Correlation of steady-state and time-dependent studies of a two-phase isotactic polystyrene gel

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(Received 16 April 1991; revised 21 October 1991; accepted 13 January 1992)

Time-resolved fluorescence emission spectra of isotactic polystyrene/benzyl alcohol (iPS/BA) gel annealed at 318 K are reported. Time-resolved spectra and analysis of the fluorescence decay parameters on fresh gel, crystalline isotactic polystyrene together with data from the gel allow identification of two excimer components. Good agreement between the steady-state fluorescence emission spectrum with a theoretically predicted excimer emission spectrum, constructed on the basis of a mechanism that assumes the existence of separate domains, was observed. The dependence of the emission intensity of components is discussed in terms of the effectiveness of photo energy transfer and energy migration.

(Keywords: time-resolved fluorescence; excimer fluorescence; lifetime; two phase gel; polystyrene gel)

INTRODUCTION

Studies of photo energy transport and trapping by excimer structures in polymeric systems are important in the understanding of the photophysical properties[1–4]. Investigation of the photophysics of the excimer state has proven to be an excellent method for the study of miscibility and phase separation in aromatic vinyl polymer blends[5–8]. Time-dependent fluorescence measurements have also been used in such studies. However, it is still not clear whether a detailed correspondence exists between the decay parameters characterizing the excimer states and the morphology and chain conformation of the polymer[1,2]. In order to be able to extend the application of the fluorescence method to phase-related problems, it is necessary to establish a direct correlation between the steady-state and transient spectral data and the morphological structure of a polymer system. In this paper we describe a study of a model heterogeneous isotactic polystyrene gel and attempt to carry out such a correlation.

EXPERIMENTAL

Materials

Isotactic polystyrene (iPS) of molecular weight $M_w = 9.1 \times 10^5$ was obtained from Shell Chemicals (batch 439/12) and was purified to remove antioxidants and low-molecular-weight additives. The tacticity of the polymer was determined using Bruker 250 MHz ^{1}H n.m.r. and the structure was found to be 95% isotactic.

Benzyl alcohol (BA) obtained from Aldrich Chemical company was used as solvent. The purity of the solvent was checked using fluorescence spectroscopy. Solutions of 10 wt% of iPS in BA were prepared by heating the mixture to 443 K under nitrogen. The solutions were transferred onto precooled quartz plates and quenched to 273 K. Clear gel films of 40 μm thickness were obtained and after 24 h of storage in a refrigerator were annealed under nitrogen at 318 K.

The thermal characteristic of the iPS/BA gels and the crystallites formed after evaporation of solvent were obtained using a Du Pont differential scanning calorimeter equipped with a TA200 data processing unit.

Fluorescence measurements

Benzyl alcohol was chosen as solvent in our photophysical studies of iPS gel[9,10] because, although there is spectral overlap between the polystyrene monomer emission and the absorption spectrum of benzyl alcohol, no concentration effect on the fluorescence spectra of iPS in the excimer region has been observed.

The steady-state fluorescence emission spectra were recorded using a Perkin–Elmer LS-50 spectrofluorophotometer with a 2.5 nm slit width and 257 nm excitation wavelength. The films were mounted at 45° to the excitation beam and a polarizer in the emission beam at the magic angle was used to separate out the scattered light.

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0032-3861/92/173552-06

A time-correlated single-photon-counting fluorometer was used for fluorescence decay measurements. Decay data were collected with 10^4 counts in the peak using 10 nm slit width. The reconvolution analysis has been carried out using a non-linear least-squares method with χ^2 as criterion for goodness of fit[9,10].

Characterization of thermally initiated phase separation and crystallization

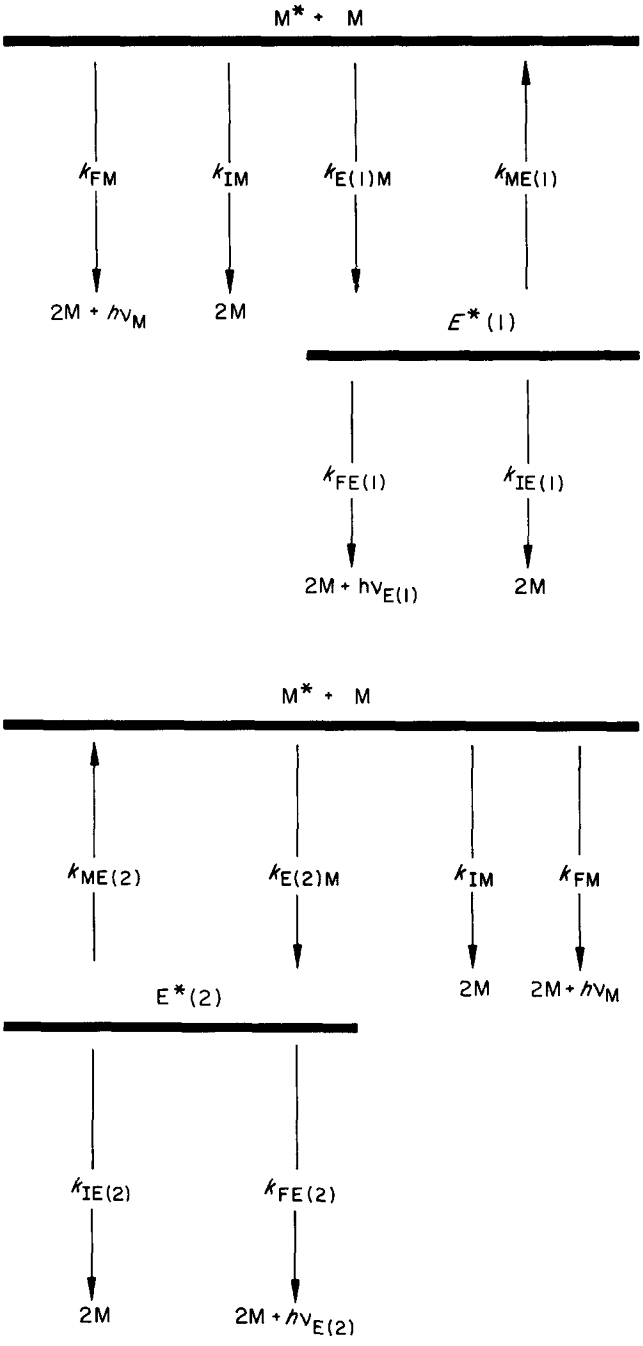
The procedure used to prepare the gel leads to a metastable state in which the polymer chains are frozen in an extended conformation[11–13]. Annealing allows the polymer chains to undergo phase separation into regions that are lean and rich in polymer[14]. The polymer-rich phase can be thermally transformed into a crystalline phase with a characteristic, three-fold helix conformation[10–13]. The phase separation step is determined at a fixed concentration by two factors: temperature and time. The annealing measurements were carried out at 318 K and this temperature was chosen because it lies sufficiently close to the glass transition temperature, reported to be at 323 K[11,15], to allow effective production of a heterogeneous two-phase system within a reasonable timescale. After 15 min of annealing, domains of approximately 50–100 μm (*Figure 1a*) can be observed using polarized optical microscopy. Simultaneously, the polymer-rich phase may also form a partially crystalline phase with a pin-cushion morphology (*Figure 1b*), as well as a range of less well defined topographies (*Figure 1c*). The d.s.c. thermograms of the gel after annealing for half an hour at 318 K (*Figure 2*) contain a peak at 494 K (curve 1), similar to the melting peak reported in the literature for the three-fold helix crystalline conformation of iPS obtained by crystallization of the gel at 383 K[10–13,16]. The fresh iPS gel thermogram (curve 3) shows a broader feature associated with loss of solvent from the gel. Assuming that the observed peak is associated with the melting of the three-fold helix conformation and accepting that its heat of fusion is $\Delta H = 80\,\mathrm{J\,g^{-1}}$ (ref. 17), then the percentage crystallinity of the gel annealed at 318 K for 30 min and at 383 K for 3 h are respectively 23% and 68%.

PHOTOPHYSICS OF A TWO-PHASE SYSTEM

In this mechanism it is proposed that the photophysical processes result as a consequence of excimer emissions from different domains within the sample. The assumptions of this model, which have been confirmed by experimental studies of photo energy migration in heterogeneous polymer blends[6–8], are as follows:

(i) there is no energy transfer between the different domains;
(ii) the exciton can migrate inside a particular phase but becomes trapped at interfaces without escaping.

The two-phase photophysical process can be represented by *Scheme 1* and has a similar form to that previously proposed for a single phase[1,9]. k_{FM}, k_{FE} and k_{IM}, k_{IE} are the rate constants of radiative and non-radiative decay for respectively the monomer and the excimer. The rate constant k_{EM} is very complicated and contains the effects of intramolecular excimer fluorescence resulting from internal rotation of the chain and energy migration. For the gel state the first process is negligible and the energy migration plays the dominant role. Similarly, the rate constant k_{ME} describes the decay of excimer fluorescence and contains all the elements associated with energy migration.



Scheme 1

The photoemission rate equations corresponding to any domain are described as follows:

$$d[^1M^*]/dt = I_a + k_{ME}[^1E^*] - (k_{EM} + k_M)[^1M^*] \quad (1)$$

$$d[^1E^*]/dt = k_{EM}[^1M^*] - (k_E + k_{ME})[^1E^*] \quad (2)$$

where $k_M = k_{FM} + k_{IM}$ and $k_E = k_{FE} + k_{IE}$.

Assuming stationary-state illumination conditions, the above equations have the following solutions[1,5]:

$$[^1M^*] = I_a(k_E + k_{ME})/[(k_M + k_{EM})k_E + k_{ME}k_M] \quad (3)$$

$$[^1E^*] = I_a k_{EM}/[(k_M + k_{EM})k_E + k_{ME}k_M] \quad (4)$$

Using the above equations, the intensities of monomer

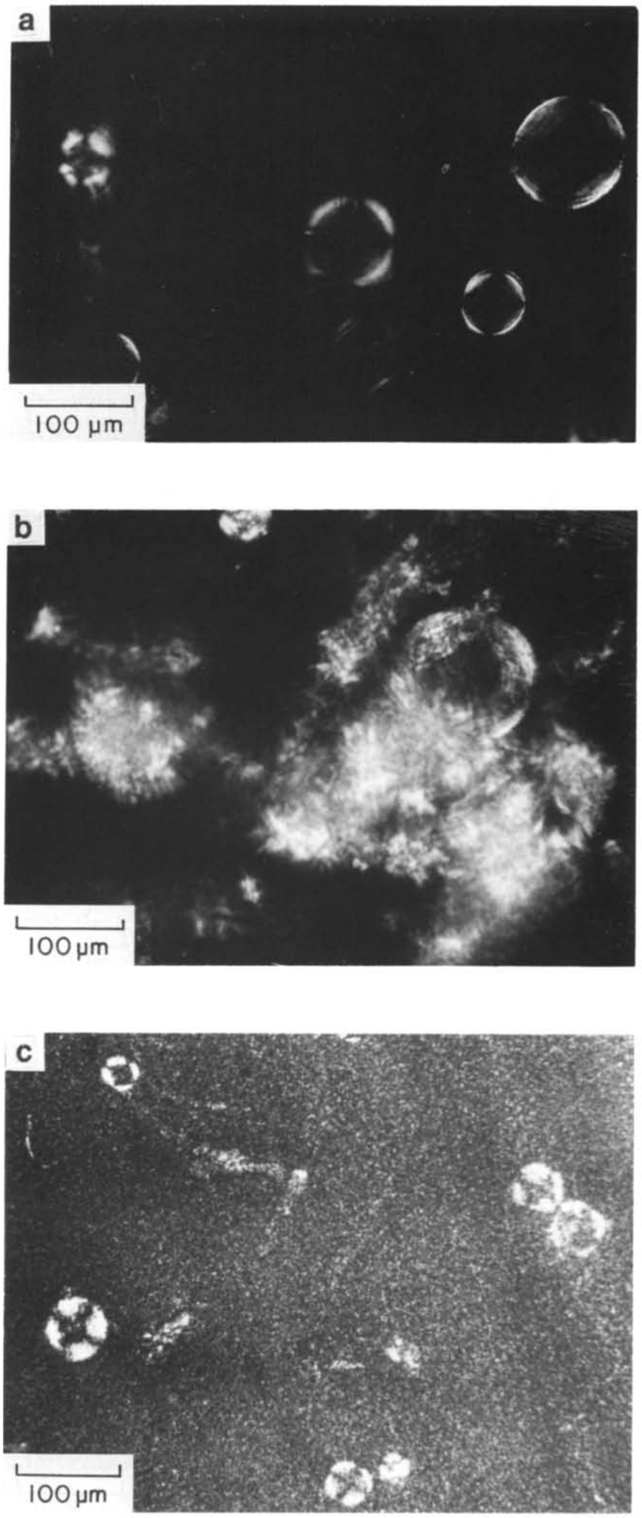


Figure 1 Optical micrographs of iPS gel annealed at 318 K: (a) phase-separated structures; (b) pin-cushion morphology of the phase-separated states; (c) miscellaneous structure

and excimer emission can be described as follows:

$$I_M = k_{FM}[^1M^*] = k_{FM}I_a(k_E + k_{ME})/[(k_M + k_{EM})k_E + k_{ME}k_M] \tag{5}$$

$$I_E = k_{FE}[^1E^*] = k_{FE}I_a k_{EM}/[(k_M + k_{EM})k_E + k_{ME}k_M] \tag{6}$$

In a two-phase system we must consider that the observed emissions arise from not only different states but also different phases and the processes are simultaneous and independent. Thus:

$$I_E = I_{E(1)} + I_{E(2)} \tag{7}$$

$$\begin{aligned} I_E = {} & k_{FE(1)}I_a k_{E(1)M}/[(k_M + k_{E(1)M})k_{E(1)} + k_{ME(1)}k_M] \\ & + k_{FE(2)}I_a k_{E(2)M}/[(k_M + k_{E(2)M})k_{E(2)} + k_{ME(2)}k_M] \end{aligned} \tag{7a}$$

Solutions of the above equations (1) and (2) under transient decay conditions, and assuming $[^1M^*] = [^1M^*]_0$ and $[^1D^*] = 0$ at $t = 0$, have the form:

$$I_M(t) = k_{FM}M_0 \exp(-t/\tau_M) \tag{8}$$

$$I_E(t) = k_{FE}k_{EM}\tau_M\tau_E M_0[\exp(-t/\tau_E) - \exp(-t/\tau_M)]/(\tau_E - \tau_M) \tag{9}$$

If the excimer state has a long lifetime, then the second term in equation (9) is negligible.

For excimers corresponding to the same energy state but associated with different phases, then:

$$I_E(t) = I_{E(1)}(t) + I_{E(2)}(t) \tag{10}$$

and subsequently equation (9) can be written:

$$\begin{aligned} I_E(t) = {} & k_{FE(1)}k_{E(1)M}\tau_M\tau_{E(1)}M_0 \exp(-t/\tau_{E(1)}) \\ & + k_{FE(2)}k_{E(2)M}\tau_M\tau_{E(2)}M_0 \exp(-t/\tau_{E(2)}) \end{aligned} \tag{10a}$$

Both of the equations describing the intensity of emission, under stationary and transient conditions, depend on the rate constants k_{EM} and k_{ME}, which include the effects of energy migration. The effectiveness and/or the probability of energy migration occurring depends on the topology of the donor–acceptor pairs and the environment around them.

The observed decay may be calculated by means of a

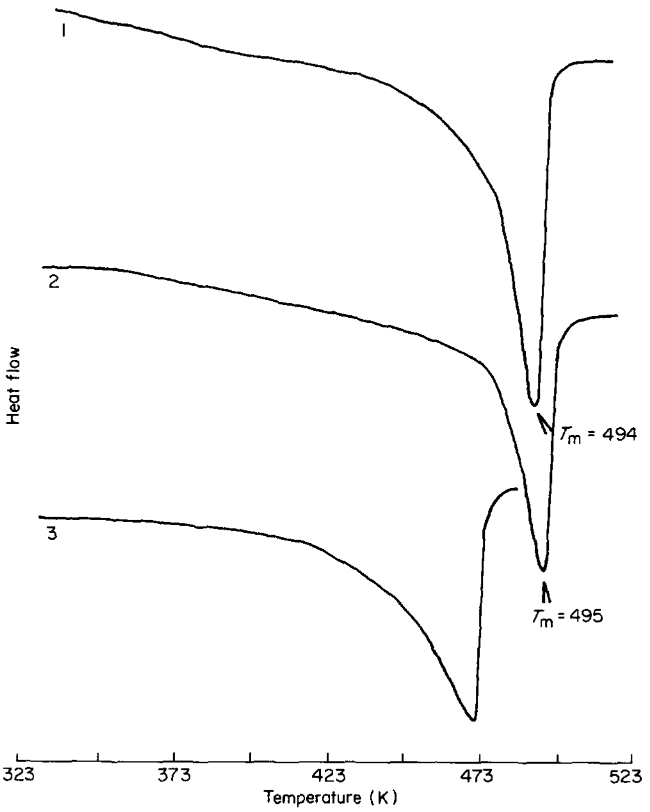


Figure 2 D.s.c. thermograms: (1) iPS gel after 0.5 h of annealing at 318 K (then evaporated at room temperature); (2) crystalline iPS gel (evaporated); (3) fresh iPS/BA gel (not evaporated)

reconvolution of a function of the type:

$$I(t)=\sum_i B_i \exp(-t/\tau_i) \qquad (11)$$

where τ_i is the fluorescence lifetime of component i and B_i is the pre-exponential parameter. In the case of fluorescence of a two-component system, then the value of B_i is proportional to the percentage emission from a particular component and $\sum_i B_i = 100\%$.

RESULTS AND DISCUSSION

The change of the steady-state emission spectrum of iPS gel during annealing at 318 K (*Figure 3*) indicates an increase in the intensity of the red-shifted excimer emission with increasing time. The fluorescence emission decays of a sample of iPS gel annealed for half an hour required two exponential functions to obtain a good fit of the experimental decays. The photophysical parameters obtained at a series of wavelengths are presented in *Table 1*. A small amount of monomer emission from the annealed iPS gel would not necessarily result in a third component in *Table 1*, but could cause a considerable decrease in the lifetime of the short-lived component.

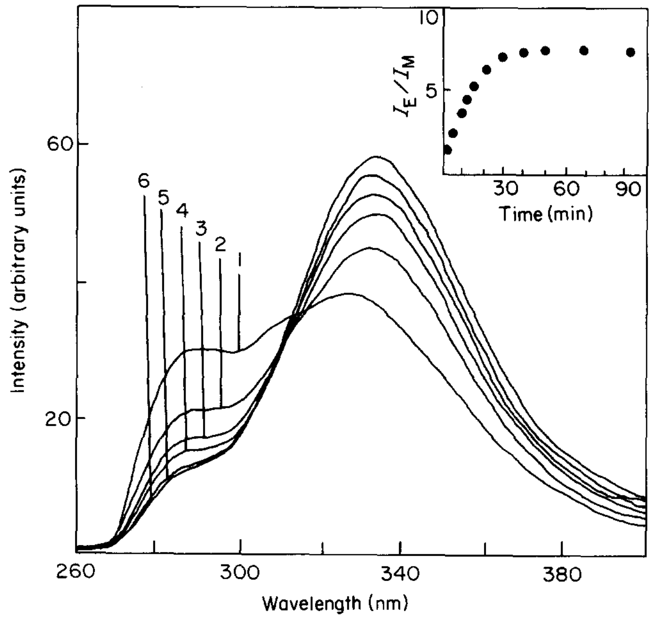


Figure 3 Changes in the fluorescence emission spectrum of iPS gel during annealing at 318 K: (1) 0 min, (2) 4 min, (3) 9 min, (4) 14 min, (5) 20 min, (6) 30 min. Insert: dependence of ratio I_E/I_M on time of annealing

Table 1 Fluorescence decay parameters for iPS gel after annealing at 318 K, fresh gel and crystalline iPS

λ_{EM} (nm)	τ_1 (ns)	τ_2 (ns)	B_1 (%)	B_2 (%)	χ^2
iPS gel after 0.5 h of annealing at 318 K					
310	8.6±0.5	18.5±0.6	59.6	40.4	1.35
330	11.3±0.3	24.5±0.2	60.1	39.9	0.98
340	12.7±0.4	25.9±0.6	56.8	43.2	1.26
Fresh gel before annealing					
310	5.4±0.3	18.3±0.2	31.6	68.4	1.17
330	5.9±0.5	18.5±0.2	19.8	80.2	1.15
350	11.6±1.3	19.6±0.5	18.4	81.6	1.19
Crystalline iPS gel					
310	3.7±0.6	19.6±0.6	27.2	72.8	1.27
330	5.2±0.3	21.0±0.3	11.9	88.1	0.99
350	4.7±0.6	21.6±0.2	6.9	93.1	1.09

Changes in the lifetime parameters with change in the emission wavelength suggest that more than one excimer structure may be contributing to the emission spectrum. Previous studies have established that the fresh iPS gel is frozen in an extended conformation and that the crystalline iPS has a three-fold helix conformation[11–13]. The introduction in the iPS/BA of crystalline material before quenching leads to a system that contains both extended and three-fold helix types of conformations. Time-resolved emission spectra of iPS gel after annealing at 318 K (*Figure 4a*), and for comparison the time-resolved spectra of a quenched mixture of crystalline and gel material (*Figure 4b*), show a strong similarity between these systems. Component 1 (*Figure 4b*) was identified with the short-lived excimer associated with the extended conformation of the chain. Component 2 has an excimer emission of 21 ns (*Table 1*) and corresponds to the three-fold helix conformation in the crystalline phase[10]. The time-resolved spectrum of component 2 is similar to that of the steady-state fluorescence spectrum of the 68% crystalline iPS gel ('dotted' curve in *Figure 4b*). The time-resolved spectrum in *Figure 4a*, obtained immediately after excitation and with time interval 7 ns, agrees well with component 2 in *Figure 4b*. This emission is associated with the crystalline phase of the iPS gel. Spectrum 2 in *Figure 4a* obtained with delay 46 ns and time interval 46–128 ns and spectrum 3 with time interval 88–244 ns are identical and agree with component 3 in *Figure 4b* and are associated with the polymer-rich phase generated after phase separation. This excimer structure has been observed in the fluorescence studies of phase separation of the gel at low temperatures and studied over long times, and are discussed separately[18].

A linear combination of components 2 and 3 using the parameters obtained from the decay analysis (*Table 1*) may be used to predict the theoretical spectrum for the two-phase excimer emission. The total intensity (*Figure 5*, curve 1) was calculated using:

$$I = 0.6(\text{component 2}) + 0.4(\text{component 3}) \qquad (12)$$

and can be compared with the experimental spectrum of the annealed iPS gel. Comparison of the experimental and theoretical curves indicates that differences are observed at short wavelength due to monomer and to some degree the extended conformation contributing to the spectrum and not included in the theoretical curves. The generally good agreement between the theoretical and experimental curves supports the assumption that the emission arises from a two-phase system. Previous investigations have shown that crystalline iPS is very effective at fluorescence and may be attributed to the specific topography of the chain. In the crystalline three-fold helix conformation of the chain, parallel phenyl groups are separated by a distance of 6.63 Å[12] and packed into a lamellar structure about 57 Å thick with an interchain distance of 7.3 Å[19], which is too large for excimer formation but is close enough for efficient energy migration[1]. The structure of the crystalline phase favours exciton energy migration along the helix to the lamellae boundary where it is finally trapped in the interphase region. It has been established that all of the chromaphores associated with the crystalline and only 20% of those in the amorphous state participate in the excimer

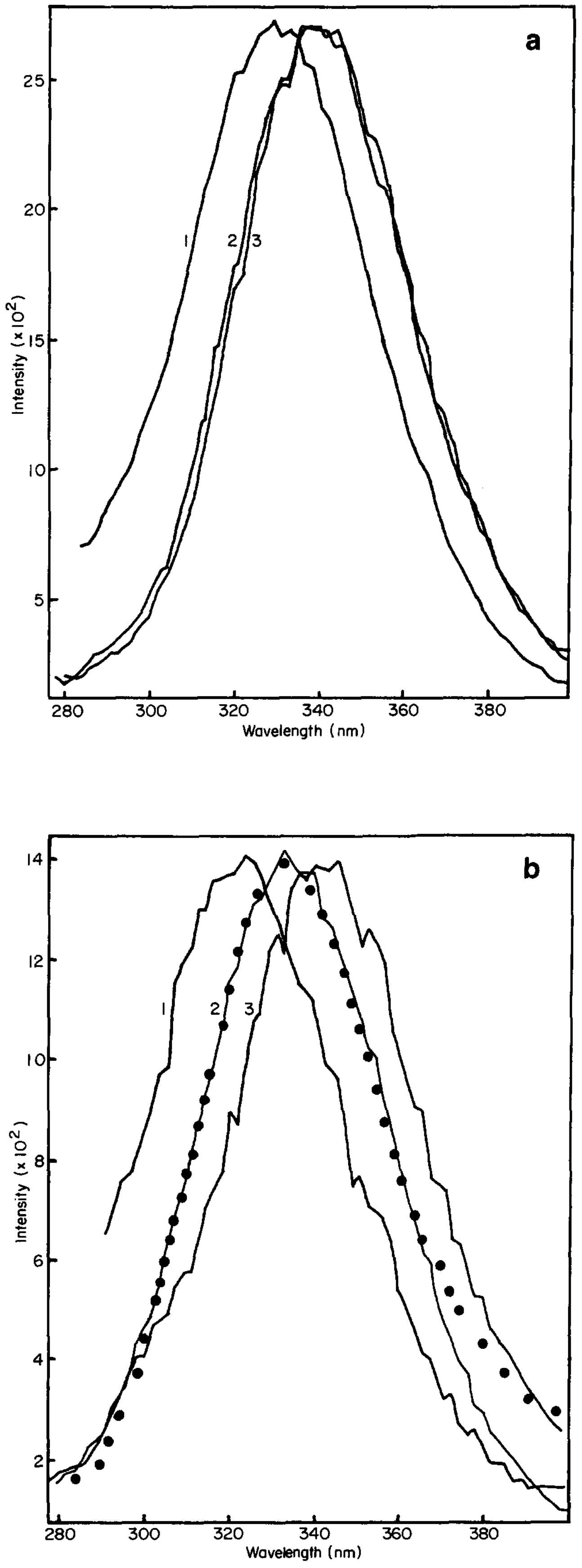


Figure 4 Time-resolved fluorescence emission spectra: (a) iPA gel after annealing at 318 K. Spectra obtained with time intervals: (1) 0–7 ns, (2) 76–128 ns, (3) 88–277 ns. (b) Modelled fresh iPS gel with suspended crystalline material. Spectra obtained with time intervals: (1) 0–5 ns, (2) 7–16 ns, (3) 71–149 ns. The 'dotted' curve is the steady-state fluorescence of crystalline (68%) iPS gel

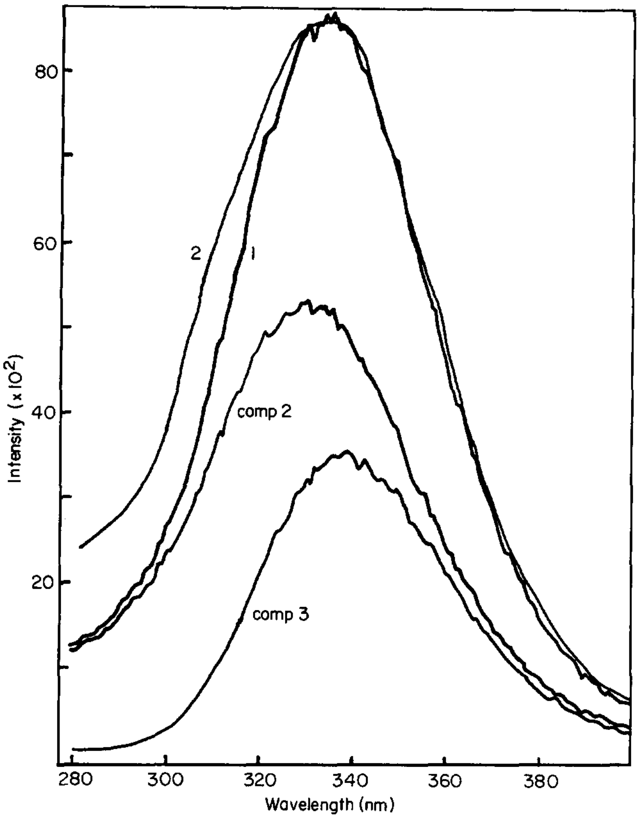


Figure 5 The spectrum estimated using the equation $I = 0.60$(comp 2)$+0.40$(comp 3) is shown as curve 1; the steady-state fluorescence emission spectrum of iPS gel after 0.5 h of annealing at 318 K is shown as curve 2

emission. Using this information the probable percentage of the emission of the crystalline phase of a gel annealed at 318 K (*Figure 4b*, curve 2) can be calculated as being 60.5% and there is a red-shifted component (curve 3) which corresponds to 39.5%. These percentages agree well with similar estimates based on analysis of the fluorescence decay data (*Table 1*).

CONCLUSIONS

Good agreement is observed between the theoretical spectrum and the steady-state excimer emission spectrum of iPS gel annealed at 318 K (*Figure 5*), confirming the validity of the two-phase photophysical mechanism proposed in this paper. Consideration of the structure of the crystalline helical conformation suggests that there are no pre-excimer sites inside the lamellae and all the emission occurs at the interfacial boundary. The interfacial region is rich in pre-excimer sites, which trap the excitons, and inhibit escape of photo energy to the other phases.

ACKNOWLEDGEMENTS

One of us (BW) wishes to thank the Royal Society and the University of Strathclyde for financial support during part of this study.

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