could be a consequence of enhanced oxygen quenching; however, an increase in excimer emission intensity suggests that this is not the case. Increase in the excimer emission intensity occurs initially at 330 nm; however, at longer times the intensity at higher wavelengths increases consistently with a shift of the maximum in the intensity, the rate at which the shift occurs increasing with increasing temperatures.

The gel obtained by quenching a solution from an initial temperature of between 383 and 393 K produces iPS, crystallizing in a 3-fold helix structure. A sample of iPS gel annealed at 383 K for 3 h formed the 3-fold helix structure and has a characteristic excimer emission at 330 nm (Figure 5b). After annealing for 3 h at 353 K, two types of excimer can be distinguished (Figure 5c): an excimer occurring at 330 nm associated with the 3-fold helix structure and a red-shifted excimer with a maximum located at 345 nm ascribed to an extended structure. The two excimer bands belong to two thermally selected conformations associated with different ordered chain structures.

Infrared (FTIR) Spectroscopic Studies. Infrared measurements[1,22] have identified bands at 1298, 1199, 1181, 1081, 1052, 922, and 899 cm^{-1} and are characteristic of the 3-fold helix structure. A band at 981 cm^{-1} is associated with intermolecular interactions, while bands at 1062, 1069, 894, and 916 cm^{-1} characterize the extended conformation. Benzyl alcohol, fortunately, has a relatively weak absorption spectrum in the above region, and spectral subtraction

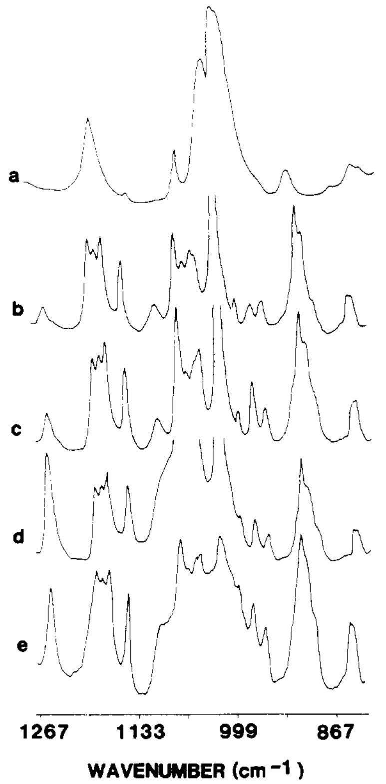

Figure 6. FTIR spectra of solvent–benzyl alcohol (a), iPS/benzyl alcohol gel quenched at 273 (b) and at 303 K (c) and iPS/benzyl alcohol gel annealed at 318 K for 30 min (d) and annealed at 318 K for 60 min (e). (Spectra were obtained after evaporation of solvent and in the case of solution with subtraction of the solvent absorption.)

is easily carried out quantitatively.

The FTIR spectrum (Figure 6c) of the gel quenched at 303 K in comparison with the gel formed at 273 K (Figure 6b) shows an increase in the intensity of the bands at 922 and 899 cm^{-1}, characteristic of the 3-fold helical structure, and bands at 916 and 894 cm^{-1}, characteristic of the extended structure. Annealing the gel at 318 K over a period of 30–60 min results in no major changes in the spectral intensity. However, significant differences were observed between the sample annealed at 318 K and those quenched to 273 and 303 K, indicating changes in the nature of the phenyl ring interactions. Sundararajan et al.[2-4,17,18] have proposed that these shifts are the result of specific interactions between the aromatic solvent and the phenyl groups of the polymer backbone involved in the extended chain structure. Comparison of the FTIR and excimer fluorescence data allows assignment of the excimer at 330 nm to the 3-fold helix structure and the band at 345 nm to an extended structure that incorporates a solvent molecule.

Annealing the gel at 343 K for 3 h (Figure 7) increases the 3-fold helix concentration; however, annealing at 343 K produces the extended structure.

Fluorescence Decay Studies of iPS Gel. Steady-state fluorescence data on the gel can be divided into three regions: monomer emission intensity having a maximum at 285 nm and excimer emission intensities at 330 nm, characteristic of the 3-fold helix form, and at 345 nm, associated with the extended conformation (Figure 8). Fluorescence decay profiles obtained at different emission wavelengths corresponding to different characteristic conformations of the gel state of iPS in benzyl alcohol were measured Table II. Fluorescence decay curves obtained for the initially formed gel in the region of the monomer and excimer emission intensity are similar to those for atactic polystyrene. Gupta et al.[27] using methylene chloride as solvent found a monomer lifetime of 0.72 ns and an excimer lifetime of 12.5 ns with a value of 20.0 ± 2.5 ns in the solid state. In the gel state, the monomer emission at 285 nm is slower than that in polystyrene solution;[25,26] however, the excimer lifetime is comparable to that for the solid, reflecting a slowing down of motion in the gel. Variation of the excimer lifetime with wavelength reflects a range of closely related excimer structures.[25-27]

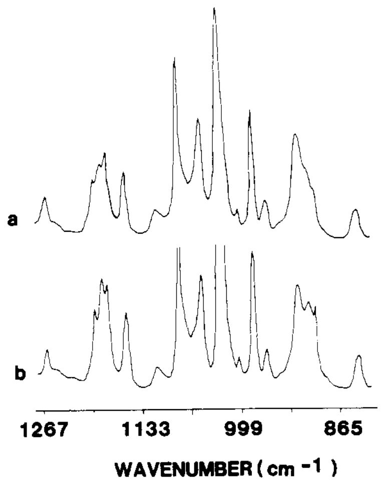

Figure 7. FTIR spectra of the iPS/benzyl alcohol gel after annealing for 3 h at 343 K (a) and after annealing for 3 h at 383 K (b). (Spectra were obtained after evaporation of solvent and in the case of solution with subtraction of the solvent absorption.)

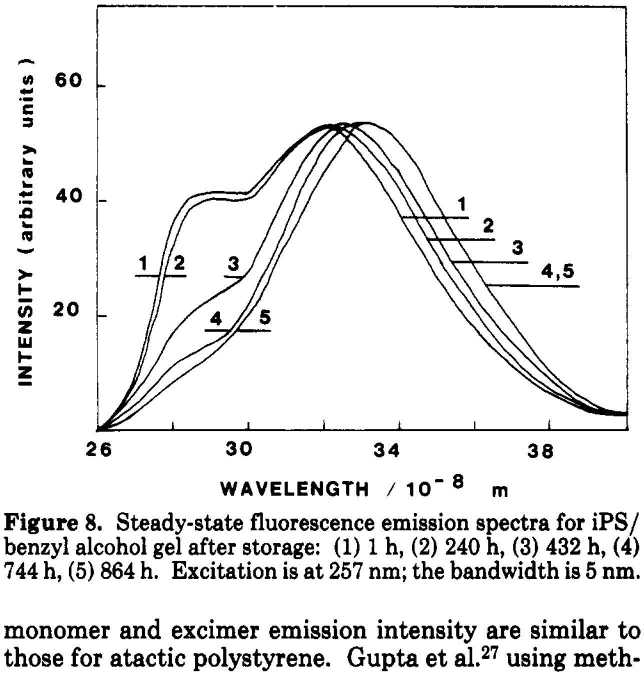

Figure 8. Steady-state fluorescence emission spectra for iPS/benzyl alcohol gel after storage: (1) 1 h, (2) 240 h, (3) 432 h, (4) 744 h, (5) 864 h. Excitation is at 257 nm; the bandwidth is 5 nm.

Annealing of the gel at 318 and 343 K increases the concentration of red-shifted excimer at 345 nm. Analysis of the fluorescence decay at 350 nm requires a third exponential with a lifetime of ≥30 ns (Table III), indicative of the iPS/BA exciplex with incorporated solvent. The gel annealed at 383 K (Table IV) exhibits a maximum in its emission intensity at 330 nm and can be adequately fitted by two components. The lifetimes indicate that the lower intensity component corresponds to the monomer and the longer lived component to the 3-fold helix form. Similar red shifts were observed[28] in the excimer fluorescence of stretched films of atactic polystyrene and increase the lifetime of the long component from 21.0 ns in the unstretched to 22.6 ns in the stretched film.

Table II
Fluorescence Decay Data for iPS/BA Gel before and after Thermal Treatment[a]

λ_{EM}/nm	τ_1/ns	τ_2/ns	τ_3/ns	B_1/%	B_2/%	B_3/%	χ^2
Initial Gel, after 2 days at 293 K							
285	6.1 ± 0.9	17.2 ± 0.6		79.0	11.2		1.5
310	6.4 ± 0.9	18.6 ± 0.9		58.5	41.5		0.81
330	7.3 ± 0.3	19.7 ± 0.2		34.1	66.0		1.12
340	12.9 ± 0.9	20.6 ± 0.4		45.3	54.7		1.15
Gel after Annealing at 318 K							
310	4.0 ± 0.4	20.5 ± 0.3		15.2	84.8		1.06
330	8.8 ± 0.8	21.3 ± 0.2		25.6	74.4		1.03
350	2.2 ± 0.6	19.5 ± 1.2	34.6 ± 1.8	4.0	74.3	21.7	1.10
Gel after Annealing at 383 K							
310	3.7 ± 0.6	19.6 ± 0.6		27.2	72.8		1.27
320	4.3 ± 0.4	20.5 ± 0.4		16.7	83.3		1.16
330	5.2 ± 0.3	21.0 ± 0.3		11.9	88.1		0.99
340	5.1 ± 0.9	21.3 ± 0.4		9.9	90.0		1.11
350	4.7 ± 0.6	21.6 ± 0.2		6.9	93.1		1.09

[a] Data have been taken at 298 K using an excitation wavelength 257 nm and a bandwidth 10 nm.

Table III
Fluorescence Decay Data for iPS/BA Gel Annealed at 318 K[a]

λ_{EM}/nm	τ_1/ns	τ_2/ns	τ_3/ns	B_1/%	B_2/%	B_3/%	χ^2
0.5 h of Annealing							
310	8.6 ± 0.5	18.4 ± 0.5		59.6	40.4		1.30
330	11.0 ± 0.3	24.5 ± 0.2		60.1	39.9		0.98
350	12.7 ± 0.6	25.9 ± 0.4		56.8	43.2		1.26
3 h of Annealing							
310	4.0 ± 0.4	20.5 ± 0.3		15.2	84.8		1.06
330	8.8 ± 0.8	21.3 ± 0.2		25.6	74.4		1.03
350	8.3 ± 1.3	24.3 ± 0.3		14.9	85.0		1.90
350	2.2 ± 0.6	19.5 ± 1.2	34.6 ± 1.8	4.0	79.3	21.7	1.10

λ_{EM}/nm	τ_1/ns	τ_2/ns	B_1/%	B_2/%	χ^2
72 h of Storage					
310	3.9	20.9	11.5	88.5	1.02
330	4.1 ± 0.4	21.8 ± 0.2	7.2	92.8	1.22
350	8.0	23.5	9.5	90.5	2.63
350	1.8	21.6	2.5	97.5	1.21
678 h of Storage					
310	4.3 ± 0.3	20.6 ± 0.3	23.5	76.5	1.27
330	5.2 ± 0.6	21.9 ± 0.2	10.7	89.3	1.41
330	3.2 ± 0.5	20.5 ± 0.2	6.1	93.9	1.25
350	6.6 ± 0.8	23.4 ± 0.3	9.9	90.1	1.47
350	2.1 ± 0.2	23.6 ± 0.6	3.4	96.6	1.15

[a] Data have been taken using an excitation wavelength 257 nm and a bandwidth 10 nm. [b] A three-exponential fit gives $\tau_1 = 2.2 \pm 0.9$, $\tau_2 = 17.9 \pm 2.7$, $\tau_3 = 28.9 \pm 1.2$, $B_1/\% = 3.2$, $B_2/\% = 55.7$, and $B_3/\% = 41.1$ with $\chi^2 = 1.15$.

Long-Time Relaxation of the Gel. In order to ensure that long-time effects observed over a period of up to 1656 h (Table V) are a consequence of the structure of the gel and not of changes in the solvent concentration, the samples were stored in an environment saturated with solvent. This ensures that any solvent lost from the gel is a consequence of shrinkage induced by conformational change rather than solvent evaporation. Initially the excimer is independent of wavelength, indicative of only one conformation being present. Systematic changes in the lifetimes are observed, resulting from changes in the distribution of conformations contributing to the excimer spectrum at 330 nm (Figure 9). The increased lifetime correlates with the macroscopic observation of densification of the gel. After 432 h of storage, the emission spectrum (Figure 8) exhibits the red-shifted excimer reflected in an increase in the lifetime of the emission at 350 nm, and approximately 30% of the excimers have changed into the long-lived component, with a characteristic lifetime of 27 ns (Table IV), and reflect change of the extended conformation into the solvated 3-fold helix form.

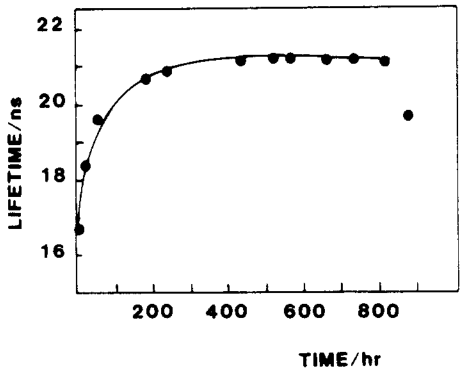

Figure 9. Dependence of the lifetime of the excimeric fluorescence emission at 330 nm on time of storage.

Time-Resolved Emission Spectra. Changes in the distribution of excimer states can be explored by using time-resolved emission spectra[28-31] (Figure 10). The red-shifted excimer emission at 345 nm is clearly identified by using a time window of 79–152 ns, which covers the whole of the emission spectra of the long-lived component. The

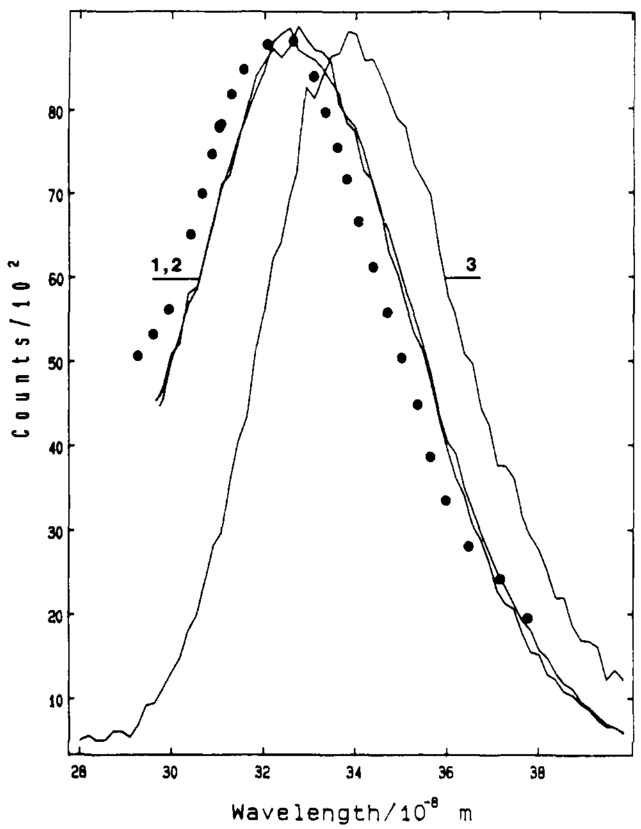

Figure 10. Time-resolved emission spectra for iPS/benzyl alcohol gel stored to 270 h: (1 and 2) $t = 0$, time window 9 ns; (3) $t = 79$ ns, time window = 73 ns. Dotted curve steady-state fluorescence emission spectrum for iPS/BA gel after pressurization. Excitation is at 257 nm; bandwidth is 2 nm.

curve shown dotted (Figure 10) is the steady-state fluorescence emission spectrum for the gel immediately after it was formed. A very close correspondence of this line shape with that of the short-lived component confirms that the extended form is the predominant species formed initially. The red-shifted solvated excimer is only generated after a period of time. After a period of 744 h (Figure 11), a red-shifted excimer with a maximum at 345 nm is observed by using a time window of 96–198 ns. The excimer component at 325 nm is reduced in intensity, being transformed to a new structure at 330 nm. After 1656 h, the whole of the gel was transformed into the lowest energy structure and exhibits a maximum at 330 nm.

The number of solvent molecules per monomer unit calculated from densification data (Figure 12a) can be correlated with the change in lifetime of the component at 330 nm (Figure 12b). The decrease in the number of solvent molecules per monomer is consistent with the idea that the final form has excluded solvent from the gel.

Study of Model Gel Systems. A model isotactic polystyrene gel (iPS) was prepared by placing a crystalline sample of isotactic polymer, produced at high temperatures, into a hot solution of iPS and BA and immediately quenching the mixture to a solid gel.[33] The steady-state fluorescence emission spectra of the resultant clear gel and the crystalline material used in forming the mixture were obtained (Figure 13). Time-resolved emission spectra obtained by using different delay times (Figure 14) indicate the existence of three excimer states. Curve 1 maximum at 325 nm is associated with the high-energy excimer, curve 2 maximum at 330 nm is the extended structure, and curve 3 maximum at 345 nm is the red-shifted excimer. Good agreement exists between the time-resolved and steady-state spectra; the differences between the curves at higher wavenumber are a result of the occurrence of other excimer species in the gel state.

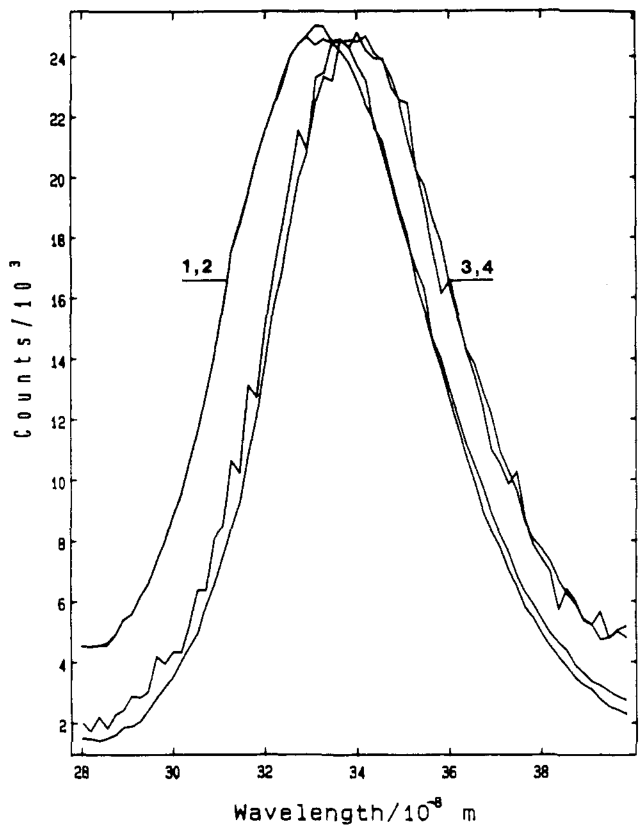

Figure 11. Time-resolved emission spectra for iPS/BA gel stored for 744 h: (1 and 2) t = time window 0–8 ns; (3 and 4) t = time window 96–198 ns.

Curve 2 in Figure 3 shows good agreement with the steady-state fluorescence emission spectrum of an iPS gel obtained after heating for 3 h at 383 K (Figure 5). During this thermal annealing process the higher temperature extended conformation is transformed into the 3-fold crystalline conformation[3] and is characterized by an emission maximum at 330 nm. Aging of the gel at 318 K for 3 h produced fluorescence decays in which the excimer structure due to the helix conformation can clearly be resolved (Table II).

Considering the general characteristics of the excimer at 345 nm and the various structural possibilities available in the isotactic structure[35–37] leads us to propose that it is formed by the interaction of a benzyl alcohol molecule with a helical dimer structure. The solvent will be involved in the π–π overlap between neighboring rings and, hence, induces the red shift characteristic of this species. The longer lifetime is probably a consequence of the fact that the lifetime of this species will be intimately connected with exchange of energy between the polymer solvation sheath and solution and has a time constant of tens of nanoseconds. The fluorescence decay parameters of the crystalline material (Table II), which has been stored in solvent vapor, will reflect the interaction of solvent with the pendant phenyl groups of the polymer. The occluded solvent molecules will cause the increase of lifetimes and distributions (Table IV).

Guenet[5,6] has recently performed a detailed investigation of the structure of isotactic polystyrene near the gelation threshold using a combination of X-ray and neutron diffraction measurements. The main feature that arises from this study is that evidence is obtained for the intercalate polymer–solvent compound. This observation

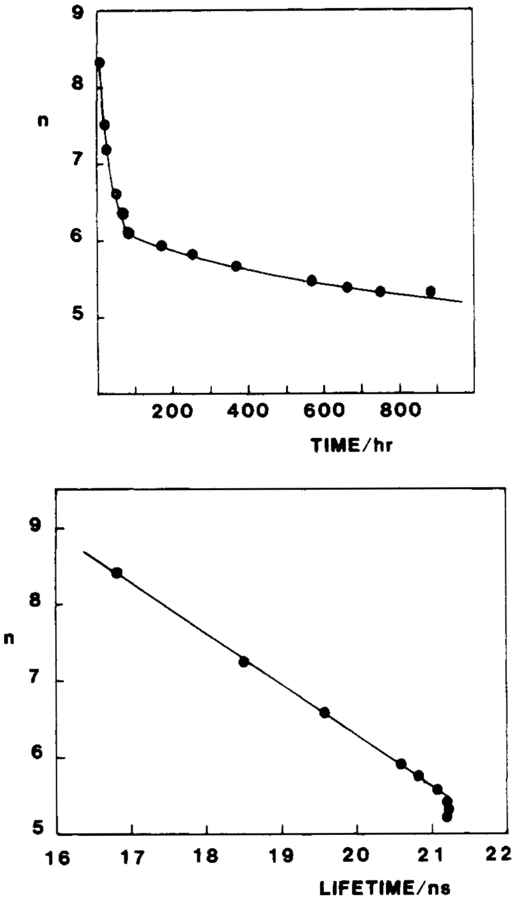

Figure 12. (a) Number of solvent molecules per monomer unit in the chain of isotactic polystyrene as a function of time of storage of the iPS/benzyl alcohol gel. (b) Change correlation of the lifetime of excimer fluorescence emission and the number of solvent molecules per monomer unit in the iPS chain.

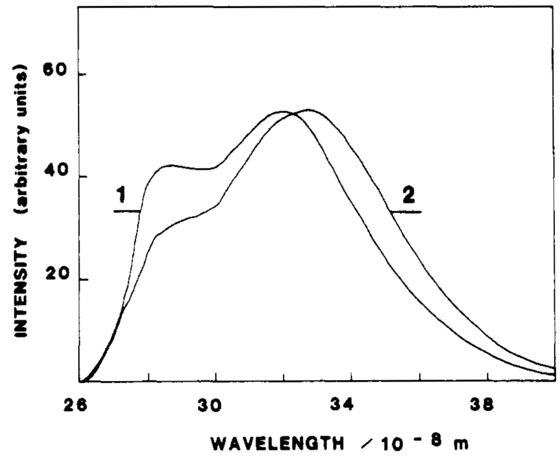

Figure 13. Steady-state fluorescence emission spectra of iPS/BA gel after preparation (1) and the gel model with suspended crystalline material (2).

is consistent with the spectroscopic data in which we interpretate the excimer at 345 nm as associated with a solvated helix structure.

Related temperature-dependent ^{1}H and ^{13}C NMR studies[34] of the gels confirm the importance of the polymer–solvent complex and reinforce the diffusional character of the time-dependent process (Figure 4). These data are consistent with the model proposed here for the gel state of isotactic polystyrene and confirm the proposition that the dynamics are important in understanding the various features observed.

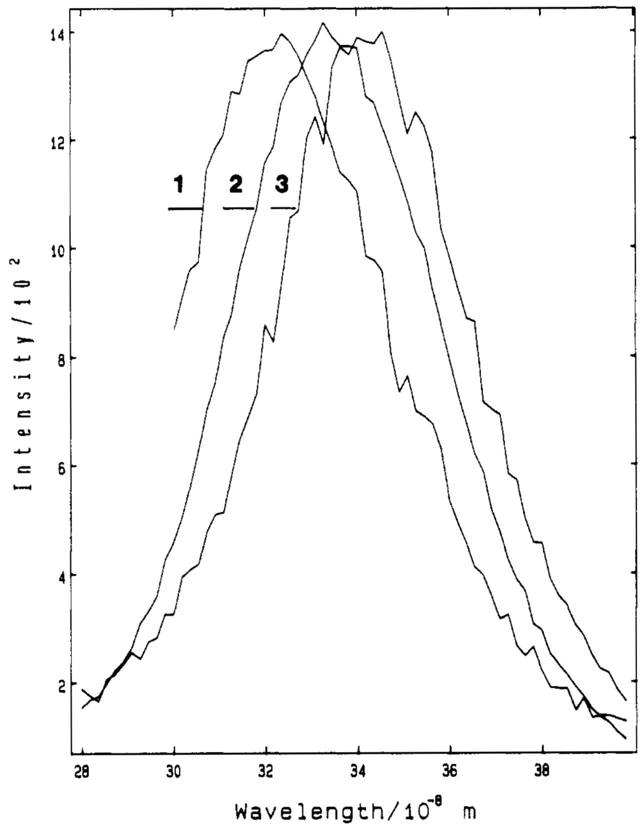

Figure 14. Time-resolved emission spectra for iPS/BA gel model with suspended crystalline material: (1) time window 5 ns, (2) time window t = 7–16 ns, (3) time window t = 71–149 ns.

Table IV
Fluorescence Decay Data for iPS/BA Gel after Heating at 353 K for 3 h

λ_{EM}/nm	τ_1/ns	τ_2/ns	B_1/%	B_2/%	χ^2
310	3.7 ± 0.6	19.6 ± 0.6	27.2	72.8	1.27
320	4.3 ± 0.4	20.5 ± 0.4	16.7	83.3	1.16
330	5.2 ± 0.3	21.0 ± 0.3	11.9	88.1	0.99
340	5.1 ± 0.9	21.3 ± 0.4	9.9	90.0	1.11
350	4.7 ± 0.6	21.6 ± 0.2	6.9	93.1	1.09

Growth of Crystallites in the Gel. Optical examination of the gels used to obtain the above measurements indicated that the crystallites growing had different structures (Figure 15) and depend on the time and/or temperature used in annealing. The gel annealed at 313 K exhibits a ringed spherulitic structure with a diameter of approximately 20 μm. Similar observations have been made when iPS amorphous films were exposed to hexahydroindane vapor.[3] The ringed spherulitic structure corresponds to the conformation that is identified with the red-shifted excimer. The long-lived component has a broader distribution of lifetime components compared with the other excimers, the distribution itself being a function of the time and conditions used to anneal the sample. The gel annealed for 3 h at 383 K (Figure 15) exhibits a regular spherulitic morphology with a diameter of 5 μm and the chains in 3-fold helix structure, which cluster and align as a result of external constraints imposed during the formation of the gel. This type of orientational effect has been previously reported for polyethylene.[36]

Model for the Gelled State of Isotactic Polystyrene. The gel structure can result from two types of interaction: normal chain entanglement and also preferential alignment of helical segments of the chain. The topography of the gel will be frozen when the solution is quenched. Below 318 K significant reptation of the chains on the time scale

Table V
Fluorescence Decay Data for iPS/BA Gel after Different Periods of Storage[a]

time/h	λ_{EM}/nm	τ_1/ns	τ_2/ns	B_1/%	B_2/%	χ^2
1	285	5.1 ± 0.4	14.4 ± 0.2	89.0	11.0	1.14
	310	5.1 ± 0.2	16.3 ± 0.4	76.6	23.9	1.14
	320	5.3 ± 0.2	17.2 ± 0.7	63.5	36.5	1.05
	330	5.2 ± 0.3	16.9 ± 0.4	61.6	48.4	1.07
24	285	5.3	18.2	55.7	45.7	1.19
	310	5.4	18.3	31.6	68.4	1.17
	330	5.9	18.5	19.8	80.2	1.15
	350	11.6	19.6	18.4	81.6	1.19
48	285	6.1 ± 0.9	17.2 ± 0.6	79.0	11.2	1.05
	310	6.4 ± 0.9	18.6 ± 0.9	58.5	41.5	0.81
	330	7.3 ± 0.3	19.7 ± 0.2	39.1	66.0	1.12
	350	12.4 ± 0.9	20.6 ± 0.4	45.3	54.7	1.15
74	310	5.3 ± 0.2	18.3 ± 0.2	49.3	50.7	1.00
	330	6.3 ± 0.6	19.5 ± 0.2	20.7	79.3	1.42
	350	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
	330	8.1 ± 0.6	20.7 ± 0.3	22.8	77.2	1.30
	350	17.9 ± 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
	330	5.6 ± 0.4	19.9 ± 0.2	19.7	80.3	1.22
	350	11.4 ± 0.4	21.7 ± 0.4	25.8	74.2	1.18
432	310	5.7	18.2	44.7	55.3	1.12
	320	6.1	19.7	28.6	71.7	1.21
	330	8.2 ± 0.9	21.1 ± 0.2	23.6	76.7	1.25
	340	13.3 ± 1.5	23.2 ± 0.4	37.5	62.5	1.07
	350	17.5 ± 1.2	27.7 ± 0.2	72.5	27.5	1.15
528	330	7.4 ± 0.7	21.1 ± 0.8	17.7	82.3	1.22
	350	18.5 ± 0.3	29.7 ± 5.0	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	10.1	80.9	1.28
	350	11.7 ± 0.3	22.8 ± 0.6	25.4	74.6	1.23
744	330	7.7 ± 0.6	21.1 ± 0.2	20.2	79.8	1.19
	350	11.2 ± 2.7	21.8 ± 3.3	17.2	82.8	1.18
816	330	6.6	20.7	17.6	82.4	1.05
	350	9.6	21.5	18.4	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	1.17
1656	330	4.9 ± 0.3	19.0 ± 0.2	18.3	81.7	1.32
	350	6.8 ± 0.9	19.9 ± 0.2	15.2	84.8	1.18

[a] Data have been taken at 298 K using an excitation wavelength 257 nm and a bandwidth of 10 nm.

of several hours or even days is inhibited and the changes in the conformation are constrained by the chain–chain interactions to being "local". Changes in the conformational distribution as a function of temperature are the result of redistribution of the 3-fold helix form. Increasing the population of the ordered structure will induce strain in other regions of the gel and will be the driving force for reptation-like motion. The strain released will destroy some regions of intermolecular interaction and cause others to be formed. The temperature of 318 K is associated with the onset of reptation motion and also the generation of solvent-inserted exciplex. Raising the temperature to 383 K causes a decrease in the strength of the solvent–polymer interaction and once more observation of the more compact structure.

Conclusions

This paper indicates the nature of the local structural changes that occur when iPS gel is annealed and indicates that there are two quite distinct temperature regions. Below 310 K, the gel is stable and redistribution of the structural forms occurs within chains that are effectively locked in space. Above 310 K, the extended structure is generated and the chains undergo reptation motion. The processes in this region are irreversible, and the gel properties depend on the thermal history of the sample. The time-resolved emission spectra reveal the existence of a third excimer peak, and the densification process of the gel involves the excimer transforming into a red-shifted solvated exciplex, which itself transforms into the compact 3-fold helical conformation. As these processes occur, the matrix undergoes densification with the exclusion of solvent, which implies a change in the solvent sheath around the polymer. Adiabatic compressibility measurements on similar systems have shown that the solvent will interact with the polymer chain for a period of 10^{-5} s, which is sufficient for it to influence the lifetime of fluorescence[5] and is also consistent with the NMR data.[34]

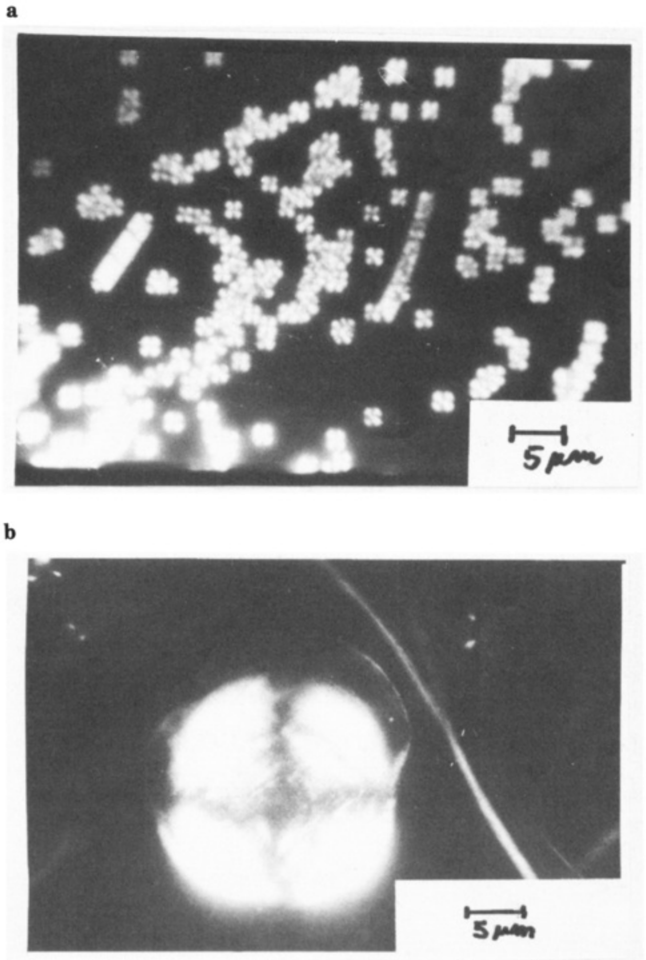

Figure 15. Morphological structures observed by optical polarize microscopy for iPS/BA annealed at 383 K (a) and at 313 K (b).

Comparison of infrared, X-ray, and fluorescence data indicates that the red-shifted exciplex structure is an extended helical structure in which solvent is incorporated. This paper illustrates how fluorescence techniques can provide an insight into the nature of the structures responsible for the formation of iPS gels.

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