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Studies of the Photophysics of Poly[(10-phenyl-9-anthryl)methyl methacrylate] Using Synchrotron Radiation

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ABSTRACT: Evolution of well-characterized macromolecules containing aromatic substituents whose excited-state decay kinetics can be adequately described by simple models would be invaluable in attempts to evaluate the conjunct roles adopted by energy and material diffusions within intramacromolecular energy-transfer processes. Achievement of simple temporal dependences, even under the conditions of the high local chromophore concentrations encountered within coiled polymers in fluid solution, might be sought either through structural design of the macromolecule or by incorporation of chromophores of appropriate photophysics, such that self-quenching interactions are precluded. In this context, it has been reported (Hargreaves, J. S.; Webber, S. E. *Macromolecules* 1984, *17,* 235) that the time-resolved fluorescence behavior of the "phenyl-anthracene-based" polymer system poly[(10-phenyl-9-anthryl)methyl methacrylate], PPA, may be adequately modeled by a first-order decay law. In this paper, it is shown that rigorous analysis of PPA fluorescence decays recorded under magic angle sampling conditions following pulsed excitation using the Synchrotron Radiation Source (Daresbury, UK) reveals that the excited-state decays are not single exponential in character. It is proposed that the observed complexities might have origins in the formation of an excited-state complex of low emissivity.

Introduction

The advent of time-resolved fluorescence techniques in the examination of macromolecular photophysics exposed[1-5] the considerable complexities apparent in phenomena such as intramolecular excimer formation, which prior to ca. 1980 were largely treated as a simple extension of the behavior of low molar mass analogues. The high local concentrations of chromophore encountered in a coiled polymer in solution encourage excimer formation. The presence of such intrinsic energy traps leads to complex decay kinetics either as a consequence of microstructural heterogeneity leading to multiexponential decay behavior or through the influence of diffusive[6] and/or migrative[7] terms leading to time-dependent rate coefficients and consequent deviations from first-order time dependence of the excited-state concentration. The area has been reviewed,[8] and various aspects of the photophysical behavior of both macromolecules and bichromophoric model compounds have appeared in recent workshop[9] and conference[10] proceedings.

The complexities of photophysical response induced in excimer-forming systems by the very presence of the energy trap itself has led to the search for polychromophoric assemblies in which intramolecular excimers might be avoided. In such systems it should prove possible to introduce copolymerized energy traps such that the time dependence of intramolecular trapping phenomena might be studied in the absence of competitive trapping by excimers. This in turn would yield information pertinent to considerations of the nature of the photophysical behavior of polymers exhibiting intramolecular excimer formation and could indicate the relative importance of approaches adopting functions based upon multiexponential or transient diffusive terms in analysis of emission decays. In addition, the absence of excimer sites as intrinsic energy traps would enhance energy migration in systems used as antenna[11] polymers and thereby lead to increased trapping efficiency and photochemical storage in "photozyme" systems.

In these contexts, enhancement of energy migration has been sought by using chemical modification of the chromophoric repeat unit to reduce excited-state complex formation as in the case of naphthyl[12] donors or through the use of comonomer[13-15] alternation to reduce the probability of excimer formation. Alternatively, reduced trapping may be sought through the agency of donor chromophores such as phenanthrene,[11,16-18] which has been long known[19,20] to have little propensity for excimer formation even when present as pendant chromophore in polymers,[21] or bisaryloxadiazoles,[22,23] whose reluctance to associate in an excimer form is supported in theory[24] but not in practice.[25,26]

In the current work we reexamine the photophysical behavior of a polymer for which it has been reported[27] that the absence of excimer formation results in excited singlet states whose temporal existence is governed by a first-order decay law. This macromolecule, poly[(10-phenyl-9-anthryl)methyl methacrylate] (PPA), was of interest to the Toronto group as a basis of a photozymic light-harvesting polymer to promote electron-transfer reactions and to the Edinburgh group as a system for testing the complexities of fluorescence decays induced by intramolecular energy trapping by copolymerized acceptor species. Unfortunately for the latter aspiration, the photophysical behavior of PPA is not as simple as might have been expected and indeed, as described below, exhibits fluorescence decays that are as complex as shown by macromolecules in which extensive excimer formation *is* apparent.

Apart from the earlier observation for PPA,[27] the absence of excimer formation in the polymer might have proven

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surprising in view of the fact that bichromophoric ether-linked systems containing the (10-phenyl-9-anthryl)methyl species show excimer emission from fluid (methylcyclohexane) solutions at temperatures near ambient.[28]

Experimental Section

Materials. The monomer (10-phenyl-9-anthryl)methyl methacrylate was synthesized via a three-stage route as follows:

(a) **10-Phenyl-9-anthracenecarboxaldehyde** (I) was prepared via a Vilsmeier–Haack reaction whereby 9-phenylanthracene (5.08 g, 20.0 mmol) was refluxed with phosphorus oxychloride (5.36 g, 35.0 mmol) and *N*-methylformanilide (5.40 g, 40.0 mmol) in *o*-dichlorobenzene (5 mL) for 1 h. The cooled mixture was neutralized with aqueous sodium acetate (35 g in 60 mL of H_2O) and subsequently subjected to a rapid steam distillation to remove *o*-dichlorobenzene and methylaniline. The crude solid was isolated and washed with 6 M HCl (50 mL) followed by H_2O (100 mL) and finally purified by column chromatography (silica gel, 50/50 v/v chloroform/toluene). Yield 64%; mp 166–168 °C; NMR ($CDCl_3$) δ 7.25–7.85 (m, 11 H), 8.95 (m, 2 H), 11.58 (s, 1 H); *m/e* 282.

(b) **(10-Phenyl-9-anthryl)methanol** (II): I (2.82 g, 10 mmol) was reduced to II by refluxing (30 min) with sodium borohydride (0.46 g; 12 mmol) in 95% ethanol (80 mL). II was purified by recrystallization from ethanol. Yield 86%; mp 168–169.5 °C (lit.[27] mp 149–151 °C); NMR ($CDCl_3$) δ 1.87 (s, 1 H), 5.70 (s, 2 H), 7.2–7.75 (m, 11 H), 8.46 (m, 2 H); *m/e* 284.

(c) **(10-Phenyl-9-anthryl)methyl methacrylate** (III): The monomer III was prepared by adding freshly prepared methacryloyl chloride (2 mL) over 30 min to a solution of II in dry pyridine (8 mL). The mixture was stirred at 0–5 °C for 1 h followed by 3 h at 25 °C. Following addition of dilute aqueous ammonium hydroxide the mixture was extracted with ether. The combined ether layer was washed with dilute HCl, aqueous $NaHCO_3$, and saturated NaCl prior to drying overnight over $MgSO_4$. Following solvent removal the product was purified by column chromatography (silica gel, toluene) and recrystallization from ethanol. Yield 59%; mp 131–133 °C (lit.[27] mp 129–130 °C); NMR ($CDCl_3$) 1.85 δ (s, 3 H), 1.95 (t, 1 H), 5.48 (m, 1 H), 6.08 (d, 1 H), 6.26 (s, 2 H), 7.2–7.8 (m, 11 H), 8.45 (m, 2 H); *m/e* 352.

(10-Phenyl-9-anthryl)methyl 2-methylpropanoate (PMP) was prepared from II and isobutyryl chloride in the manner described in (c) above for production of the methacrylate monomer. The product was purified by recrystallization from ethanol. Yield 80%; mp 170–172 °C (lit.[27] mp 161–163 °C); NMR ($CDCl_3$) δ 1.18 (d, 6 H), 2.56 (m, 1 H), 6.20 (s, 1 H), 7.1–7.9 (m, 11 H), 8.37 (m, 2 H); *m/e* 354.

Poly[(10-phenyl-9-anthryl)methyl methacrylate] (PPA) was prepared by free-radical polymerization in benzene under high vacuum using AIBN initiator. The polymer was purified by multiple reprecipitation from benzene into methanol. High and low molar mass portions [PPA(H) (DP > 100) and PPA(L) (DP ~30), respectively] were produced by fractionation. Molar masses were determined by GPC and were expressed in polystyrene equivalents.

Solvents and Solutions for Spectroscopy. Toluene (BDH) was purified immediately prior to use by refluxing over and distillation from phosphorus pentoxide. Dichloromethane (May and Baker) was purified immediately prior to use by distillation from phosphorus pentoxide.

Luminescence Measurements. Solutions were prepared such that the optical density (OD) with a 1-cm path length was less than 0.1. Degassing was accomplished by the freeze/pump/thaw technique.

Steady-state fluorescence measurements were made on Perkin-Elmer MPF3 and MPF44 spectrometers. Total fluorescence contour representations were generated on a Baird Fluorocomp TLS system comprising a PDP 11/34 minicomputer interfaced to a Baird SFR100 fluorimeter.

Time-resolved fluorescence measurements were made using the technique of time-correlated single-photon counting. In the Edinburgh laboratory an Edinburgh Instruments 199 spectrometer was used. In Toronto a spectrometer whose construction has been described previously[29] was used. Both spectrometers employ gas discharge lamps as excitation sources. Experiments involving synchrotron radiation were performed at the SERC Daresbury, Warrington U.K. The Synchrotron Radiation Source (SRS) and detection system are described briefly as follows:

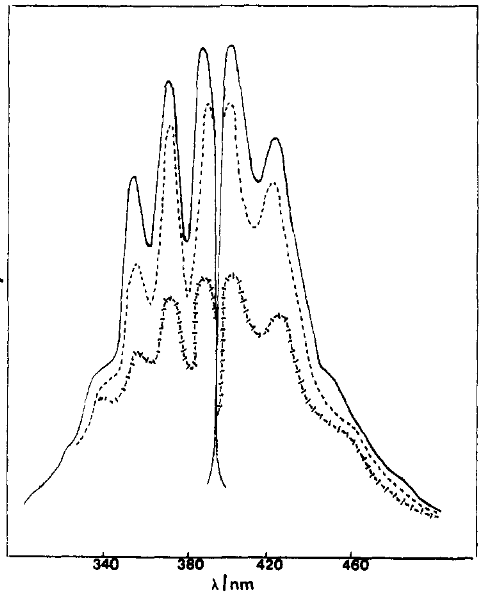


Figure 1. Fluorescence excitation and emission spectra of PPA(H) (—), PPA(L) (- - -) and PMP (-|-) in toluene at 298 K.

The electron storage ring, operating in single bunch mode, delivered light pulses of ca. 200-ps duration at a repetition frequency of 3.1 MHz. Monochromation and excitation wavelength selection was accomplished using a Spex 1500 Czerny–Turner monochromator. Fluorescence was detected, at right angles to excitation and with a polarizer set at the magic angle of 54.5° to the vertical plane of excitation polarization, by a Philips XP2020Q photomultiplier. Analysis wavelengths were isolated by means of interference filters.

Adequacy of fitting of decays by model functions was assessed by the conventionally accepted limits[29] of reduced χ^2 and serial correlation coefficient (Durbin–Watson parameter), randomly dispersed residuals, and autocorrelation of residuals.[29] Modeling of the observed decay profiles involved iterative reconvolution using a model function and the instrument response profile recorded (scatter from Ludox) at the wavelength of fluorescence analysis.

Results and Discussion

Steady-State Fluorescence Excitation and Emission Spectroscopies and UV Absorption Spectroscopy. Figure 1 shows the fluorescence excitation (action) and emission spectra of toluene solutions (OD < 0.1 for a 1-cm path length) of both polymer samples PPA(L) and PPA(H). For comparison, the corresponding spectra for the model compound, PMP, also are shown. Clearly, the spectra are remarkably similar except for a small red-shift in those for the PPAs relative to that of PMP. Significantly, as observed by Hargreaves and Webber,[27] not only do the excitation (and UV absorption) spectra of the polymers indicate the absence of extensive interactions between the pendant chromophores, but also there is little evidence of the spectral broadening of the emission spectra that would be anticipated in the event of excited-state involvement in the creation of an emissive excimeric complex. The absence of spectral evidence for the formation of an emissive excited-state complex is demonstrated in a more convincing fashion by reference to Figure 2, which compares the total luminescence spectral profiles of PMP and PPA over the entire excitation/emission wavelength array.

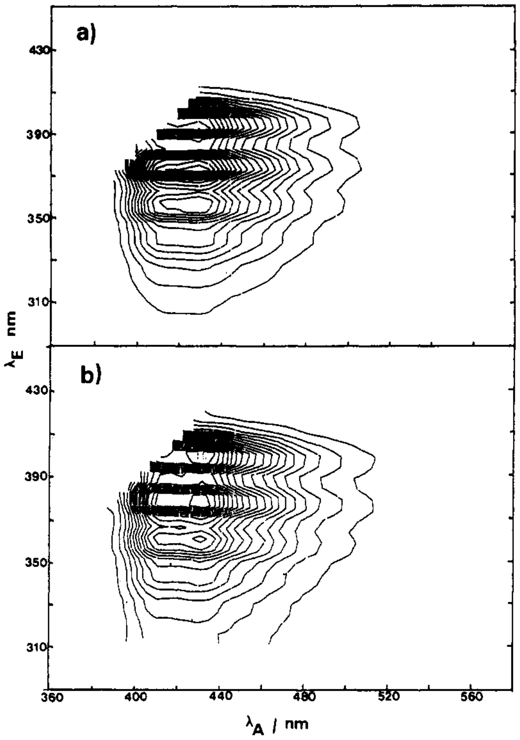


Figure 2. Total luminescence contour representations of fluorescence matrices of (a) PMP and (b) PPA(H) in toluene.

Similar considerations apply to spectra obtained from solutions of model compound and polymers in dichloromethane.

Time-Resolved Fluorescence Spectroscopy following Flashlamp Excitation. Fluorescence decays were collected to a minimum of 10 000 counts in the channel of maximum population for samples dissolved in either dichloromethane or toluene solvents from excited states created by flashlamp excitation on the time-correlated single-photon-counting systems in both the Toronto and Edinburgh laboratories. Data obtained bore a good correlation between samples (in a given solvent) and location.

Fluorescence temporal profiles of the model compound PMP were well described ($\chi^2 < 1.3$, random distribution of residuals, SCC > 1.4) by a first-order decay law regardless of solvent or analysis wavelength. The resultant excited-state lifetimes were independent of both analysis wavelength and fitting range employed. Lifetimes of 8.6 (±0.2) and 8.3 (±0.2) ns were obtained in CH_2Cl_2 and toluene, respectively. In contrast, fluorescence decays from the polymer samples in either solvent proved to be more complex.

Table I lists fitting parameters resultant upon application of a single-exponential trial function to the fluorescence decay data obtained for the PPA polymers. It is obvious that, according to generally accepted statistical criteria, single-exponential decay functions are not capable of furnishing adequate descriptions of the empirical data. Fits to decays obtained from solutions in dichloromethane were particularly inadequate and showed marked deviations between data and fit in the region of the peak of the fluorescence profile. Consequently "tail fitting" procedures were adopted for these samples where only the decaying portion of the fluorescence was fitted. Even in this instance, single-exponential functions proved inadequate descriptors of the data as the χ^2 values in Table I show. A typical fit is shown in Figure 3.

These observations would seem to contradict previously reported trends.[27] However, the data analysis routines adopted by Hargreaves and Webber[27] addressed somewhat restricted data ranges involving a mere 6-fold decay in intensity from that channel *adopted* as corresponding to $t = 0$. In the current work, adoption of similarly restricted regions of interest in analysis resulted in improved (but yet unacceptable by our chosen criteria) fits using single-exponential functions. Apparently unquenched lifetimes (compared to the PMP model compound) could also be obtained by this method when the analysis region concentrated on the earlier time portion of the *decaying* intensity profile. However, consistent with the reality of a more complicated deactivation mechanism, the "fluorescence lifetime" obtained was dependent upon the fitting range chosen.

Table I
Parameters Resultant upon Single-Exponential Fitting to Selected Fluorescence Decay Data Sets for PPA
(λ_{ex} = 380 nm; Flashlamp Excitation)

sample	solvent	λ_a/nm	τ/ns	χ^2
PPA(L)	toluene	410	8.4	3.0
		450	8.4	4.0
PPA(H)	toluene	410	7.8	8.9
		450	7.8	3.3
PPA(L)	CH_2Cl_2	410	9.2[b]	6.0
		500	9.0[b]	3.9
PPA(H)	CH_2Cl_2	420+[a]	8.8[b]	7.4
		520+[a]	9.8[b]	5.4

[a] Cutoff filters (passing all wavelengths greater than stipulated) applied in analysis channel. [b] Tail fits (employing a fitting range beginning two channels after peak). See text.

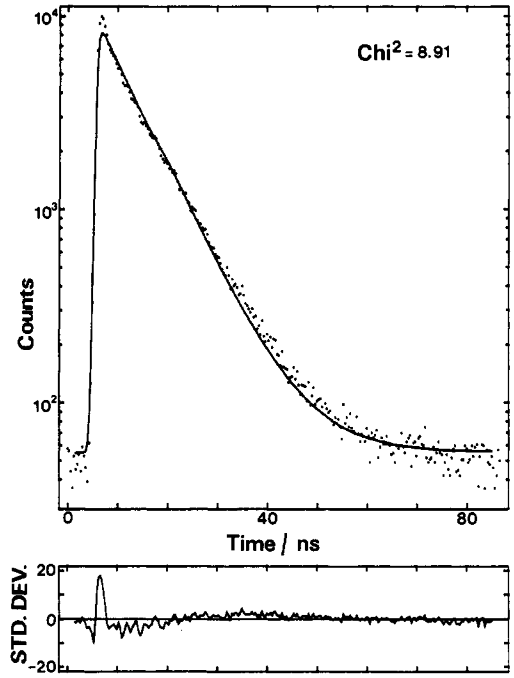


Figure 3. Fluorescence decay profile, "best fit" to a single-exponential model function, and resultant residuals plot for PPA(H) in toluene following H_2 discharge lamp excitation (Edinburgh Instruments system; λ_{ex} = 380 nm, λ_a = 410 nm).

Reconvolution analyses using dual-exponential decay functions of the form

$$i(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \qquad (1)$$

resulted in improved fitting statistics. A typical fit is shown in Figure 4. As Table II demonstrates, the fits cannot be deemed totally adequate. In general the fits become less satisfactory at longer wavelengths and the resultant decay parameters also display a dependence upon analysis wavelength.

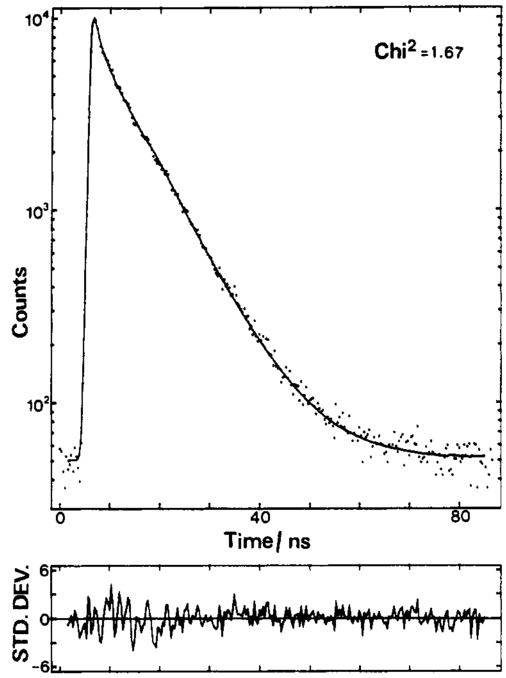


Figure 4. Fluorescence decay profile shown in Figure 3 fitted to a dual-exponential decay model with resultant residuals.

Table II
Decay Parameters Resultant upon Dual-Exponential Fitting the Data Sets Featured in Table I

sample	solvent	λ_a/nm	τ_1/ns	τ_2/ns	χ^2
PPA(L)	toluene	410	1.0	8.6	1.7
		450	1.1	8.7	2.1
		480	1.5	8.5	5.1
PPA(H)	toluene	410	1.0	8.4	1.7
		450	1.8	8.3	1.9
PPA(L)	CH_2Cl_2	410	4.5[b]	11.0	2.1
		500	7.3[b]	14.9	2.2
PPA(H)	CH_2Cl_2	420+[a]	6.1[b]	13.8	2.7
		520+[a]	7.5[b]	21.7	2.1

[a] Cutoff filters applied (cf. Table I). [b] Tail fits (cf. Table I).

Examination of the "residuals" to the fit revealed that marked deviations occurred in the rising edge of the fluorescence–time profiles when dual-exponential analyses were attempted. Such distortions might originate from a number of effects:

(i) Contamination of the decays by scattered excitation would make the emission decay behavior appear to be more complex than actuality. This was not considered to be the major cause of the inability of single- and double-exponential functions to provide adequate fits since it was felt that the wavelength selection arrangements employed on the two lifetime spectrometers involved in these studies were such as to preclude leakage of stray excitation to the analyzing photomultiplier. In addition, attempts to fit the decays with functions of the form

$$i(t) = \sum_i A_i \exp(-\lambda_i t) + CP(t) \qquad (2)$$

(where $P(t)$ is the instrument response function and $i \leq 2$) did not improve the quality of fit.

(ii) Anisotropy effects can distort decay profiles over time ranges in which rotational relaxations of the chromophore are significant. Since segmental motion of the PPA is likely to occur on a nanosecond timebase, distortions of this sort are a potential cause of the problems experienced in fitting the decays.

(iii) The excited-state existence might not be governed by either single- or dual-exponential decay laws. Such deviations from "expected" behavior could be resultant upon either the heterogeneity of microhabitats of the chromophore within the polymer or from excited-state interactions. In the latter instance the decay behavior might be expected to be multiexponential as evinced by other macromolecular species[8] or might adopt a different temporal dependence as a consequence of, e.g., rotational sampling of[6] or energy migration to[7] intrinsic energy traps.

So that the possibilities described in iii might be explored, it was decided that greater confidence would be generated if superior signal-to-noise ratios than readily attainable by using flashlamp excitation could be achieved. In addition, adoption of stringent monochromation conditions allied to excitation with polarized radiation and analysis under "magic angle" conditions would eliminate fears of distortion from either of the effects described in i or ii. In this respect, the high-frequency, short-pulse characteristics of the SRS Daresbury made it an attractive excitation source.

Time-Resolved Fluorescence Spectroscopy following Synchrotron Excitation. Fluorescence decays were collected from toluene solutions (OD < 0.1) of PPA(H) and PPA(L) under "magic angle" analysis conditions following excitation with polarized radiation from the SRS Daresbury. A typical decay profile is shown in Figure 5a. Attempted fitting to these decays using single- or dual-exponential model functions proved inadequate as clearly demonstrated by the plots of the "residuals" (Figure 5b) and their autocorrelation functions (Figure 5c) resultant upon such fits. Resort to a triple-exponential model function affords a superior representation of the experimental data as demonstrated by the residuals and autocorrelation plots shown in Figure 5, parts b and c, respectively. Data resultant from such analysis are shown in Table III.

It is apparent that if functions comprising sums of exponential terms are deemed appropriate for the description of the decay behavior of PPA, then three exponential terms must be regarded as the minimum requirement for adequate representation. [Inspection of the data in Table III reveals that, according to the stringent criterion of attainment of $\chi^2 < 1.3$, triple-exponential functions are not "adequate" in this respect. The fit to the data shown in Figure 5a is characterized by a serial correlation coefficient of 1.61 (compared to values of 0.49 and 1.24 for single- and double-exponential fits, respectively), further testament to the fact that triple-exponential functions are "barely adequate" (a satisfactory triple-exponential fit should result in a Durbin–Watson parameter in excess of 1.8).] Furthermore, a wavelength dependence of the resultant "lifetime" parameters is apparent, reflecting the tendency for the fluorescences of both PPA(L) and PPA(H) to become longer lived as the analysis wavelength is extended. Interestingly, a dominant component of "lifetime" in the region of ca. 8 ns is consistently recovered in triple-exponential analyses of these decays. This value is similar to that of the unquenched model compound. The presence of this significant component of the overall decay explains why analysis over restricted data ranges produces an "unquenched lifetime".

Photophysical Behavior of the PPA System. In contrast to our anticipation, the fluorescence decays of the PPA samples display degrees of complexity comparable to those observed[8] in macromolecular systems in which excimer formation is evident. As discussed above the complexities might be consequent upon a number of effects.

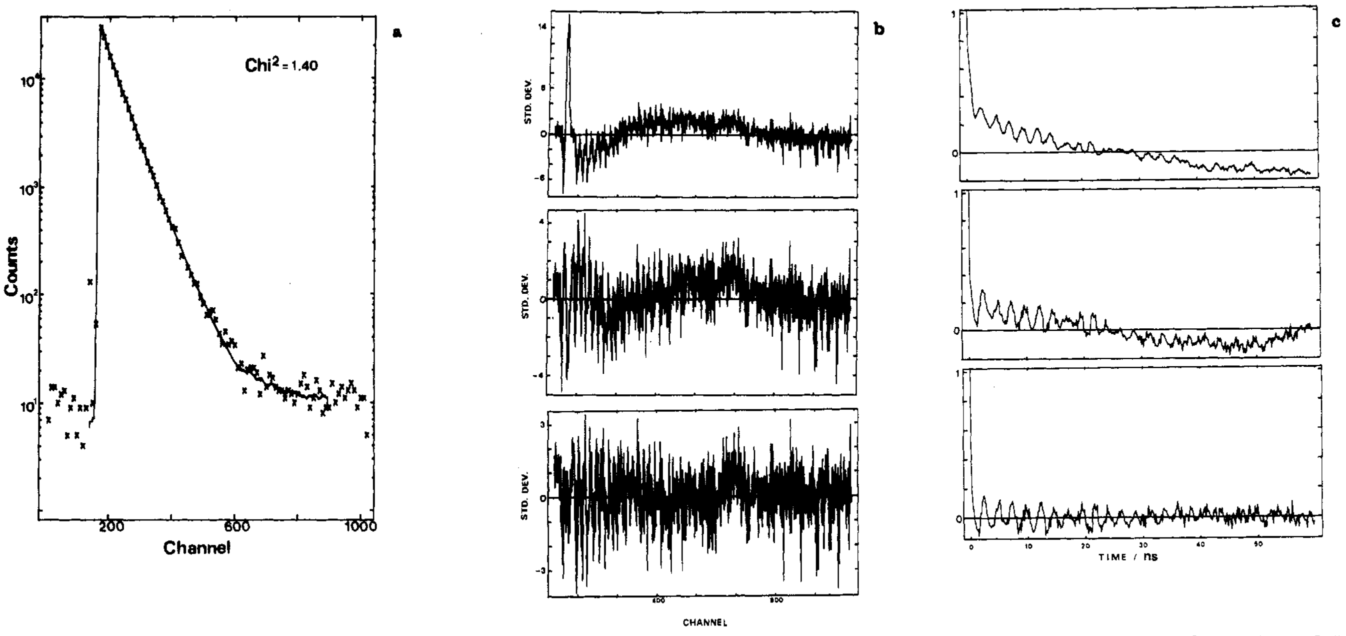


Figure 5. (a) Fluorescence decay data (×) and "best fit" to a triple-exponential model upon synchrotron excitation and "magic angle" analysis. (For clarity the fluorescence data have been edited to display only the contents of every fifth channel. For analysis all 1024 channels of the MCA memory were data storage.) (b) Plots of residuals resultant upon single-, double-, and triple-exponential analysis of the decay data represented in a. (c) Plots of the autocorrelation of residuals resultant upon single-, double-, and triple-exponential fittings to the decay data represented in a.

Table III
Parameters Resultant upon Triple-Exponential Fitting to Fluorescence Decays of PPA (λ_{ex} = 380 nm; Synchrotron Excitation; Solvent = Toluene; 298 K)

sample	λ_a/nm	τ_1/ns	τ_2/ns	τ_3/ns	A_1	A_2	A_3	χ^2
PPA(L)	410	0.7	7.4	10.3	0.17	0.39	0.17	1.41
	450	1.3	8.1	16.1	0.05	0.18	0.008	1.21
	520	1.0	8.2	27.7	0.05	0.04	0.002	1.50
PPA(H)	410	0.6	3.6	8.7	0.16	0.06	0.52	1.55
	450	1.1	8.2	12.2	0.05	0.16	0.015	1.42
	520	0.7	8.1	16.8	0.07	0.34	0.003	1.57

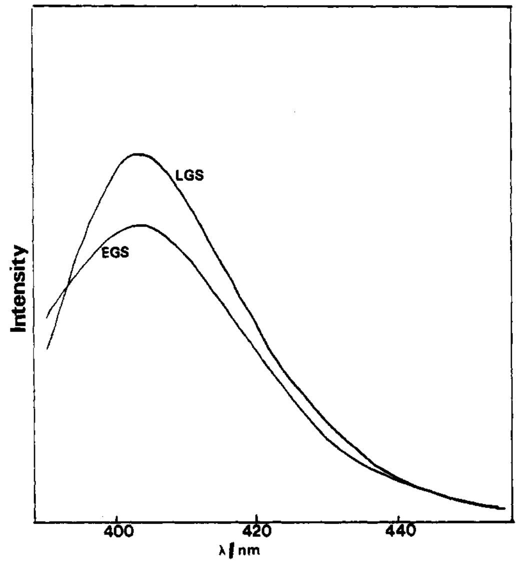
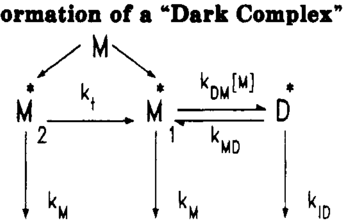


Figure 6. Early (EGS) and late (LGS) gated fluorescence spectra of PPA(H) in toluene recorded by using the Edinburgh Instruments system (λ_{ex} = 380 nm). (EGS emission recorded between 0 and 5 ns following excitation; LGS emission recorded between 27 and 47 ns following excitation.)

If the complexities in the photophysics originate in the existence of a heterogeneity of chromophore environments within the polymer coil, it is evident that the distribution of ground and excited states is not such that a significantly broadened distribution of absorption or emission energies results. There are no wavelength effects evident in either excitation or emission spectra in that the spectral *profiles* are not dependent in either case upon the arbitrary choice of fixed-wavelength parameter for analysis or excitation, respectively. This is clearly demonstrated in a concise fashion by the total fluorescence contour plot for the PPA system shown in Figure 2b. Under these conditions where the kinetic distinctions between microhabitats would originate solely from differences in the relative rates of radiationless quenching between one environment and another, the observed wavelength dependence of the decay profiles and consequent triple-exponential "lifetime terms" (which would merely serve to parametrize the decay) might appear surprising. In support of this argument time-resolved spectra (Figure 6) do not show a spectral shift to lower energies at longer sampling times of the photon distribution. It is likely therefore that the observed decay complexities cannot be explained simply on the grounds of configurational differences within the polymer chain.

The similarities between the transient fluorescence behavior of PPA and those of excimer-forming macromolecules are conducive to consideration of the possibility that an intrinsic energy trap is either present in the polymer or is created within the excited-state lifetime. The invariance of the excitation spectral profiles with analysis wavelength (Figure 2) mediates against implication of ground-state complex formation, whereas both steady-state (Figures 1 and 2) and time-resolved fluorescence spectra (Figure 6) indicate that an emissive excimeric moiety is not formed in this polymer. However, if a "dark complex" were to be formed, as depicted in Scheme I, both quenched and longer-lived emissions could result provided the complex furnishes a feeder mechanism for the quenched excited-state M_1* through dissociation. This scheme is that adopted by Phillips et al.[2,8] to rationalize the intramolecular concentration dependence of fluorescence decays obtained in the region of monomer emission for *certain* vinylaromatic copolymer systems with the provision that, for PPA, k_{FD} is zero. M_2* represents "kinetically isolated" species that cannot access confor-

Scheme I
Formation of a "Dark Complex"[a]



[a] The notation adopted for identification of rate coefficients is that of Birks.[19] [M] represents the unknown intramolecular concentration of the reservoir of unassociated phenylanthracene chromophores accessible by the monomeric excited state M_1^*.

mations conducive to excimer formation. In the instance where "communication" with the M_1 reservoir is not possible ($k_t = 0$), the scheme reduces to that proposed by Holden et al.[3] to describe the photophysical behavior of poly(2-naphthylmethyl methacrylate). Application of Scheme I under such circumstances would imply the existence of three decay terms: an unquenched monomer fluorescence from M_2^* and a biexponential monomeric decay from M_1^* that would analyze to give a quenched "lifetime" and a further decay parameter whose magnitude would be controlled by the time of existence of the excited-state complex D*.

At first sight Scheme I seems an attractive proposition in explanation of the observed photophysics of PPA (cf. Table III) provided triple-exponential functions are regarded as satisfactory in description of the fluorescence decays. However, the wavelength dependence of the decay parameters means that Scheme I (or, indeed, *any* model based upon a three-excited-state system) cannot serve as a model for the photophysical behavior. Similar wavelength dependences of the lifetimes associated with triple-exponential analysis of fluorescence decays from several macromolecular systems (in which emissive excimeric species are produced) have been observed.[22,25,31] The inadequacies of Scheme I in dealing with such wavelength dependences might be alleviated somewhat if it is proposed that a distribution of excimer states exist that are of differing stability with respect to "reverse dissociation" to M_1^*. Clearly, decays analyzed in the excimer region would contain a "lifetime" component characteristic of the entire population, whereas those collected in the region of monomer fluorescence would reflect the existence solely of excimeric species that do dissociate to monomer. Time-resolved spectral evidence for the existence of excimer states of differing stability has been obtained in polymers containing highly fluorescent short-lived chromophores (produced from vinyl scintillators).[22,25] Studies continue on copolymers of vinylnaphthalene (to the photophysics of which Scheme I has been applied[2,8]) and the applicability of a modified Scheme I, in which a distribution of excimer sites is considered, to the overall photophysical behavior of these polymers will be addressed elsewhere.[31] However, such a proposal *cannot* explain the wavelength dependence of the fluorescence decays of PPA. There is no mechanism whereby a monomeric emission band would reveal the details of its origins in the form of an energy dependence of its decay kinetics.

If the proposal that an excimeric complex is formed is to retain any credibility in the face of the time-resolved data, it must be concluded that the complex is not truly "dark". However, it would have to emit *weakly* at wavelengths longer than that of the unassociated chromophore such that the emission is obscured within the fluorescence envelope of the monomeric emitter, *even* in the low-resolution late-gated spectra (exemplified in Figure 6). Such a postulate, involving the existence of an excited-state complex of low quantum efficiency, would be consistent with the fact that the longest lived component of the fluorescence decay (characterized by the lifetime τ_3) makes a small contribution to the overall fluorescence intensity (cf. Table III). Why such a component should be unable to access conformations in the polymer that would allow the extent of molecular orbital overlap achieved in low molar mass ether-linked analogues[28] and should experience a concomitant relative enhancement of nonradiative deactivation is not apparent at this time.

If the suggestion that the observed increases in "average fluorescence lifetime" with wavelength of analysis have their origins in excited-state interactions leading to complex formation is pursued, it could be argued that the triple-exponential functions employed merely serve to parametrize the decay and have limited physical significance. Again, it might be arguable that in this respect the polymer PPA is no different from any other polymer system and that sums of exponentials never provide a "proper" description of the excited-state temporal characteristics and that other mathematical models are appropriate. In this context, it has been argued that diffusive terms consequent upon transition vector displacement through either energy migration[7] or rotational motion[6] might result in fluorescence time dependences (in the region of monomer emission) of the form

$$i(t) = A_1 \exp(-at - bt^{1/2}) + A_2 \exp(-ct) \tag{3}$$

where A_1, A_2, a, b, and c are constants. A_2 has a finite value in the instance of excited-state monomer regeneration via excimer dissociation. However, application of model functions of the form of eq 3 in iterative reconvolution was not entirely successful in production of adequate fits to the decay curves. Difficulties were experienced in achieving convergence of χ^2 when all five fitting parameters were allowed free variance. So that the fitting procedure be aided, it was reasoned that if transient diffusive terms play a significant role in the behavior of the excited state, such will be apparent only at short sampling times. Consequently, dual-exponential functions were applied to fitting of the *tails* of the decaying portions of the transient fluorescence profiles. The resultant decay parameters were then used as initial estimates of a^{-1} and c^{-1}, respectively in eq 3. Unfortunately, "whole curve" fits using model functions of this form where $A_2 = 0$ were statistically inadequate (and inferior to dual-exponential fitting to the same data set). Furthermore, use of the complete functional form of eq 3 resulted in fits that were not only statistically inferior to triple-exponential fitting of the same data set but that gave meaningless estimates of a^{-1} (which, dependent upon the mechansim of diffusive term involvement, should be either equal to or less than the unquenched chromophore lifetime). In addition, fits of this type showed an emission wavelength dependence (*itself* to be expected in view of the fact that the average "decay time" does increase with wavelength of analysis) but markedly nonuniform trends in the values of a^{-1}, c^{-1}, and b so derived.

Conclusions

Contrary to expectation[27] and aspiration, the photophysical behavior of poly[(10-phenyl-9-anthryl)methyl methacrylate], PPA, is complex. Through the agency of synchrotron radiation for excitation in time-resolved studies, it has been shown that the complexities observed in the decay profiles are neither the product of the potential distortions that could be induced through the leakage of exciting radiation into the analyzer channel nor those that might result from anisotropic emission phenomena accompanying chromophore reorientation. Consequently, it is clear that the generation of a macromolecular system in which energy trapping by an emissive excimer is not apparent in its steady-state fluorescence does not, in itself, produce truly single-exponential decay behavior.

The complex decay kinetics evinced by PPA might result from the heterogeneity of environments experienced by the chromophores in the macromolecular assemblage. We have argued against such an interpretation on the basis of the independence of the fluorescence characteristics of the PPA system of excitation wavelength. As an alternative explanation of the observed photophysics we have invoked creation of an excimeric state of low fluorescence efficiency and stabilization energy.

Whatever the root of the complex photophysics, it is apparent that functions based upon sums of exponential terms are superior in describing the fluorescence decays of PPA than models based upon transient terms leading to $t^{1/2}$-dependent diffusive contributions. If additive combinations of simple exponential terms are considered appropriate descriptors of the transient photophysical behavior, it is apparent that triple-exponential functions are the least complex functions that may be deemed adequate.

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