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**ENERGY MIGRATION, MOTION AND ORDER
IN SYNTHETIC POLYMERS**

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Seventh Periodic Report

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This report is on the final phase of the three year programme of work supported under the terms of this contract. The report is divided into two sections, that dealing with evanescent wave-induced fluorescence of polymer-surface interactions, and that dealing with the fluorescence of synthetic polymers in solution.

Evanescent wave-induced fluorescence spectroscopy

Earlier work describing the setting up and performance of a time-resolved evanescent wave-induced fluorescence spectrometer has been fully written up¹, and a copy of the paper (in press) is appended.

The emission properties of soluble polydiacetylenes have received considerable attention over the past few years, since they exhibit dramatic solvato, thermo and electrochromic effects. The evidence for 1D exciton diffusion in conjugated polymeric systems of this type promotes investigations for the theoretical modelling as well as the technological importance in optical molecular electronics.

The mechanisms responsible for the spectral shifts in both absorption and emission (where observable) is attributed to the degree of disorder in the conjugated π -electron backbone. In the disordered systems such as those induced by higher solubilities of high temperature solutions or better solvents, the conjugation is disrupted which reduces the effective conjugation length and results in a shift to higher energy of both the absorption and emission spectra.² Conversely, a reduction in the solubility causes order in the polymer backbone and results in a shift to lower energies of the absorption and emission spectra, although in some cases the increased order also reduces the fluorescence quantum yield to an undetectable level. The structural deformations responsible for the observed changes in conjugation is an area of controversy.³ In disordered systems it is not clear whether the forms, the existence of solvated single chains is debated.

Polymers based on fully conjugated backbones exhibit large non-linear optical

effects. The technological importance of this property is one of the major driving forces for a greater understanding of the relationship between the microscopic molecular properties and the macroscopic optical effects. The preparation of good quality optical waveguides based on these materials is essential to the evaluation of the non-linear properties. Soluble forms of the polymers provide a means for the preparation of the waveguides by the simple spin coating technique, where solutions of the polymers are spun onto a glass substrate. However, the solvating side-group can be a major influence on the extent of conjugation.

The aim of the present study was to use the well known fluorescence properties of 4BCMU as a method of studying the molecular influence on the quality of the thin films used for the optical waveguides. In particular, the interfacial region between the 4BCMU and the glass substrate was of interest as it is a major influence on the optical guiding properties of the film.

Using evanescent-wave induced fluorescence spectroscopy, emission from the soluble polydiacetylene, 4BCMU, has been studied at a fused silica/2-methyltetrahydrofuran solution interface.⁴

Figure 1 shows that the red (R) form of 4BCMU in poor solvent (CHCl_3 /Hexane) gives a fluorescence centred at 550nm, and that in the evanescent wave experiment, where the bulk solution is probed (marked ewif in Figure 1), an identical result is obtained. The yellow (Y) form of 4BCMU in good solvent (2MeTHF) has a fluorescence at 525nm, which is reproduced in the ewif experiment in the bulk (Figure 2).

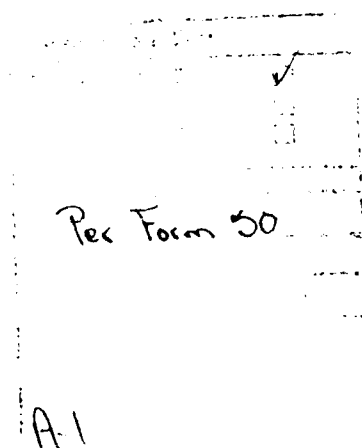


Figure 1

Bulk and Evanescent-Wave induced Fluorescence Spectra
of an R-Form 4BCMU solution. (CHCl₃/Hexane)

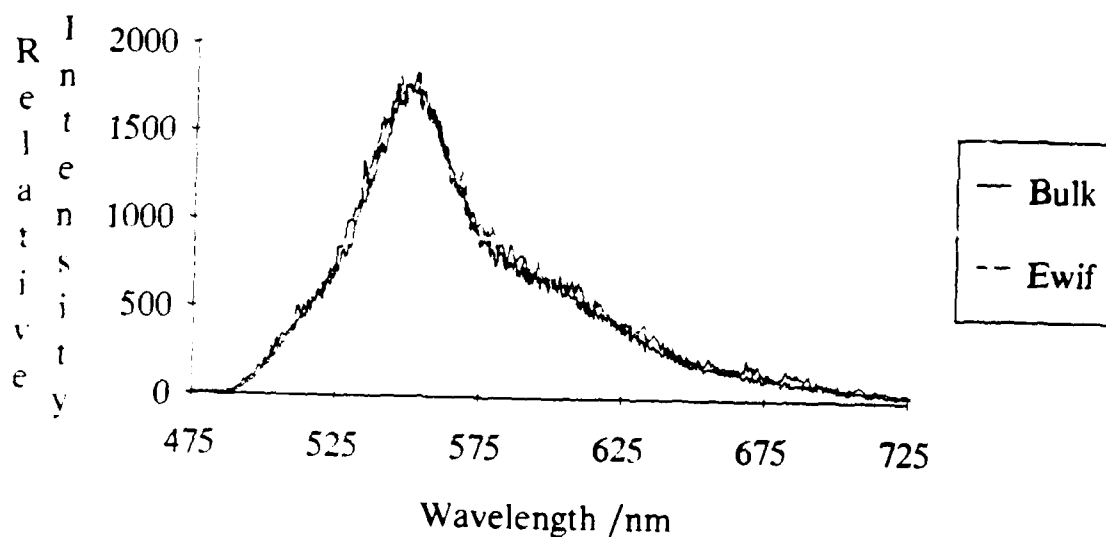


Figure 3 shows the emission spectra at the interface for a Y solution of 4BCMU presented to a clean fused silica surface. The emission spectra are seen to change for up to three hours from the time when the interface is first made. Initially, the emission has a maximum at 520nm, which rapidly shifts to 550nm and then reduces to an equilibrium profile. Two spectrally distinct species can be identified which correlate with the ordered (R) and disordered (Y) forms of the polymer. The changes in spectra are related to the conformational reorganisation of the polymer at the solid solution interface, with evidence for polymer folding.

Figure 2

**Bulk and Evanescent-Wave induced Fluorescence
Spectra of a Y-Solution of 4BCMU. (2MeTHF)**

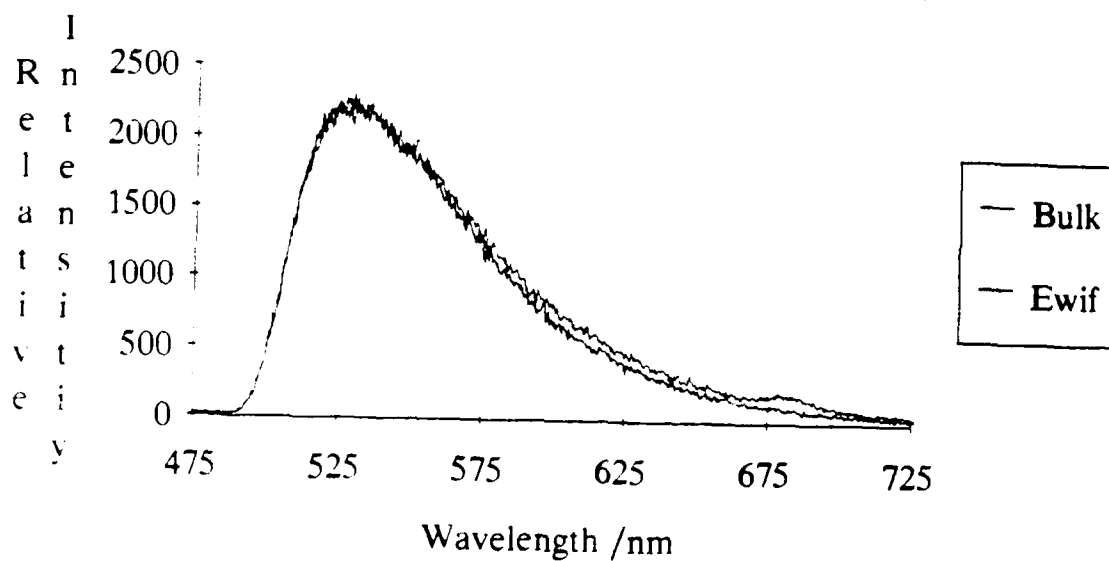
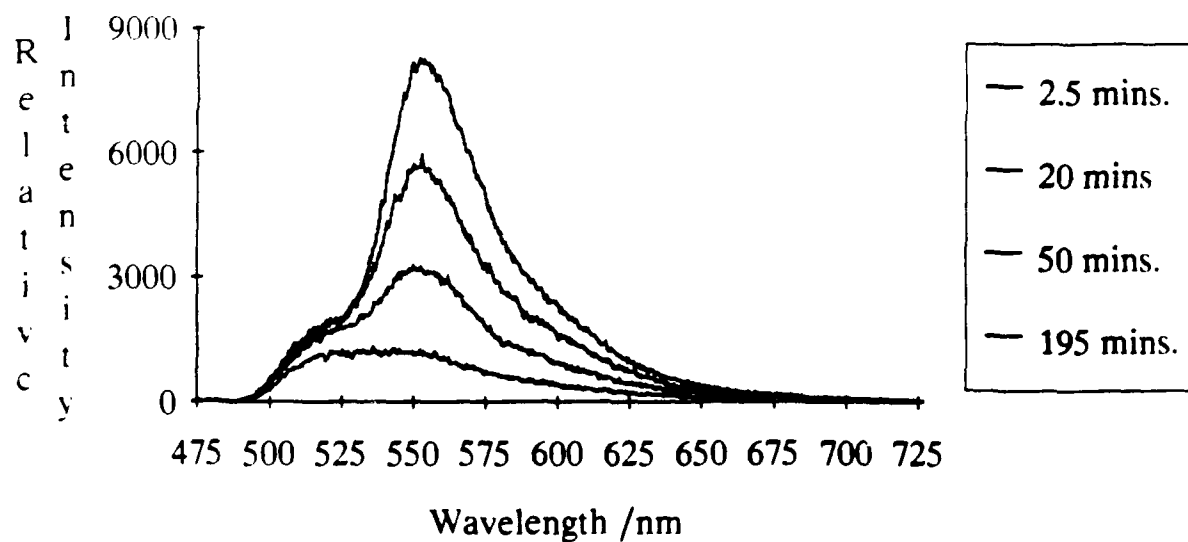


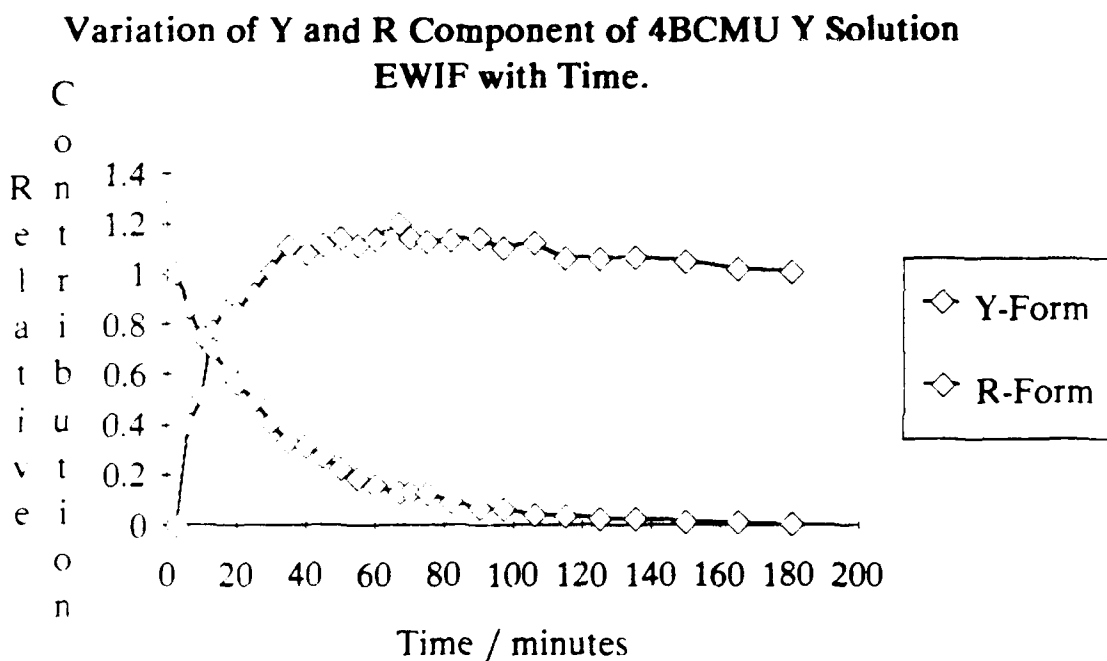
Figure 3

**Evanescent-Wave induced Fluorescence Spectra of
a Y-solution of 4-BCMU.**



The changes from red to yellow forms which occur near the surface on a time-scale of 3-300 minutes follow first-order kinetics, as shown in Figure 4. The implication of these results are still being assessed, and will be included in the final technical report of this contract, due shortly.

Figure 4



Luminescence in vinyl (aromatic) polymers

As outlined briefly in the Fifth periodic report on this grant, results obtained on poly(styrene) are at odds with earlier results concerning the extent to which electronic energy migration contributes to the population of 'excimer' sites in poly(vinyl aromatic) polymers in solution and bulk phases. A critical evaluation of the reverse dissociation

in poly(styrene) in solution using better time resolution has led to the conclusion that this process is absent in this polymer, despite earlier evidence that it occurred. A brief paper reporting this is in press (copy appended)⁵. A full review of the implications of our recent findings upon the reinterpretation of the relative importance of energy migration and segmental motion in populating excimeric trap sites in polymers is in preparation, and will be included in the final report on this contract.

A brief study has also been carried out on the fluorescence from atactic poly(styrene) films, cast from solution. In this study, care was taken to avoid continuous exposure of the film to excitation radiation at 257.25nm, as this has been shown to give rise to fluorescent products which complicate subsequent analysis.

At 298 K, the total fluorescence spectrum is dominated by excimer emission, whereas at 77 K, the spectrum is dominated by monomeric emission, as is that of attractive polystyrene dispersed in poly(vinyl methyl ether). The propensity for excimer formation is thus strongly correlated with the freedom of motion of the aromatic moiety. This could be due to there being low rotational energy barriers to inter molecular excimer formation, or a temperature dependence to intermolecular energy migration in these solids. An attempt was made to investigate this by close analysis of the kinetics of the excimer forming process using picosecond laser excitation. Fluorescence decay data recorded in the excimer region could be well fitted to a single experimental decay with a lifetime of 20ns. That a risetime was also present was established (thus indicating a time-dependence of population, i.e. excimer sites are not preformed), but the details of this risetime were beyond the resolving power (100ps) of the present apparatus.

References

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Derivations in the fluorescence lifetime of tetrasulphonated aluminium

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(2) Papers submitted or published during the period June 1990-November 1990 which acknowledged US Army support.

(i) Time-resolved evanescent wave-induced fluorescence spectroscopy I
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A.J. Brown, G. Rumbles and D. Phillips, JCS Faraday. 1991 (in press) (copy appended).

(ii) Excimer dissociation in dilute solutions of poly(styrene) and poly(2-vinyl naphthalene).

C.F.C. Porter, G. Rumbles and D. Phillips, Polymer, 1991 (in press) (copy appended).

(iii) Time-dependent surface induce chromism in the soluble poly(diacetylene) 4BCMU : an evanescent wave-induced fluorescence study.

G. Rumbles, A.J. Brown, D. Phillips and D. Bloor, Chem. Phys. Letters (to be submitted shortly).

(3) During this period US Army funds were used for laser optics, computing hardware and software, chemicals, refrigerants, laser dyes and other consumable items.

(4) —

(5) Annex (a) Amount of unused funds remaining in contract at end of report -Nil-
(b) No important new property was acquired during this period.

Time-resolved Evanescent Wave Induced Fluorescence Spectroscopy

Part 1.—Deviations in the Fluorescence Lifetime of Tetrasulphonated Aluminium Phthalocyanine at a Fused Silica/Methanol Interface

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Evanescent wave induced fluorescence spectroscopy and time-correlated single-photon counting have been combined to provide a method of studying the fluorescence decay profiles of fluorophores at a solid/solution interface. Using these techniques the photophysical properties of tetrasulphonated aluminium phthalocyanine (AIS₄Pc) in methanol and water solution have been studied at fused silica interface. In a poor solvent, such as methanol, AIS₄Pc is shown to form an adsorbed monolayer on the fused silica surface and exhibit a fluorescence decay profile that deviates from the simple, first-order, single-exponential kinetics of the bulk solution. By changing the solvent to water, which is a good solvent for AIS₄Pc, the surface/bulk differences are not observed.

The ability of time-resolved fluorescence spectroscopy to distinguish between concentration and quantum-yield effects on evanescent wave induced fluorescence intensity, is clearly demonstrated.

When light in a medium of refractive index, n_1 , encounters a medium of lower refractive index, n_2 , two processes can occur when the angle of incidence is less than the critical angle Θ_c , defined by Snell's law as $\Theta_c = \sin^{-1}(n_2/n_1)$, refraction occurs; for angles of incidence $> \Theta_c$ total internal reflection occurs. The name total internal reflection (TIR), however, is a misnomer, as it implies that all of the light remains within the more refractive medium. This is not the case, as predicted by Maxwell's equations of electromagnetic radiation,^{1,2} since a small amount of light penetrates the lower refractive medium in the form of a standing wave that decays exponentially in intensity with distance from the interface and is known as an 'evanescent' wave. If the lower refractive medium contains a chromophore that can absorb the wavelength(s) of light that are incident at the interface, then they can absorb the light within the evanescent wave. This principle can be combined with conventional spectroscopic techniques, such as IR,³ UV-visible,^{2,3} Raman^{4,5} and fluorescence spectroscopy,⁶⁻³⁴ to study molecules of interest at a solid interface, at distances that are a fraction of the wavelength of the incident light. The less refractive medium can take the form of a fluid solution, a solid film or even a gas, with the only limitation being that the refractive index is lower than that of the solid medium, for the wavelength of light used (IR, visible, UV). It is also possible to modify the nature of the surface without unduly affecting the nature of the evanescent wave, this therefore provides a method of studying surface interactions with simple spectroscopic techniques. Early experiments were based on IR and UV-visible absorption spectroscopies and developed under the name of attenuated total internal reflection (ATR) and have been well reviewed.² As with most spectroscopic absorption techniques, it was necessary to develop methods of overcoming the inherent insensitivities, which were further hindered by the small interaction length between the light and the absorbing solution. These were overcome in a number of ways, the most common of which was the use multiple reflections, with a number of elaborate experimental configurations leading finally to the use of planar dielectric waveguides.^{9,35} However, in recent years there has been a renewed interest in

the application of single-reflection techniques promoted by the availability of intense laser light sources and improvements in signal detection equipment. Total internal reflection fluorescence (TIRF), or more precisely, evanescent wave induced fluorescence (EWIF) spectroscopy, as well as a Raman analogue have been employed by a number of scientific disciplines, ranging from biophysics¹⁰⁻¹⁹ to polymer photophysics.²⁰⁻²⁸

One of the most recent controversies in the field of EWIF concerns the effects of the surface on the photophysical properties of the fluorophore. Steady-state measurements assume that the properties close to the surface, specifically the fluorescence quantum yield,²¹⁻²⁶ are the same as in the bulk. In addition, there are incidences where the knowledge of the homogeneity of a solution from the bulk to surface is required, in order to provide a reference for more complex systems. This often requires modification of the surface in order to render it inert.^{21-27,36} Time-resolved fluorescence spectroscopy has the potential of resolving some of these controversies and confirm assumptions, since any changes in the photophysical properties of the chromophore will be reflected in the fluorescence decay profile.^{20,29-32} Indeed, it has shown that the photophysical properties of the scintillator, POPOP, differ as a function of the proximity to a solid surface when dissolved in a polymer matrix.^{20,29} In this paper we use time-resolved evanescent wave induced fluorescence, (TREWIF), spectroscopy to investigate the photophysical properties of tetrasulphonated aluminium phthalocyanine (AIS₄Pc) in methanol and water solutions. AIS₄Pc is a well characterised dye that exhibits a simple single-exponential decay profile in dilute solution and has interesting binding properties with applications in photomedicine³⁷ and molecular electronics.³⁸

Experimental

Fluorescence decays were recorded by time-correlated single-photon counting³⁹ using a cavity-dumped, synchronously pumped, mode-locked dye laser (Coherent Antares/701-3CD 7220) as an excitation source ($\lambda_{ex} = 590$ nm). The light, polarised perpendicular to the plane of excitation and detection (s-polarised), was focused, using a 15 cm focal length lens, onto the interfacial region. Fluorescence was collected perpendicular to excitation using an f collection lens, which

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focused the emission onto an iris and was detected subsequently using a red-sensitive photomultiplier tube (Hamamatsu R955) with a cut-off filter (Schott RG645) placed in front of it to remove any scattered laser light. To record spectra, the cut-off filter was replaced by a 1.4 m monochromator. Although the pulses from the laser are 10 ps in duration, the slower response of the detection electronics results in a convoluted instrument response function of ca. 500 picoseconds. The sample was contained in a modified cuvette which allowed the solution to come into contact with the flat side of a hemispherical prism (Spanoptic, $n_1 = 1.46$). A detailed characterisation of the set-up can be found elsewhere.³³ The surface of the prism was thoroughly cleaned with sulphuric acid and water, but was otherwise untreated. AlS_4Pc was obtained by the sulphonation of aluminium phthalocyanine and purified by medium-pressure liquid chromatography.⁴⁰ Water and methanol (BDH HPLC grade) were tested to ensure that no extraneous emission was observable and were used without further purification. Fluorescence decays on the bulk of the sample were recorded by using the prism to refract the light into the sample cuvette, and the collection optics translated to ensure that no emission from evanescent region could be simultaneously detected. All decays were recorded to a minimum of 20 000 counts in the channel of maximum intensity and analysed by a non-linear least-squares iterative deconvolution program, with global analysis,⁴¹ using the reduced χ^2 , serial correlation coefficient, and plots of weighted residuals and autocorrelation function as a method of determining the quality of fit.

Theory

To understand fully the implications of the concentration and angle effects, discussed later, it is necessary to outline some of the mathematics which define the relationship between the evanescent wave and the observed fluorescence intensity.^{2,34}

For vertically or s-polarised light, the intensity of the evanescent wave as a function of distance, z , perpendicular to the interface is given by

$$I_{\text{evan}}(z, \Lambda) = U(\Theta) \exp(-z/\Lambda) \quad (1)$$

where Λ is termed the penetration depth and is related to the wavelength of the light, λ , the refractive index of the solution, n_2 , the angle of incidence Θ_i , and the critical angle for the prism, Θ_c , by

$$\Lambda = \frac{\lambda}{4\pi n_1 \sqrt{(\sin^2 \Theta_i - \sin^2 \Theta_c)}} \quad (2)$$

and $U(\Theta)$ is the energy density at $z = 0$, and is also related to the angle of incidence and refractive indices, by

$$U(\Theta_i) = 4 \cos^2 \Theta_i [1 - (n_2/n_1)^2] \quad (3)$$

From eqn (2) it can be seen that there are two limiting cases for Λ . As Θ_i deviates from the critical angle and approaches 90° , a limiting penetration depth given by

$$\Lambda_{\text{lim}} \rightarrow \lambda [4\pi n_1 \sqrt{(1 - \sin^2 \Theta_c)}] \quad (4)$$

is attained and for the system described here is 780 Å, assuming that the concentration of the AlS_4Pc is sufficiently dilute, so as not to affect the refractive index of the solvent. As Θ_i approaches Θ_c , Λ approaches infinity and refraction occurs. The total intensity of the evanescent light at any angle of incidence greater than Θ_c , is given by

$$I_{\text{tot}}(\Lambda) = \int_0^\infty U(\Theta) \exp(-z/\Lambda) dz \quad (5)$$

Therefore for a fluorophore dissolved in the solvent, the intensity of fluorescence that would result from $I_{\text{tot}}(\Lambda)$, would be

$$I_{\text{fl}}(\Lambda) \propto \int_0^\infty \phi(z) c(z) U(\Theta) \exp(-z/\Lambda) dz \quad (6)$$

Where $\phi(z)$ and $c(z)$ are the fluorescence quantum yield and the concentration profile of the fluorophore in the interfacial region. For homogeneous solutions that extend up to the surface, such that $\phi(z)$ and $c(z)$ are independent of z and are therefore constant, and eqn. (6) reduces to

$$I_{\text{fl, hom}}(\Lambda) \propto U(\Theta) \phi c \Lambda \quad (7)$$

If this assumption is valid, then measurements of fluorescence intensity from the evanescent wave can be used to verify the existence of the evanescent wave and prove the theory which describes it.^{21-27,34}

A more general treatment, without the assumptions above, can be developed as follows. The fluorescence quantum yield, ϕ , and lifetime, τ_f , are related by:

$$\phi = k_r \tau_f \quad (8)$$

where k_r is the rate constant for radiative decay of the fluorophore. Assuming that k_r is independent of environment, then eqn. (6) can be rewritten as:

$$I_{\text{fl}}(\Lambda) = k_r \int_0^\infty \tau_f(z) c(z) U(\Theta) \exp(-z/\Lambda) dz \quad (9)$$

Results and Discussion

Fluorescence decays of AlS_4Pc in bulk methanol and water, were well described by a single-exponential decay function with lifetimes of 5.8 ± 0.1 and 6.0 ± 0.1 ns, respectively. These results demonstrate the purity of the samples, the ability of the instrument to record simple decays, and also provide a functional form of decay from which any surface induced deviations can be easily compared.

Concentration Effects

Using methanol as a solvent ($n_1 = 1.328$) a series of decays were recorded at different bulk concentrations using the evanescent wave as the excitation source, at the limiting penetration depth of 870 Å ($\Theta_i \approx 77^\circ$). Starting with an initial absorbance of 1.0 and reducing the concentration by a factor of two between measurements, 10 decays were recorded, four of which are shown in Fig. 1 and are normalised to the channel of maximum intensity. The most noticeable observation is the asymptotic approach, with successive dilutions, to

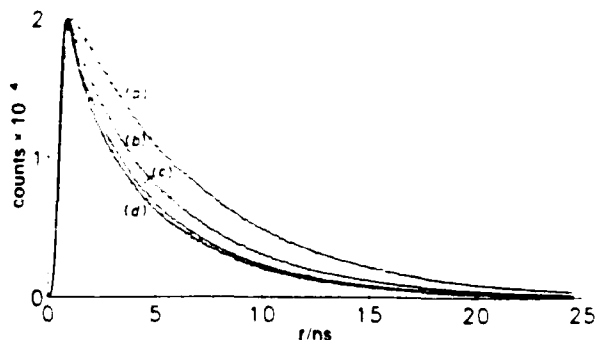


Fig. 1 Evanescent wave induced fluorescence decay profiles of AlS_4Pc in methanol at a penetration depth of 870 Å and at a bulk concentration (absorbance) of: (a) 1.0, (b) 0.063, (c) 0.004 and (d) 0.00.

the decay recorded at infinite dilution, at which point no appreciable amount of sample resides in the bulk of the solution. This indicates that the AlS_4Pc must be binding to the surface of the fused silica prism. Indeed, repeated flushing of the surface with methanol failed to eliminate the fluorescence signal. The second observation is the difference in the functional form of the decays as a function of bulk concentration. If the solution were homogeneous up to the surface, then no difference in the decays would be observed, with decays exhibiting single exponential behaviour at all concentrations.

Angular Dependence

Using a sample with an absorbance of 0.1, the influence of the angle of incidence on the decay profiles was studied, the results from which are shown in Fig. 2. The angle of incidence influences the intensity profile of the evanescent wave,

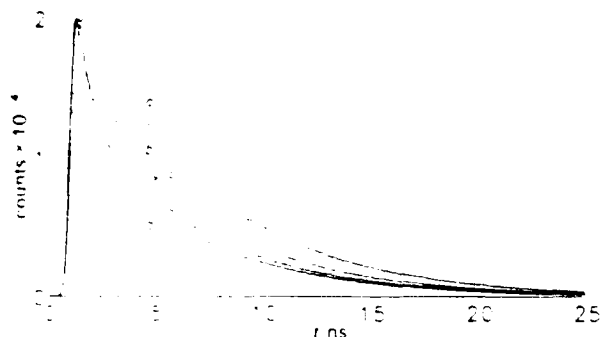


Fig. 2. Evanescent wave induced fluorescence decay profiles of AlS_4Pc in methanol at a bulk concentration (absorbance) of 0.1 and at angles of incidence: (a) 64.42° , (b) 66.67° , (c) 70.13° and (d) 77.42° , corresponding to penetration depths of: (a) refraction, (b) $1990 \text{ \AA}$, (c) $1230 \text{ \AA}$ and (d) $870 \text{ \AA}$.

as discussed in the theory section, and is summarised by eqn (1) and (2). In a similar fashion to the concentration data, the decay profiles change with increasing angle, asymptotically approaching a common profile in the limiting case as the angle of incidence approaches 90° . The dependence of the decay profile on the angle, once again demonstrates the effects of the interface on the transient photophysical properties of the AlS_4Pc . Unlike fluorescence intensity measurements, the fluorescence decay profiles are independent of $U(\theta)$ and depend only upon the penetration depth, Λ .

Two conclusions can instantly be drawn from these data: first, the AlS_4Pc is adsorbed on the fused silica and the concentration at the surface is independent of the bulk concentration. Secondly, the fluorescence lifetime of the AlS_4Pc , at the surface, differs from the bulk value. Since the fluorescence lifetime and quantum yield are related, any changes in the lifetime, as a result of a change in a radiative or non-radiative rate of decay, will also be reflected in the quantum yield. Therefore the assumptions made in simplifying eqn. (6) to eqn. (7), in the theory section, cannot be made here.

To quantify the changes in the fluorescence decay profile as a function of concentration and angle, the decays were analysed in terms of a sum of exponentials, i.e.

$$I_n(t) = \sum_{i=1}^{n-1} A_i \exp(-t/\tau_i) \quad (10)$$

The results of this analysis are given in Table 1. In all cases the number of exponentials, n , required to describe the fluorescence decays, was the minimum required for achieving a good fit. In the majority of cases the number was three, with the major component, $>80\%$, having a lifetime of $ca. 5.5 \pm 0.6 \text{ ns}$. This value is similar to the value derived from bulk measurements. The next most significant lifetime is $ca. 1.6 \pm 1.0 \text{ ns}$, constituting $ca. 10\%$ of the decay, and finally a third component of $ca. 0.4 \pm 0.3 \text{ ns}$. The lifetimes recovered are similar from both the concentration data and the angle

Table 1. Experimental analysis of fluorescence decays

	c_{bulk}	A_B	yield _B (%)	τ_1	A_1 ps	yield ₁ (%)	τ_2	A_2 ps	yield ₂ (%)
concentration (absorbance units)									
1	6004	0.97	99	1050	0.03	1	0	0.00	0
0.5	5555	0.95	99	1461	0.05	1	0	0.00	0
0.25	567	0.88	97	1178	0.12	3	0	0.00	0
0.125	5525	0.67	94	1552	0.12	5	117	0.27	1
0.063	5513	0.50	90	1620	0.16	9	129	0.34	1
0.031	5155	0.52	87	1705	0.20	11	225	0.28	2
0.016	5035	0.45	86	1669	0.21	12	184	0.31	2
0.008	4975	0.45	85	1676	0.22	13	220	0.30	2
0.004	4917	0.45	83	1714	0.21	14	209	0.34	3
0	4979	0.38	79	1844	0.22	17	220	0.40	4
angle*									
77.42	5510	0.26	83	1392	0.15	12	161	0.58	5
72.42	5507	0.30	87	1417	0.16	12	179	0.05	1
72.42	5496	0.29	84	1342	0.16	11	162	0.55	5
71.28	5525	0.31	84	1481	0.16	11	183	0.54	5
70.13	5617	0.33	85	1486	0.15	10	181	0.53	4
68.99	5614	0.33	87	1452	0.14	9	163	0.53	4
67.85	5647	0.36	89	1398	0.13	8	147	0.51	3
66.67	5671	0.41	90	1517	0.11	7	163	0.48	3
65.79	5683	0.51	94	1296	0.09	4	142	0.39	2
65.56	5670	0.41	97	1215	0.04	2	59	0.56	1
65.45	5747	0.58	98	1480	0.03	1	87	0.38	1
65.35	5767	0.41	98	1692	0.02	1	41	0.57	1
65.11	5832	0.95	976	3556	0.05	3	0	0.00	0
64.42	5784	1.00	100	0	0.00	0	0	0.00	0
57.42	5778	1.00	100	0	0.00	0	0	0.00	0
47.42	5795	1.00	100	0	0.00	0	0	0.00	0

* At a penetration depth, Λ_{ev} , of $870 \text{ \AA}$. * At a bulk concentration, c_{bulk} , of absorbance = 0.1

data. The relative fluorescence intensities that correlate with each lifetime can be calculated from:

$$\text{yield}_i = A_i \tau_i / \sum_{j=1}^{j=n} A_j \tau_j \quad (11)$$

In many instances the number of measured lifetimes is a reflection of the number of non-interacting fluorescent species contributing to the decay. On this basis there are three different AlS_4Pc species in the interfacial region. The major component represents a species whose properties are similar to those of the bulk, whilst the other two represent two quenched species, perhaps one adjacent to the interface and the other fixed on it. On this basis the relative contribution of the 5.5 ns component to the decay, would decrease in yield, as the penetration depth decreased or as the concentration was decreased, reflecting the percentage of the evanescent wave probing the bulk of the solution. Coinciding with the decrease in the major component, an increase in the percentage yield of the minor components would also be observed, and indeed this is the case, lending credibility to this hypothesis. However, this theory does not give any reasoning for the change in lifetimes as a function of angle or concentration. For example the lifetime of the 'bulk' species is 5.0 ± 1.0 ns at infinite dilution but increases to 6.1 ± 0.1 ns at the highest concentration. It must be recognised that all the parameters are derived from a non-linear least-squares fit to the measured data, which, although it is of exceptional quality, does require a minimum of six variable parameters to describe it. Consequently, any apparent trend of any lifetime or percentage yield with angle or concentration, may be a consequence of the fitting procedure, which does not give any indication of the correlation between the parameters. If the three non-interacting species theory is correct, then all three lifetimes recovered from a set of experiments should be the same, independent of angle or concentration, and the differing amounts

of each species reflected in the pre-exponential A factors. To test this theory, all the fluorescence decays from both the angle and concentration data were analysed globally,⁴¹ where three lifetimes common to all the decays were calculated. In every case an excellent fit was obtained, with an average reduced χ^2 of <1.1 and no single decay having a reduced χ^2 >1.2. The results of this analysis are given in Table 2 with the three common lifetimes of 6.1, 3.4 and 0.6 ns.

For the AlS_4Pc molecules bound to or in the vicinity of the interface, the interaction of the surface could induce a change in the fluorescence spectrum. To examine this idea, two emission spectra were recorded and these are shown in Fig. 3. Spectrum (a) corresponds to spectra recorded at early time (0–10 ns) on the infinite dilution sample, while spectrum (b) corresponds to a total fluorescence spectrum of the bulk species. The total fluorescence spectrum of the bulk species peaks at 680 nm, whilst spectrum (a) is red shifted, by 10 nm, to 690 nm. This indicates that the species which emit at early

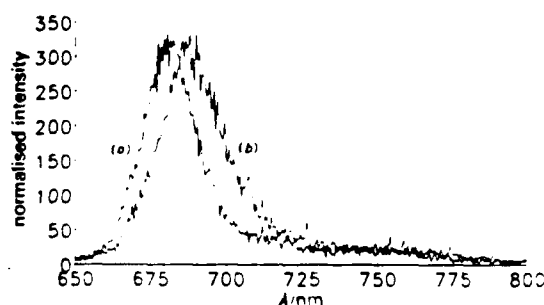


Fig. 3 Fluorescence spectra of AlS_4Pc in methanol, recorded (a) under refraction conditions, corresponding to a 'bulk' spectrum and (b) an early gated (0–10 ns), evanescent wave induced fluorescence spectrum, recorded at a penetration depth of 870 Å and a bulk concentration (absorbance) of 0.004

Table 2 Global analysis of fluorescence decays

concentration ^a (absorbance units)	yield ₁ (%)	yield ₂ (%)	A_0	A_1	A_2	$\lambda/\text{Å}$
1.00	99	0	1	0.040	0.000	0.003
0.50	95	4	1	0.040	0.003	0.003
0.25	88	11	1	0.030	0.007	0.004
0.125	80	18	2	0.050	0.020	0.010
0.063	71	27	2	0.022	0.016	0.008
0.031	61	35	4	0.017	0.017	0.008
0.016	58	38	4	0.014	0.017	0.009
0.008	53	42	5	0.013	0.018	0.010
0.004	54	42	4	0.013	0.019	0.011
0.002	50	44	6	0.007	0.012	0.008
angle ^b						
77.42	67	24	9	0.025	0.017	0.030
72.42	68	23	9	0.018	0.011	0.017
72.42	69	23	8	0.020	0.012	0.022
71.28	69	24	7	0.030	0.018	0.025
70.13	73	20	7	0.023	0.012	0.021
68.99	74	20	6	0.024	0.011	0.015
67.85	77	18	5	0.026	0.011	0.016
66.67	80	16	4	0.036	0.013	0.014
65.79	85	12	3	0.042	0.011	0.012
65.56	88	12	0	0.067	0.016	0.035
65.45	90	9	1	0.040	0.007	0.001
65.33	91	9	0	0.040	0.007	0
65.11	92	8	0	0.045	0.008	0
64.42	94	6	0	0.038	0.005	0
57.42	93	7	0	0.056	0.009	0
47.42	93	7	0	0.036	0.006	0

$\tau_0 = 6.1 \pm 0.1$ ns $\tau_1 = 3.4 \pm 0.3$ ns $\tau_2 = 0.6 \pm 0.3$ ns ^a At a penetration depth, λ_{im} , of 870 Å. ^b At a bulk concentration, $c_{\text{b, im}}$, of absorbance = 0.1. ^c Calculated using $\lambda = 590$ nm, $n_1 = 1.47$, $n_2 = 1.33$

times, and which are in the vicinity of the interface, are spectroscopically different from those that exhibit bulk phase properties and emit at later times. Spectroscopically there is evidence for only two non-interacting fluorescent species, although the contribution from the species assigned to the shortest lifetime is small and may not be spectroscopically observable.

In the case of infinite dilution, if it is assumed that the adsorbed layer(s) of AIS₄Pc are instantly formed on addition of the high-concentration solution, then the fluorescence decay corresponding to this case originates from the adsorbed layer only and can be considered as the 'surface' decay. The contribution of the 6.1 ns component to the 'surface' decay is ca. 50%, therefore even at infinite dilution there is a species within the evanescent wave that reflects the bulk environment. This is not too surprising, since even under these conditions some AIS₄Pc molecules will be desorbed from the surface into solution to set up a dynamic equilibrium. Assuming that the absorption coefficient of the adsorbed species is identical to that of the solution species, then the ratio of the measured pre-exponential factors are a direct measure of the ratio of adsorbed AIS₄Pc molecules to solution phase molecules within the evanescent wave.

The fluorescence decay from the adsorbed layer is biexponential and has been justified in terms of two non-interacting fluorescent species. This, however, may not be the case. The photophysical properties of an adsorbed species can be complex, with the possibility of self-quenching and energy transfer, as well as unusual polarisation effects that can lead to a non-exponential decay. The two lifetimes may therefore only be parametrising a more complex functional decay form. The approximation of two species is sufficient for the discussions here and future experiments will be aimed at elucidating the origins of the biexponentiality.

The conclusions drawn so far indicate that there exists an adsorbed layer of thickness, d , the concentration of which, on the timescale of these experiments, is independent of the bulk concentration, but may be related to the concentration of the original high-concentration solution. The fluorescence quantum yield within the adsorbed layer is constant and ca. one third of the bulk phase value. Beyond the adsorbed layer the solution resembles that of the bulk of the solution. If the concentration gradient between the two phases is small in comparison with the thickness of the adsorbed layer and the penetration depth of the evanescent wave, then the fluorescence intensity can, from eqn. (6), be written as

$$I_f(\lambda) = I_{ad}(\lambda) + I_{bulk}(\lambda) \quad (12)$$

$$= \phi_A c_A U(\Theta) \int_0^d \exp(-z/\Lambda) dz + \phi_B c_B U(\Theta) \int_d^\infty \exp(-z/\Lambda) dz \quad (13)$$

where $\phi_{A/B}$ is the fluorescence quantum yield of adsorbed/bulk species and $c_{A/B}$ is the concentration of adsorbed/bulk species. On integration, this reduces to

$$I_f(\lambda) = \phi_A c_A U(\Theta) \Lambda [1 - \exp(-d/\Lambda)] + \phi_B c_B U(\Theta) \Lambda \exp(-d/\Lambda) \quad (14)$$

Hence the ratio of fluorescence from the surface to that of the bulk is

$$\frac{I_{ad}(\lambda)}{I_{bulk}(\lambda)} = \frac{\phi_A c_A [1 - \exp(-d/\Lambda)]}{\phi_B c_B \exp(-d/\Lambda)} \quad (15)$$

The fluorescence intensity is proportional to the area under the fluorescence decay curve, i.e.

$$I \propto \int_0^\infty A \exp(-t/\tau) dt = A\tau \quad (16)$$

and for a biexponential decay

$$I \propto A_1 \tau_1 + A_2 \tau_2 \quad (17)$$

Therefore,

$$\frac{A_1 \tau_1 + A_2 \tau_2}{A_B \tau_B} = \frac{\phi_A c_A [1 - \exp(-d/\Lambda)]}{\phi_B c_B \exp(-d/\Lambda)} \quad (18)$$

Substituting for the quantum yield of the bulk, ϕ_B , from eqn. (8) and rearranging gives

$$\frac{A_1 \tau_1 + A_2 \tau_2}{A_B} = \frac{\phi_A c_A [\exp(d/\Lambda) - 1]}{k_t c_B} \quad (19)$$

If the thickness of the adsorbed layer, d , is much less than the penetration depth, Λ , the exponential term in eqn. (19) can be expanded into a Taylor series. By using only the first two terms in the expansion, eqn. (19) reduces to:

$$\frac{A_1 \tau_1 + A_2 \tau_2}{A_B} = \frac{\phi_A c_A}{k_t c_B} \left(\frac{d}{\Lambda} \right) \quad (20)$$

Therefore a plot of $1/\Lambda$ against $(A_1 \tau_1 + A_2 \tau_2)/A_{B \tau_B}$, at constant bulk concentration, $c_{B,lim}$, should also be a straight line with a gradient equivalent to $(\phi_A c_A/k_t d)/c_{B,lim}$. These data are shown in Fig. 4, and the line through the data points has a gradient of $2850 \pm 150 \text{ \AA ns}$. Similarly, a plot of $1/c_B$ vs. $(A_1 \tau_1 + A_2 \tau_2)/A_B$ at constant penetration depth, Λ_{lim} , should also be a straight line with a gradient of $(\phi_A c_A/k_t d)/\Lambda_{lim}$. However, in this case the value of the bulk concentration must be modified in order to take into account the small amount of bulk species resulting from the desorption process, as discussed earlier. The ratio of the gradient from the angle study, grad_a , to that from the concentration study, grad_c , is given by:

$$\text{grad}_c/\text{grad}_a = c_{B,lim}/\Lambda_{lim} \quad (21)$$

The limiting penetration depth for the concentration study, Λ_{lim} , was ca. 870 $\text{\AA}$, and the value of the concentration for the angle study, $c_{B,lim}$, was 0.1 (measured in absorbance units). Combining these values with the gradient from the angle study, grad_a , of 2850 $\text{\AA}$ implies that the gradient from concentration study should be 0.33 ns. By adding 0.05 to each concentration value the predicted linear relationship, discussed above, was obtained and is shown in Fig. 5.

The adsorbed layer, d , is assumed to be much smaller than the limiting penetration depth, Λ_{lim} (810 $\text{\AA}$), and since AIS₄Pc is ca. 20 $\text{\AA} \times 20 \text{\AA} \times 10 \text{\AA}$, this indicates that the adsorbed layer is probably a monolayer.

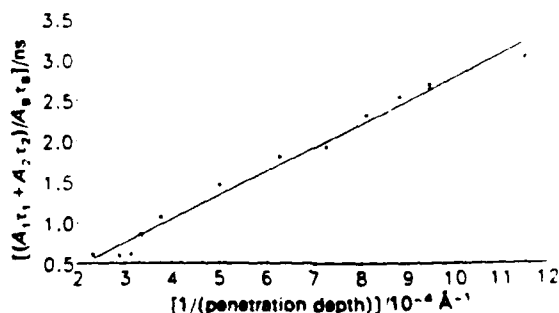


Fig. 4 Plot of $1/\Lambda$ vs. $(A_1 \tau_1 + A_2 \tau_2)/A_B \tau_B$ at a bulk concentration (absorbance) of 0.1. The straight line represents a linear regression fit to the experimental data points with a gradient of 2850 ns $\text{\AA}$.

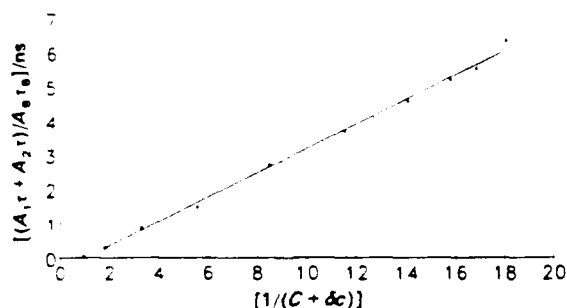


Fig. 5 Plot of $1/(C_0 + \delta c)$ vs. $(A_1 \tau_1 + A_2 \tau_2)/A_0 \tau_0$ at a limiting penetration depth of 870 Å, with a value for δc of 0.053, giving the linear relationship. The straight line, of gradient 0.352 ns, represents the predicted relationship

It has to be recognised that there are a number of assumptions in the treatment of this data, including the value of n_2 and hence Θ_c , the modification to the data at different bulk concentrations and the model itself. But in view of these simplifications, the agreement between experiment and theory is excellent.

By choosing water as the solvent, none of the effects seen in methanol solution are observed. All decays could be satisfactorily described by a single-exponential function, with a lifetime of 6.0 ± 0.1 ns. The result is probably a reflection of the better solvating properties of water on AlS_4Pc . This will be examined in the future by using the disulphonated compound AlS_2Pc , which is more soluble in methanol than in water.

The most important results from this work are the observation of AlS_4Pc binding to the fused silica prism surface and the deviation from monoexponentiality of the fluorescence decays recorded in the interfacial region. Both of these results indicate that the interpretation of steady-state fluorescence measurements may be erroneous, unless the effects observed here are taken into consideration. Returning to eqn. (6), the fluorescence quantum yield, $\phi(z)$, and the concentration profile, $c(z)$, are, in the case of AlS_4Pc in methanol, not constant and the simplification relating eqn. (6) to (7) cannot be made. Alternatively, if free AlS_4Pc were used as a reference solution for a more complex system, where the AlS_4Pc was bound to a larger molecule and acted as a probe, then the differing solvent effects on the free molecule compared with the bound molecule would not simplify the mathematics, but would complicate it. However, when water is used as a solvent for the AlS_4Pc , the assumptions are valid since the data clearly show that quantum yield is independent of penetration depth and hence eqn. (7) provides an accurate description of this particular system.

Conclusions

By combining the techniques of evanescent wave induced fluorescence spectroscopy and time-correlated single-photon counting we have developed a very powerful spectroscopic technique for investigating the properties of fluorescent molecules at a solid solution interface. By studying the fluorescence spectra and decay curves of tetrasulphonated aluminium phthalocyanine in methanol solution in contact with a fused silica surface, we have shown that: (a) the dye binds to the surface to form an adsorbed monolayer, and (b) the photophysical properties of the adsorbed layer differ from the bulk solution characteristics. In the vicinity of the surface, the fluorescence decay characteristics are not simple, with evidence for at least one kinetically different fluorophore, the reasons for which have not yet been identified, but are the subject of current investigations.

The relationship between steady-state fluorescence intensity and the evanescent wave is becoming more important in the understanding of surface-solution interactions. Fundamental to these studies is the knowledge of whether the observed changes in fluorescence intensity are a result of differing quantum yields or changes in concentration profiles. The data reported here, clearly demonstrate the ability and ease with which time-resolved fluorescence measurements can resolve these criteria.

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Excimer dissociation in dilute solutions of
poly(styrene) and poly(2-vinylnaphthalene).

by

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Abstract.

Time-resolved fluorescence spectra of purified atactic poly(styrene) in methylene chloride and methylcyclohexane and poly(2-vinylnaphthalene) in benzene, have been obtained. At late-gated times, only excimer emission is observed. Under these conditions, reverse dissociation of the excimeric species to reform singlet, excited state monomeric chromophore is thus absent.

Introduction.

The starting point for the interpretation of the fluorescence of vinyl aromatic polymers such as poly(styrene) is the Birks kinetic scheme ¹ (scheme 1), devised to explain excimer formation of free aromatic molecules in solution. A feature of the scheme is the thermally activated process represented by the rate constant k_{MD} through which the excimer, $(MM)^*$ undergoes reverse dissociation ('feedback') to reform singlet excited monomeric species M^* . The manifestation of such a process would be a long-lived component in the fluorescence decay of the monomeric species, with a lifetime characteristic of the excimer and the appearance of fluorescence in the monomer spectral region at long times after excitation, such that the monomer to excimer intensity ratio becomes constant by virtue of the equilibrium set up between the species. This phenomenon is well documented in free aromatic molecules, but the evidence for 'feedback' in poly(styrene) is conflicting (late-gated emission spectra of poly(2-vinylnaphthalene) have not been reported in the literature). In early work on this polymer, no evidence for reverse dissociation was presented ²⁻⁷, but in later studies, spectral and kinetic data suggested that the dissociation did occur to a small extent^{8,9,10}.

In view of the conflict, we have reinvestigated these systems using an apparatus with improved time and spectral resolution.

Experimental.

This has been described fully elsewhere¹¹. For the work carried out on poly(styrene), a mode-locked, cavity-dumped argon ion laser (Spectra Physics Model 165) was used with a temperature tuned ADP frequency-doubling crystal to give 150 ps duration pulses at a repetition rate of 5 MHz, and at a wavelength of 257.25 nm. Standard single-photon counting¹² detection techniques were

employed, with a Hilger Watts D330, 1/4 meter grating monochromator used to isolate emission wavelengths. An end-on photomultiplier tube (Philips XP2020Q) was used for pulse counting, giving an overall instrument response function of approximately 600 ps.

For the work carried out on poly(2-vinylnaphthalene), a mode-locked cavity-dumped, synchronously pumped dye laser (Coherent Antares-701-3/CD) was used with an angle tuned lithium formate frequency-doubling crystal to give 10 ps duration pulses at a repetition rate of 1 MHz. The laser was tuned to emit radiation at a wavelength of 283 nm. Using a Hamamatsu R1564 U-01 microchannel plate photomultiplier tube the instrument response function was around 100 ps. The steady-state fluorescence spectra were taken on a Perkin Elmer LS5B spectrofluorimeter.

Atactic poly(styrene) was obtained from BDH and purified by making up a concentrated solution using benzene (Aldrich HPLC grade) as solvent and by precipitation by addition to chilled methanol (Aldrich HPLC grade). The procedure was repeated eight times.

Poly(2-vinylnaphthalene) was obtained from Aldrich and purified by the process of impurity abstraction from the polymer film using acetonitrile (Aldrich HPLC grade).

Methylene chloride (Aldrich HPLC grade) was freshly distilled over phosphorus pentoxide. Methylcyclohexane (Aldrich, Gold Label) grade was purified by abstraction of aromatic impurities^{13,14} by sulphonation followed by successive passage through basic alumina then activated silica gel. Benzene (Aldrich HPLC grade) was used without further purification. All solvents were tested for impurities using fluorescence spectroscopy by comparison of Raman bands as a reference.

All samples were outgassed by the technique of freeze-pump-thaw cycles. All experiments were carried out at a temperature of 292 K unless otherwise stated.

Results and Discussion.

Figure 1 shows the total fluorescence spectra of poly(styrene) in outgassed methylene chloride and poly(2-vinylnaphthalene) in benzene to be dominated by the excimer contribution, as has been reported elsewhere^{2,10,15}. 'Gated' spectra for poly(styrene) are shown in figure 2a, from which it is seen that at time zero, the excimer contribution is absent but that as the monomeric contribution to fluorescence, decays, the excimer grows in importance. At 1.7ns after excitation, the monomer species is still visible. At longer times after excitation however, figure 2b, the monomeric contribution is absent, and the excimer fluorescence plotted on an energy scale (Fig. 2c) is reasonably well represented by a Gaussian function as predicted by the Frank-Condon projection of the electronic excited state, vibrational ground state, onto a repulsive electronic ground state. The same is true of poly(styrene) in methylcyclohexane at room temperature (figure 4) and the dominant excimer in poly(2-vinylnaphthalene) (figure 3).

It is clear from this work that reverse dissociation of the excimer does not occur under these conditions. Increasing the temperature (figure 4) however resulted in a blue shift of the excimer emission of 438 cm^{-1} for a temperature rise of 48 K. Coincident with the resulting spectral overlap of the excimer emission, monomer absorption, there is the appearance of a small contribution to fluorescence in the blue edge of the emission band (Figure 5). This may be due to 'feedback', however the spectral overlap between hot ground-state absorption and excimer emission cannot preclude a 'trivial' population mechanism of excimer emission followed by monomer reabsorption. The case of poly(2-vinylnaphthalene) has yet to be fully investigated.

The present poly(styrene) results differ from those reported earlier^{8,9,10} lower temporal resolution (instrument response function of 7 ns FWHM). It seems

possible that the discrepancy is due to the duration of the excitation pulse in these experiments, such that even at time-gates nominally some 20 ns after excitation, the spectra recorded contained features due to directly excited monomeric species. A more likely explanation however, would be that in the former experiments, a free molecular phenyl based impurity was present. For example, isopropyl benzene has a fluorescence decay time similar to that of the poly(styrene) excimer ¹⁶, and thus direct excitation would give a contribution in the monomer region at late gates. In the present experiments, great care was taken in the purification of the polymers. Late-gated emission spectra of poly(2-vinylnaphthalene) has not been reported in the literature.

These results show that particular care must be taken in recording and interpreting spectra and decay characteristics of these polymers, in which excimeric reverse dissociation to reform excited singlet state monomeric species is now seen to be absent in poly(styrene) and in the case of the dominant excimer in poly(2-vinylnaphthalene).

Figure 1

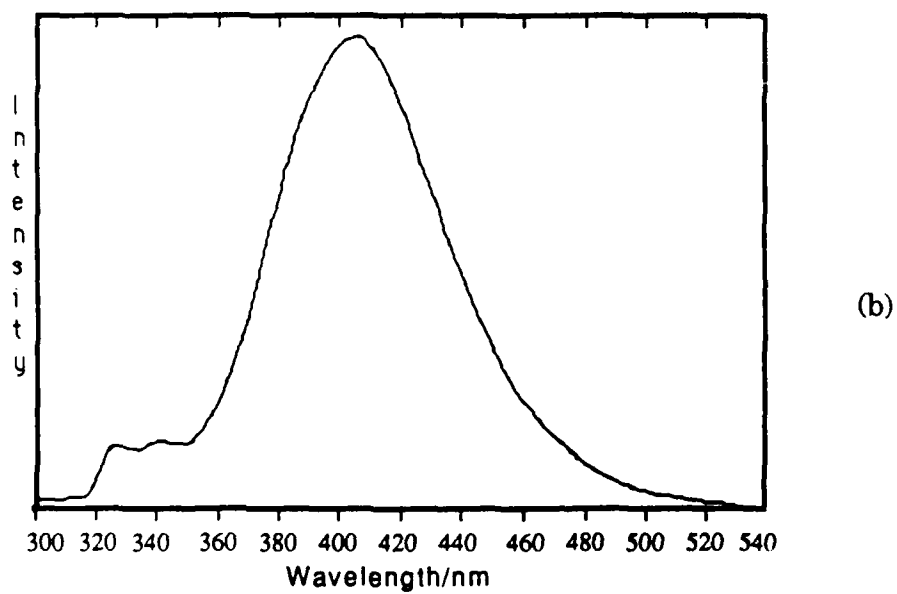
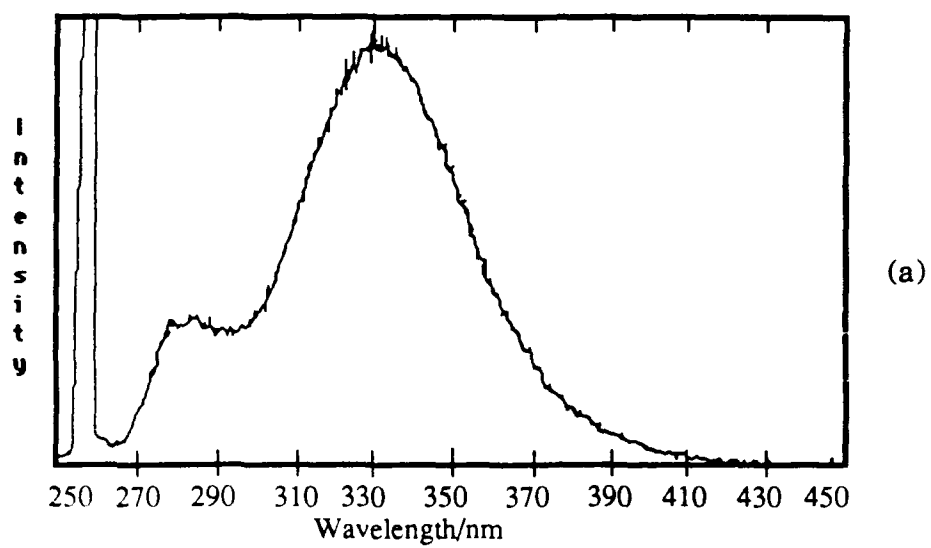


Figure 2

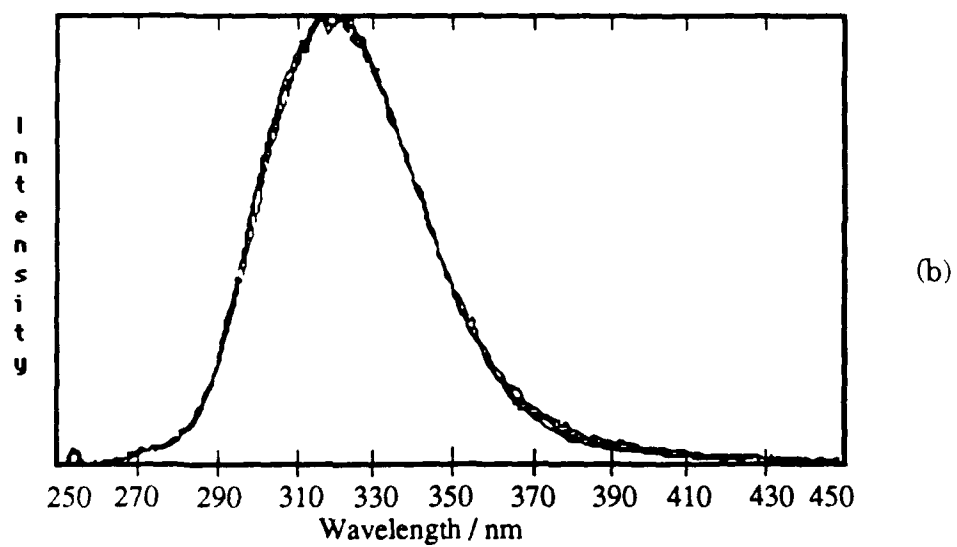
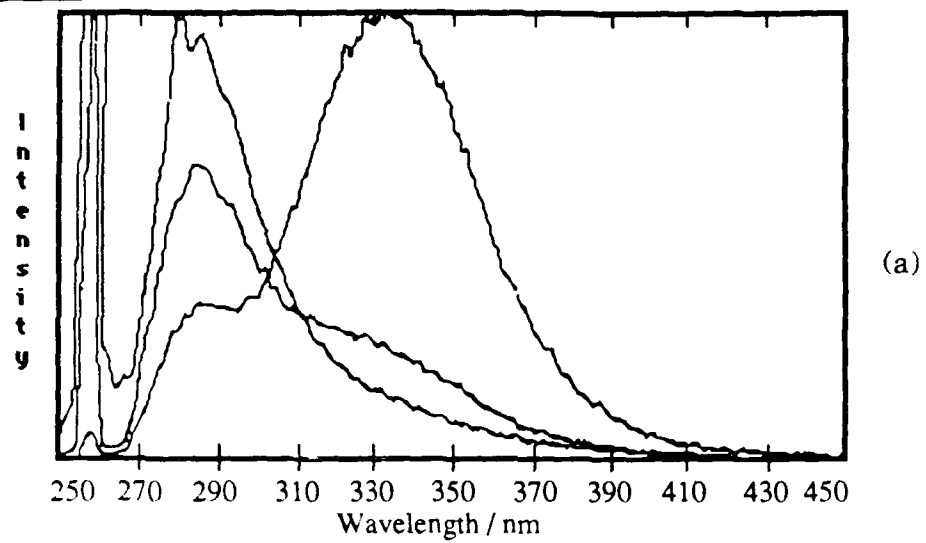


Figure 2

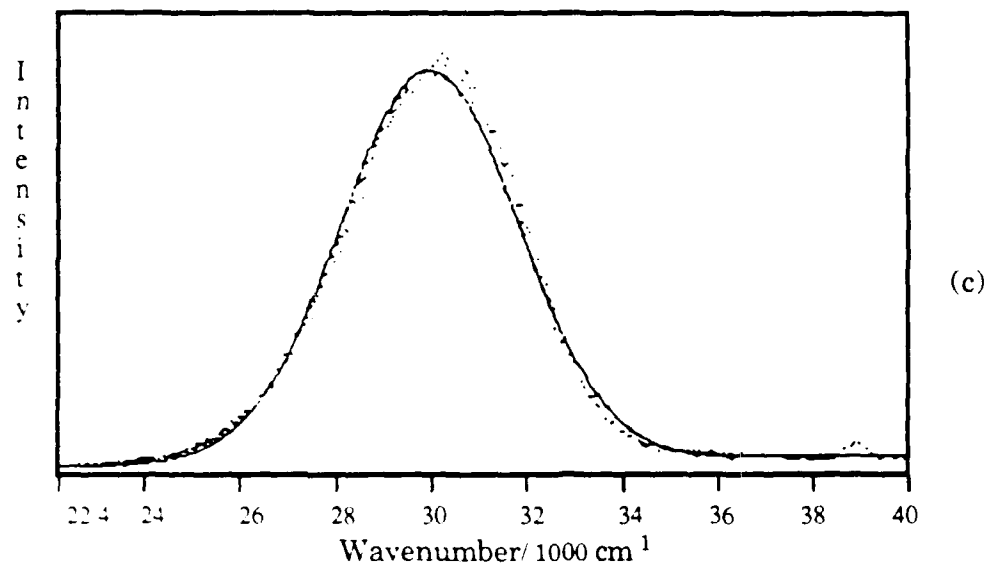


Figure 3

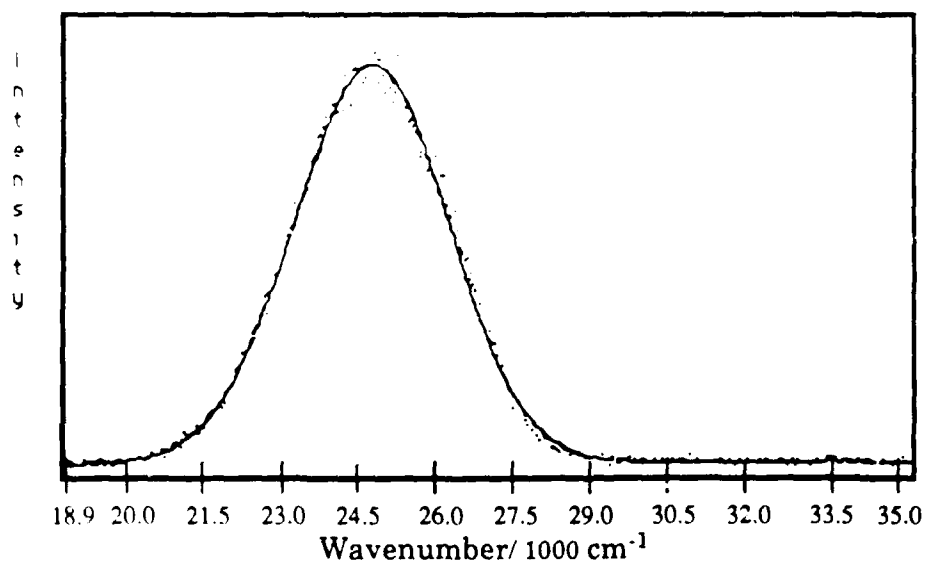


Figure 4

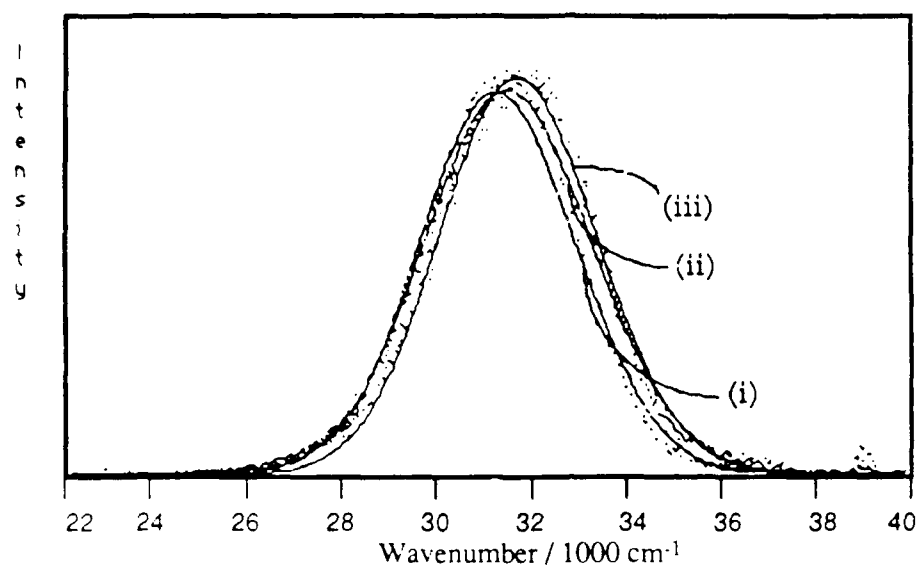
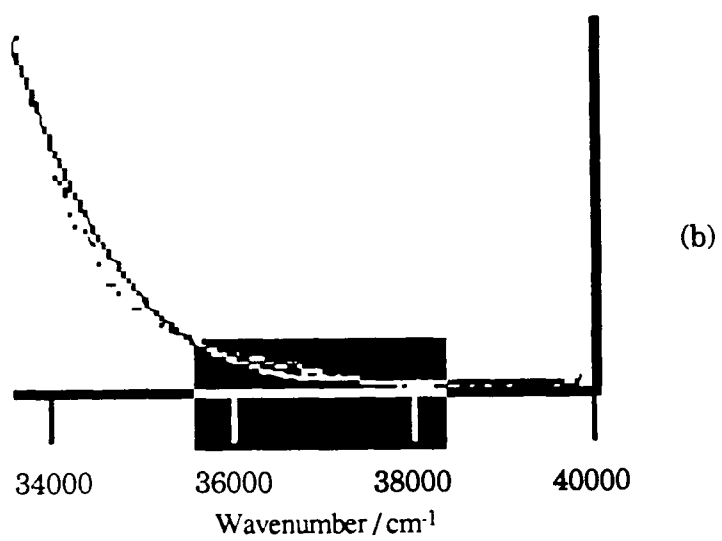
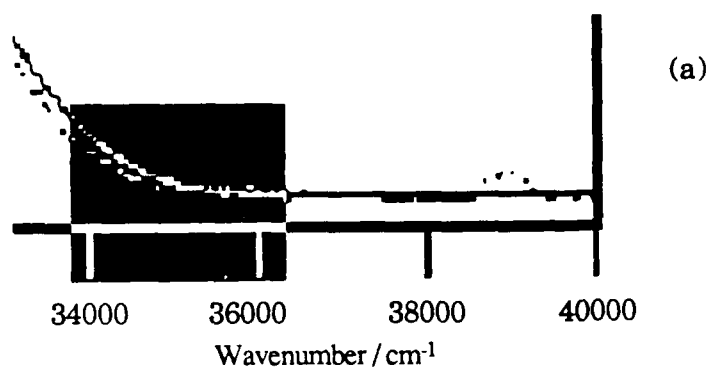


Figure 5



Scheme 1

Birks' kinetic scheme for excimer formation and decay.

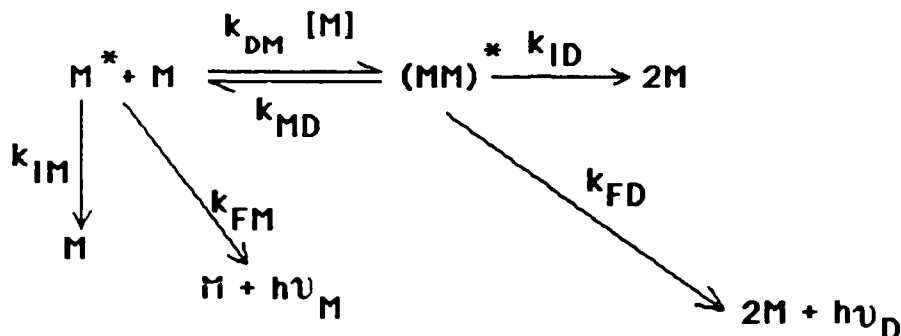


Figure 1

- (a) Total fluorescence spectrum of polystyrene dissolved in outgassed methylene chloride.
- (b) Total fluorescence spectrum of purified P2VN dissolved in degassed benzene.

Figure 2 Polystyrene dissolved in outgassed methylene chloride.

- (a) Gated spectra: Pulse width, 600 ps (FWHM) gate width, $\delta t = 0.4$ ns.
 $\Delta t = 0$ ns $\Delta t = 1.0$ ns $\Delta t = 1.7$ ns
- (b) Late-gated spectra: Pulse width, 600 ps (FWHM) gate width, $\delta t = 4$ ns.
 $\Delta t = 20$ ns $\Delta t = 30$ ns $\Delta t = 40$ ns
- (c) Late-gated spectrum plotted on an energy axis.

Figure 3 Poly(2-vinylnaphthalene) dissolved in outgassed benzene.

Late-gated spectrum plotted on an energy axis ($\Delta t = 255$ ns).

Figure 4

Late-gated spectra of polystyrene dissolved in methylcyclohexane at the temperatures of:

- (i) 292 K (ii) 322 K (iii) 340 K

Figure 5

Polystyrene dissolved in methylcyclohexane.

Detailed examination of the blue edge of the excimer emission at the temperatures of:

- (a) 292 K
- (b) 340 K

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