# Photophysics of Anthracene Polymers: Fluorescence, Singlet Energy Migration, and Photodegradation†

**John S. Hargreaves and Stephen E. Webber***

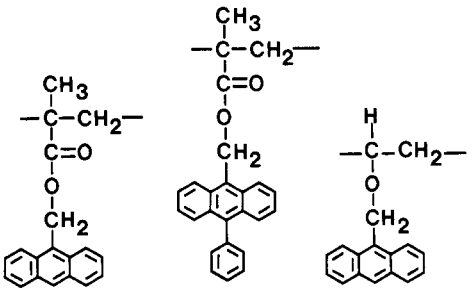
*Department of Chemistry and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712.* *Received January 21, 1983*

ABSTRACT: Poly(9-anthrylmethyl methacrylate) (PAMMA), poly[(10-phenyl-9-anthryl)methyl methacrylate] (PPA), and poly(9-anthrylmethyl ethenyl ether) (PAE) were prepared and their photophysics studied. The fluorescence spectra of these polymers are very dependent on the degree of anthracene crowding. The singlet energy migration constant ($\Lambda_s$) was estimated to exceed $2 \times 10^{-5}$ cm$^2$/s for PPA but to be essentially 0 for PAE and PAMMA (the latter displaying the largest fluorescence shift with respect to its monomeric model compound of all the polymers studied). Singlet–singlet annihilation was observed for PPA, which strengthens the finding that $\Lambda_s \neq 0$. Polymers containing ester groups were photolabile with respect to loss of anthracene groups, and PAMMA especially has a strong tendency to be photoreactive.

## Introduction

For the past few years a number of workers have studied the photophysics of polymers with pendent aromatic groups, with special emphasis on down-chain singlet or triplet energy migration (i.e., singlet or triplet intracoil "excitons"). The present paper is concerned with these processes in polymers with pendent anthryl groups. These polymer systems have been studied only slightly in previous years, usually with the anthracene moiety as a fluorescent "probe" to study macromolecular dynamics. Many of the generalizations that have been established in the field of energy transfer in molecular crystals originate from studies of anthracene crystals. Consequently it is natural to carry the study of anthracene into the regime of macromolecular photophysics. In addition, anthracene is a bulkier pendent group than many of those studied previously in macromolecular photophysics such that one can hope to further elucidate the effect(s) of chromophore crowding.

Our results are divided into four parts: (1) structure and fluorescence relations, (2) determination of $\Lambda_s$ (apparent singlet exciton migration constant) via comparative quenching studies, (3) intracoil singlet–singlet annihilation, and (4) photochemical stability. Our polymers are of two types: (1) methacrylates [poly(9-anthrylmethyl methacrylate) (PAMMA, I) and poly[(10-phenyl-9-anthryl)-methyl methacrylate] (PPA, II)] and (2) vinyl ethers [poly(9-anthrylmethyl ethenyl ether) (PAE, III)].



PAMMA (I) PPA (II) PAE (III)

## Experimental Section

**1. Synthesis of Materials. (a) 9-Anthrylmethyl Methacrylate (AMMA).** This monomer was prepared as described in the literature[1] from 9-anthracenemethanol and methacryloyl chloride (both Aldrich).

Over a period of 1 h, 2.1 mL of freshly distilled methacryloyl chloride was added to a dry solution of 9-anthracenemethanol (3 g), tetrahydrofuran (12 mL), triethylamine (3 mL), and pyridine (2 mL), which was maintained at 0 °C. After addition was complete, the mixture was warmed to 25 °C and stirred for 1 h. Water was added and the mixture was extracted with ether. The ether extract was washed with HCl, $NaHCO_3$, and saturated NaCl and dried over $Na_2SO_4$. After solvent removal, the product was recrystallized from methanol. The product is a yellow crystal (42% yield): mp 82–83 °C (uncorrected); NMR ($CDCl_3$) $\delta$ 1.85 (s, 3 H), 5.4 (s, 1 H), 5.95 (s, 1 H), 6.1 (s, 2 H), 7.2–8.5 (m, 9 H).

**(b) 9-Anthrylmethyl 2-Methylpropanoate.** 9-Anthracenemethanol and isobutyryl chloride (both Aldrich) were reacted together in a manner similar to that given for 9-anthrylmethyl methacrylate. The ester was chromatographed on activated alumina with benzene and recrystallized from ethanol to give yellow crystals (76% yield): mp 95–96 °C (uncorrected); NMR ($CDCl_3$) $\delta$ 1.1–1.2 (d, 6 H), 2.2–2.7 (septet, 1 H), 6.0 (s, 2 H), 7.2–8.3 (m, 9 H); *m/e* 278.

**(c) (10-Phenyl-9-anthryl)methyl Methacrylate. 10-Phenyl-9-anthracenecarboxaldehyde.**[2] A mixture of 9-phenylanthracene (4 g, Aldrich), DMF (2.7 mL), and *o*-dichlorobenzene (5 mL) was cooled with an ice bath, and $POCl_3$ was slowly added dropwise. Upon completion of $POCl_3$ addition the mixture was heated to 95 °C and maintained at that temperature for $2^1/_2$ h. The mixture was cooled and then neutralized with aqueous NaOAc. Water was added to the mixture, which was then stored in a refrigerator overnight. The solid was filtered and dried on a vacuum line. The crude product was eluted from a silica gel column (MCB, 60–200 mesh).

**(10-Phenyl-9-anthryl)methanol.**[3] The crude product of the above preparation (3.5 g) was dissolved in benzene (50 mL). A $NaBH_4$ solution (0.2 g in 10 mL methanol) was added dropwise until all nonfluorescent material was consumed. HCl (100 mL) was added to the solution, which was then stirred for 1 h. The benzene layer was chromatographed on a silica gel column, and the alcohol was eluted with methanol. The product is a yellow crystal (yield based on 9-phenylanthracene, 82%); mp 149–151 °C; *m/e* 284.

**(10-Phenyl-9-anthryl)methyl Methacrylate.** This monomer was prepared in a manner similar to that of 9-anthrylmethyl methacrylate except dry pyridine only was the solvent and the product was purified by eluting it with benzene from a silica gel column. The ester is a yellow crystal (yield 55%): mp 129–130 °C (uncorrected); NMR ($CDCl_3$) $\delta$ 1.85 (s, 3 H), 5.4 (s, 1 H), 6.0 (s, 1 H), 6.2 (s, 2 H), 7.2–8.45 (m, 13 H); *m/e* 352.

**(d) (10-Phenyl-9-anthryl) 2-Methylpropanoate.** This was prepared in similar fashion to that of the monomer by using, instead, (10-phenyl-9-anthryl)methanol and isobutyryl chloride (Aldrich). It was purified by chromatography using activated alumina and benzene and recrystallized from ethanol to give yellow crystals (85% yield): mp 161–163 °C (uncorrected); NMR ($CDCl_3$) $\delta$ 1.1–1.2 (d, 6 H), 2.3–2.8 (septet, 1 H), 6.15 (s, 2 H), 7.2–8.4 (m, 13 H); *m/e* 354.

**(e) 9-Anthrylmethyl Ethenyl Ether.** This monomer was prepared by vinyl transetherification of vinyl *n*-butyl ether

† Presented in part at the 38th Southwest and 6th Rocky Mountain Combined Regional Meeting of the American Chemical Society, El Paso, TX, Dec 1–3, 1982.

0024-9297/84/2217-0235$01.50/0 

(Aldrich) and 9-anthracenemethanol as described in the literature.[4]

**(f) 9-Anthrylmethyl Ethyl Ether.** This compound was synthesized by the method of Johnstone and Rose[5] for the alkylation of hydroxyl derivatives, using in this instance 1-bromoethane and 9-anthracenemethanol. After recrystallization twice from methanol the procedure gave yellow needles (85% yield): mp 72–74 °C (uncorrected); NMR ($CDCl_3$) $\delta$ 1.1–1.2 (t, 3 H), 3.5–3.8 (q, 2 H), 5.35 (s, 2 H), 7.2–8.5 (m, 9 H); *m/e* 236.

**(g) Polymerization.** Polymerization of the methacryloyl monomers was carried out in thoroughly deoxygenated benzene at 60 °C for 24 h in sealed tubes, using 2,2′-azobis(isobutyronitrile) as initiator (1 wt %). This method is similar to that used in an earlier report of PAMMA.[6] The vinyl ether monomer was polymerized cationically[7] in either toluene (MCB) (PAE-1) or dichloromethane (MCB, spectrograde) (PAE-2) by using purified, redistilled boron trifluoride etherate (Aldrich) as received. Toluene and dichloromethane were purified and dried prior to use by the methods described in ref 8. The solvent change is expected to change the tacticity of the polyether.[9] Polymerization was carried out in a vacuum-sealed tube at room temperature (to prevent crystallization of monomer) with 0.5 mol/L solutions containing 5 mol % of catalyst. The reaction was stopped after 6 h by the addition of methanol. All polymers were purified by precipitation 3 times by addition of a benzene solution into rapidly stirred methanol. Molecular weights were determined from a polystyrene calibration curve on a Waters HPLC chromatograph (with Waters $\mu$-Styragel columns, 500-, $10^3$-, $10^4$-, and $10^5$-Å or $10^2$-, 500-Å pore size and $CH_2Cl_2$ as the mobile phase). This provided a further purification procedure, as the polymer was collected as it came off the column and stored in the dark at 0 °C for future fluorescence work.

**2. Optical Characterization.** Absorption spectra were taken with a Cary 14 spectrometer. Steady-state fluorescence emission and excitation spectra were obtained on a Spex Fluorolog fluorimeter (Model 1902) with double monochromators for excitation and emission. All solutions had an OD at the excitation wavelength (365 nm) of $\leq$0.1 with a 1-cm path length; concentrations in anthracene units were less than $1 \times 10^{-5}$ mol·L$^{-1}$.

Spectrophotometric grade $CH_2Cl_2$ (MCB) was used as received for fluorimetry. MTHF (Columbia Organic Chemicals) was refluxed over $LiAlH_4$ and fractionally distilled immediately prior to use. Stern–Volmer quenching constants were measured by monitoring the decrease in fluorescence intensity at the wavelength of maximum emission with addition of quencher. Distilled carbon tetrachloride was used as quencher.

**3. S–S Annihilation Studies.** The experimental conditions are as follows. (1) The excitation source was a picosecond Nd:YAG laser (fwhm = 40 ps), operated at the third harmonic (355 nm) with a maximum power/shot of ca. 5 mJ (ca. $9 \times 10^{15}$ photons/shot). (2) As laser power was increased, neutral-density filters were placed between the fluorescent solution and the observation photomultiplier, such that the photocurrents were similar for all laser powers. (3) A Tektronix 7912 fast digitizer was used to capture the fluorescence wave form, which was transferred to a computer for data analysis (typically the decay curves are fit to single or double exponentials including a deconvolution routine to minimize the effect of the photomultiplier time response function). (4) Solutions (benzene solvent) were outgassed and prepared with an anthracene OD of ca. 0.06 at 355 nm. It was not possible to monitor the exact energy density/shot for these initial experiments.

The method used to obtain a "best fit" (in the least-squares sense) for biexponential decay was as follows. (1) The long-time portion of the fluorescence decay was fit to a single exponential. (2) The short-lived fluorescence was fit to a biexponential function ($Ae^{-at} + Be^{-bt}$) in which one of the rate constants was constrained to be equal to the rate obtained from the long-time analysis.[10] The decay curves were fit from the original intensity at $t = 0$ to a value of $t$ where the intensity had dropped approximately sixfold.

**4. Photolysis.** Photolysis of thoroughly deaerated benzene solutions of the polymers in Pyrex vessels was carried out with a Rayonet photochemical chamber reactor (RPR-100) with RPR-3500 lamps (305–425-nm spectral range). Photodegradation products were analyzed by mass spectral and visible absorption analysis and by TLC, using comparisons with known, authentic samples.

Table I
Molecular Weight of Polymers

| compd | $M_w$[a] (DP[b]) | $M_w/M_n$[a] |
|---|---|---|
| PAMMA | 26 600 (96) | 1.40 |
| PPA | 16 300 (46) | 1.44 |
| PAE-1,2 | 5 000 (21) | 1 |

[a] Based on polystyrene calibration curve. [b] Degree of polymerization.

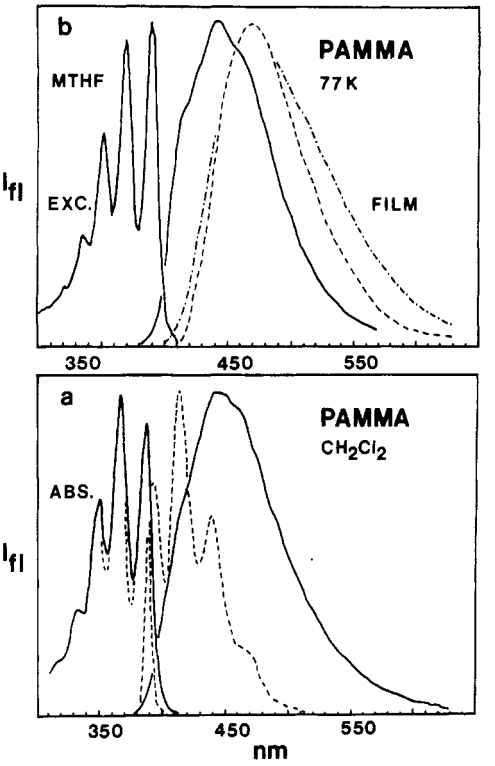



**Figure 1.** Fluorescence and absorption (or excitation) spectra of PAMMA: (a) PAMMA (solid line) and monomer model (dashed line); $CH_2Cl_2$ solution $10^{-5}$ M in anthryl groups (excitation at 365 nm); the high-energy portion of the spectrum is the absorption spectrum of polymer and model, scaled to equal maxima. (b) Spectra at 77 K (monomeric model not shown for clarity); MTHF glass (solid line), neat film at 77 K (- - -), (· - ·) neat film at room temperature.

## Results and Discussion

**1. Absorption and Fluorescence Spectroscopy. (a) PAMMA (I) and PPA (II).** These two polymers are very similar except for the somewhat higher molecular weight of PAMMA (based on the polystyrene calibration curve; see Table I) and the addition of the bulky phenyl group at the 10-position for PPA. It is well-known that 9,10 substitution on anthracene diminishes the importance of photodimerization[11] or excimer formation. Since excimer fluorescence is one of the most characteristic processes in polymer photophysics, it is of interest to understand how this 10-position "blocking" affects the anthracene polymer photophysics. As will be seen in the following, this substitution has a profound effect.

The polymer absorption and fluorescence spectra of $CH_2Cl_2$ solutions (at room temperature) or MTHF glasses (at 77 K) are summarized in Figure 1 (PAMMA) and Figure 2 (PPA). Also in these figures are the neat film and model compound spectra (the latter are shown in $CH_2Cl_2$ at room temperature only; no significant shifts are observed in going to 77 K MTHF glasses for the model compounds).

For both PAMMA and PPA we note that the absorption (or excitation) spectrum for the polymer is only slightly

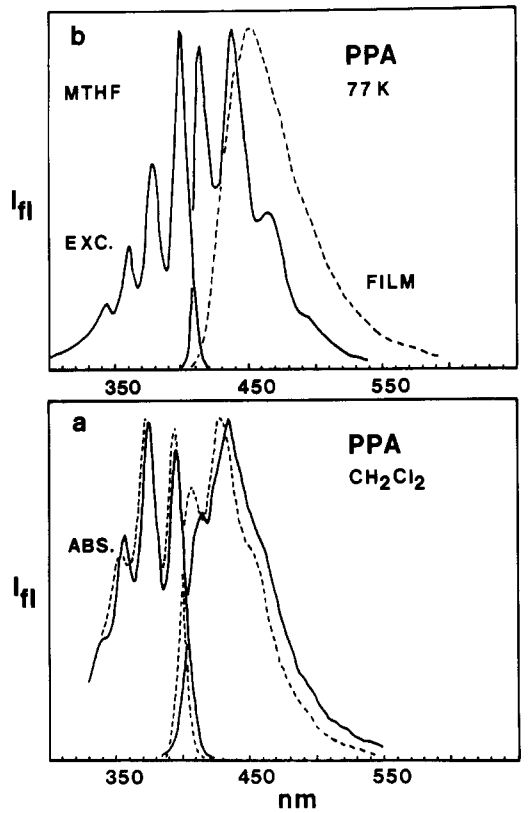



**Figure 2.** Fluorescence and absorption (or excitation) of PPA: (a) PPA (solid line) and monomeric model (dashed line) (like Figure 1a). (b) Spectra at 77 K (monomeric model not shown for clarity); MTHF glass (solid line) and neat film at 77 K (---) (no shift in PPA film in going to room temperature).

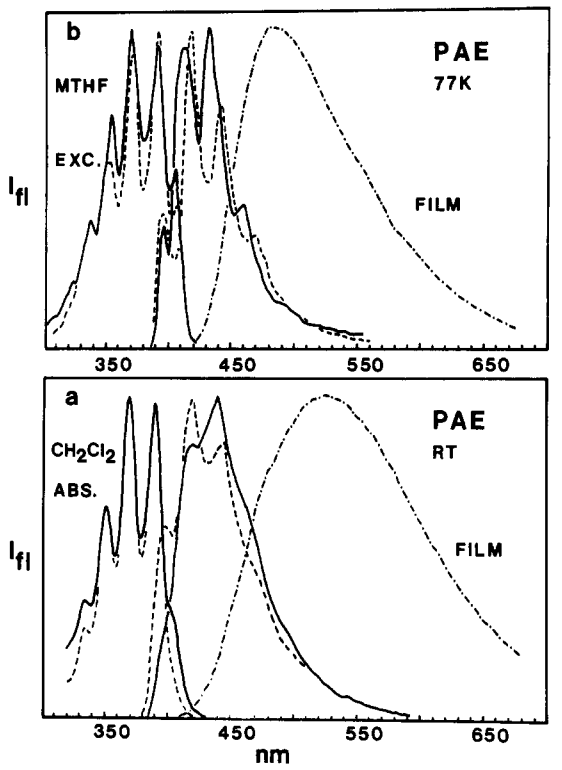



**Figure 3.** (a) PAE-1 (solid line) and PAE-2 (dashed line) in $CH_2Cl_2$ at room temperature (model compound not shown for clarity); neat film at room temperature. (b) PAE-1 (solid line) and PAE-2 (dashed line) in MTHF at 77 K; ··· is neat film at 77 K. The absorption spectra were the same as the excitation spectra in $CH_2Cl_2$.

different from that of the model ester (typically there is a red shift of a few nanometers). However, the fluorescence spectra are quite different. For PAMMA the fluorescence spectrum is broadened and red-shifted relative to the model compound. This is a typical "polymer effect" on the fluorescence of pendent aromatics and, on the basis of emission from bianthryl compounds,[12,13] we conclude that the structure giving rise to this excimer fluorescence is of two anthracene units that are only partially overlapping with each other. In other words, the excimer emission results from "partially eclipsed" chromophores. We note that the 77 K glass fluorescence is almost identical with the room-temperature spectrum, which we take as evidence that PAMMA contains a high density of "preformed excimer sites". Yet these sites are such that they result in very little ground-state dimer formation, as shown in the similar absorption spectra of PAMMA and its saturated monomer analogue. This is unlike PAE (see later).

In contrast to PAMMA, the fluorescence spectrum of PPA is very similar to that of its model, except for a 10-nm red shift. In the 77 K MTHF glass the PPA excitation and fluorescence spectra are both structured, implying that the mechanism of spectral broadening has been "frozen out" (presumably this broadening arises from the interaction of the 10-phenyl group with the anthryl moiety). However, even at 77 K there is approximately a 10-nm red shift of the polymer relative to the monomeric model (the fluorescence of the model compound is not shown in Figure 2 for clarity). Since this red shift does not seem to be the result of a thermally assisted process, it is reasonable to think of it as a kind of excitonic self-polarization (i.e., the polarization of surrounding anthryl moieties by an excited-state anthracene), as shown, for instance, in anthracene crystals.[14]

For both PAMMA and PPA the film spectra are broadened and red-shifted relative to the solution spectra. This phenomenon is quite common for polymers and is usually interpreted as an enhancement of the excimer component in the fluorescence spectrum. On the basis of the data on bianthryl compounds[12,13] and the anthracene fully eclipsed excimer,[15] we believe that the film state enhances the role of a partially eclipsed excimer state. In view of our solution-phase observations it is not surprising that the film spectrum for PAMMA is red-shifted and broadened relative to that of PPA. It is less obvious why the PAMMA film spectrum is more temperature dependent than that of PPA.

**(b) PAE-1 and PAE-2.** The poly(anthryl ethers) are distinguished from the poly(anthryl methacrylates) by (1) lower molecular weight (see Table I), (2) only a two-atom separation from the polymer backbone, and (3) some control of stereoregularity by changing solvent. On the basis of solvent dielectric constant, PAE-1 is expected to be more stereoregular than PAE-2 (see Experimental Section). The fluid phase fluorescence spectra of these two polymers do differ slightly (see Figure 3a). The polymer fluorescence is broadened and red-shifted relative to the appropriate model compound (not shown in Figure 3 for clarity). However, the absorption edge for PAE-1 extends more to the red than does that for PAE-2 and shows a definite low-energy shoulder, which PAE-2 does not. The fluorescence of PAE-1 is more weighted toward lower energy features than is that of PAE-2, although the positions of the peaks of both polymers are essentially identical. This feature is not a self-absorption effect since the spectral shapes persist as total anthracene concentration is diminished.

The spectral differences between these two polymers persist at low temperatures (see Figure 3b). Both polymers

display well-structured excitation spectra that are typical of anthracene except that both show a low-energy shoulder, which is more prominent in PAE-1 than in PAE-2. The fluorescence spectrum of PAE-1 has broader peaks than that of PAE-2, and there is significant shift between the peak positions of these two polymers. There is also an unusually large overlap of the excitation spectrum and the fluorescence spectrum. We note that excitation at 410 nm (predominant absorption by the ground-state dimer) yields a spectrum like that reported by Chandross et al.[15]

The observation of a broad shoulder to the red of the normal absorption or excitation spectrum tends to imply the existence of ground-state dimers that play a role in both absorption and fluorescence and have been observed in similar systems.[16] These ground-state dimers must not be very similar to the partially eclipsed excimer proposed for PAMMA. In fact the fluorescence of the PAE samples in $CH_2Cl_2$ solution or MTHF glasses is more similar to that of PPA than PAMMA (PAE is shifted by approximately +5 nm relative to PPA, however).

The film spectra of the PAE samples are drastically different from those of the PAMMA or PPA films but are not very different from each other. PAE film spectra are shifted by 20–30 nm to the red of PAMMA or PPA at 77 K and by as much as 100 nm at room temperature. We presume that these features arise from the fully eclipsed form of the anthracene excimer.[15] Evidently in PAE films there is sufficient "local mobility" to achieve this configuration. Furthermore, this local mobility is fairly sensitive to temperature, unlike the anthryl methacrylates (especially PPA).

**(c) Discussion of Absorption and Fluorescence Results.** The absorption/fluorescence features described above do not permit a straightforward quantitative interpretation. However, these results do demonstrate the effects of pendent group and main chain "architecture" on the photophysics of a homologous series of polymers. To summarize: (1) The fluorescence of PAMMA is the most changed relative to the monomeric model of any of the polymers studied. It seems reasonable to assign polymer fluorescence to a partially eclipsed excimer. In the film state further excimeric stabilization occurs. (2) For PPA only a modest polymer perturbation of the fluorescence is observed, implying little or no excimer formation. Even the film displays a relatively small excimeric component in the fluorescence. Evidently the blocking phenyl group at the 10-position does serve to prevent excimer formation. (3) The PAE polymers present something of an anomaly. This polymer system is evidently crowded enough to produce ground-state dimers, yet is not dominated by classical excimer fluorescence in solutions or a glassy matrix. The natural conclusion is that the structure of the ground-state dimer is significantly different from the excimer. However, in neat films of PAE the classical excimer can be formed, perhaps between anthryls on different coils or distant neighbors of the same polymer coil.

In closing this subsection we note that the solution-phase fluorescence spectra of these anthryl polymers were not very dependent on solvent. Specifically if a nonsolvent (e.g., ethanol) were added to a good solvent (e.g., $CH_2Cl_2$) or solvents of different thermodynamic quality were used, no change was observed in the fluorescence spectrum, so long as the solution remained clear.

**2. Fluorescence Quenching and Estimation of Singlet Energy Migration Rate ($\Lambda_s$).** We[10] and others[17] have estimated the singlet energy migration constant ($\Lambda_s$) by measuring the relative quenching efficiency of a contact quencher (typically $CCl_4$) for a polymer-bound species and a monomeric model compound. The relevant equations are

$$I(0)/I(Q) = 1 + k_q\tau_0[Q] \quad (1)$$

and

$$\Lambda_s/D = (k_q^{polymer} - (1/2)k_q^{model})/(1/2)k_q^{model} \quad (2)$$

in eq 1 (the Stern–Volmer equation) $k_q$ is the bimolecular rate constant for singlet-state quenching by Q, and $\tau_0$ is the (unquenched) lifetime of the excited state. Experimentally $I(0)/I(Q)$ is fit to a straight line (slope = $k_q\tau_0$), $\tau_0$ is measured independently, and $k_q$ is calculated. To derive eq 2 one assumes the applicability of a modified Smoluchowski–Einstein equation[18a]

$$k_q = 4N_0(D_Q + D_E + \Lambda_s)(PR) \times 10^{-3} \quad (3)$$

with the further assumption that the product $PR$ ($P$ = probability of reaction at collision radius $R$) is equivalent for the polymer-bound chromophore and the monomeric model. For the model compound it is assumed that $\Lambda_s$ = 0, and for the polymer that $D_E = 0$ (i.e., segmental diffusion can be ignored during the lifetime of the excited state). $D_Q$ is the diffusion constant of the small-molecule quencher. If $D_Q$ and $D_E$ are essentially equal, then eq 2 follows, where $D = (D_Q + D_E)/2$. Because of the many assumptions leading to eq 2 we interpret values of $\Lambda_s/D$ less than unity as implying little or no energy migration within experimental error. Furthermore, derived values of $\Lambda_s$ for $\Lambda_s/D$ on the order of unity are inevitably of poor accuracy and reflect the presence rather than the magnitude of singlet energy migration.

Fluorescence quenching by $CCl_4$ of $CH_2Cl_2$ solutions of the anthryl polymers and the monomeric model compounds was carried out to obtain the Stern–Volmer quenching constant ($k_Q\tau_0$). For this portion of the experiment a $CCl_4$ concentration up to 0.345 M was used. Fluorescence lifetimes were obtained with facilities described in the Experimental Section. These data are presented in Table II. The derived values of $k_q$, $\Lambda_s/D$, and $L_s$ are also given there, where $L_s$ is the excitation diffusion length derived on the basis of a one-dimensional random walk

$$L_s = (2\Lambda_s\tau_0)^{1/2} \quad (4)$$

To evaluate eq 4 $D$ was assumed to have a value of $1.5 \times 10^{-5}$ cm$^2$/s (appropriate for $CCl_4$).[18b]

The experimental results demonstrate that for PPA $\Lambda_s/D$ is greater than unity, and in fact the derived value of $L_s$ is quite significant for this polymer. However, for PAMMA, PAE-1, and PAE-2 we find $\Lambda_s/D = 0$. On the

Table II
Fluorescence Quenching of Polymers, Monomeric Models, and Derived Energy-Transfer Parameters

| compd | $k_q\tau_0$,[a] $M^{-1}$ | $\tau_0$,[b] ns | $10^{-8}k_q$, $M^{-1}$ s | $\Lambda_s/D$[d] | $L_s$,[e] Å |
|---|---|---|---|---|---|
| PAMMA | 0.82 | 5.4 (2, 9) | 1.5 | 0 | 0 |
| (model) | 1.44 | 4.5 | 3.2 | | |
| PPA | 1.67[c] | 6.7 (8.8) | 2.5 | 1.17 | 48 |
| (model) | 1.45 | 6.3 (8.6) | 2.3 | | |
| PAE-1 | 4.32 | 4.7 (4, 11) | 6.6 | 0 | 0 |
| (model) | 2.04 | 2.5 | 8.2 | | |
| PAE-2 | 6.75 | 6.3 (4, 11) | 11 | 0 | 0 |
| (model) | 2.04 | 2.5 | 8.2 | | |

[a] From slope of Stern–Volmer quenching (eq 1). [b] In aerated $CH_2Cl_2$ solutions ($\tau_0 = \tau_e$ for PAMMA and PAE). Lifetimes in parentheses are for deaerated benzene solutions. Two values are given when the decay was best fit to a double exponential. [c] From initial slope only (see text). [d] See eq 2. [e] See eq 4.

basis of apparent importance of the partially eclipsed excimer state, as discussed in the previous section, these results are not surprising. Previous results for other polymers have demonstrated that excimers act as traps for intracoil singlet excitons in the solution phase.[1,10,19]

One comment concerning the Stern–Volmer quenching curves is in order. Except for PPA, all species showed a linear quenching relationship (see eq 1) for $CCl_4$ concentrations up to 0.345 M. However, for PPA there was a supralinear dependence of $I(0)/I(Q)$ for $[CCl_4] > 0.2$ M. Such positive deviations are not uncommon. For instance, it has been interpreted as a "static quenching" in which donor–acceptor pairs act as if they were molecularly associated with an equilibrium constant $K$, so that[20]

$$I(0)/I(Q) = (1 + K[Q])(1 + k_q\tau_0[Q])$$

However, the quenching deviation we observe for PPA does not follow this relationship. We could find no evidence for ground-state complex formation, as the absorption spectrum of PPA is unchanged in the presence of $CCl_4$. Similar conclusions have been reached for $CBr_4$ quenching of anthracene.[21] This kind of dependence has also been observed for excimer states, or in the case of overlapping excimer/monomer fluorescence.[10] In these instances, however, the Stern–Volmer quenching constant is wavelength dependent. For PPA quenched by $CCl_4$ this cannot be the explanation since the spectral distribution of the fluorescence emission did not change on addition of quencher.

We do not have a ready account for this deviation in our system, although we note that Keizer[22] has recently offered an explanation for such effects for those cases where there is no molecular association and which is based on a modification of Smoluchowski's theory of diffusion effects on reactions in solution. The diffusion of excitation energy down the polymer chain in PPA may thus be the cause of the supralinear dependence we observe for this system.

In the analysis of the Stern–Volmer quenching for PPA only the initial portion of the quenching curve was used to obtain $k_q\tau_0$. We also note that of the four polymers only the fluorescence decay of PPA could be fit to a single exponential. Both PAMMA and the PAE polymers could be fit satisfactorily only if a double-exponential decay function was used. Hence the appropriate value of $\tau_0$ in eq 1 is questionable. Values of $\tau_0$ for these polymers, given in Table II and used to estimate $k_q$, are the times taken for the fluorescence intensity to fall to $1/e$ of that intensity at $t = 0$. Furthermore, any fluorescence lifetime below 5 ns is subject to some degree of error by our deconvolution method of data fitting.

**3. Observation of S–S Annihilation in PPA.** Recently, Masuhara et al. reported S–S annihilation in poly(*N*-vinylcarbazole) (PVCz) and other carbazole polymers or oligomers.[23] This is consistent with the previously reported estimate $L_s = 40$ Å for the PVCz monomeric singlet state. In a preliminary set of experiments we measured the excitation intensity dependence of the fluorescence intensity and decay of the polymers in degassed benzene solution. The fluorescence intensity of PPA was highly nonlinear at higher laser powers, showing strong saturation effects, while the model compound displayed a simple linear dependence. This nonlinearity is typically observed in the case of S–S annihilation. However, the fluorescence decay of both compounds did not depend on the laser power (time resolution ca. 1 ns). S–S annihilation in these and other polymers will be the subject of later publications.

One would expect significant S–S annihilation to occur when excitations are created along the chain at average separations of the order $L_s/l$ units (where $L_s$ is the exciton mean free path and $l$ is the average separation between chromophores). However, since we do not have a quantitative measure of the photons/shot and we are not aware of a quantitative theoretical basis for the interpretation of these decay curves in terms of $L_s$ and $l$, we will not attempt a detailed interpretation of these results. We present these preliminary results only to demonstrate that they are consistent with the hypothesis of facile singlet migration in the PPA polymer.

**4. Photostability.** While we have not attempted a systematic study of the photochemistry on the anthryl polymers discussed above, this group presents a complex array of facile photoreactions. Our photostability work has centered on PAMMA or PPA because of the higher molecular weights of these samples (see Table I) and the relatively large amount of material on hand.

We note that PAMMA tends to become insoluble after standing in solution for only a few days under normal laboratory conditions.[24] Since this does not occur in the dark, we assume that this facile formation on an insoluble product is due to photodimerization, since the absorption spectrum of the solution begins to resemble that of an anthracene dimer.[25] Certainly, solutions of this polymer have been shown to photodimerize when irradiated, the relative quantum yields of interchain or intrachain photodimerization depending on the polymer concentration.[25]

In addition to these observations, we have also noticed the formation of a complex array of small-molecular anthryl moieties, both fluorescent and nonfluorescent, on UV exposure. Certain of these have been identified by mass spectral and absorption spectroscopy and TLC analysis of the photoproducts and confirmed by reference to known, authentic samples. In aerated benzene solutions anthraquinone is, as expected from model compound studies,[26] a photoproduct for both PPA and PAMMA. In degassed benzene solutions, and even for PAMMA, which might be expected to be predominantly photodimerized, fragmentation still occurs. The vinyl monomer is one of the products, for both PPA and PAMMA, implying photo-depolymerization.[27] In addition, 9-anthraldehyde was identified in irradiated, degassed benzene solutions of PAMMA.

Since photooxidation is unlikely in degassed solutions and photodimerization unlikely for PPA or already extensively photodimerized PAMMA (where "isolated" anthracene units may be thought of as being sandwiched between two photodimers and thus unable to photodimerize with nearest neighbors),[25] the observed photoproducts probably arise from photodegradation of the carbonyl chromophore.[27] The excitation of this group can occur under our experimental conditions ($\lambda > 305$ nm) even though it might be expected that the anthracene moiety would absorb most of the light, acting as a UV screen. Further detailed work will be required to determine the relative instabilities of the two polymers and to determine the effect that solution concentration[26] or the energy of the exciting light has on the relative yield of the photoproducts.

## Summary

The main objective of the present work is to elucidate structure–photophysics relations for several anthryl polymers. We have shown that it is possible to enhance singlet energy migration by retarding the formation of partially eclipsed excimers. This was accomplished by blocking the 10-position of the anthracene moiety with a phenyl group. Facile energy migration (i.e., $\Lambda_s > 2 \times 10^{-5}$ $cm^2/s$) was found for PPA, but not for PAE and PAMMA.

In addition, evidence for S–S annihilation was found for PPA, which further implies significant singlet energy migration. Moreover, all ester polymers were found to have photolabile side groups.

**Acknowledgment.** We acknowledge the financial support of the National Science Foundation (Grant DMR-8013709) and the Robert A. Welch Foundation (Grant F-356). We also acknowledge the help of the staff and the use of the facilities of the Center for Fast Kinetics Research, which is supported jointly by the Biotechnology Branch of the Division of Research Resources of the NIH (Grant RR00886) and the University of Texas at Austin. Special acknowledgment is made to Brent Hyman, who carried out much of the monomer synthesis and polymerization for PPA and PAMMA.

**Registry No.** I, 51960-29-3; II, 88315-88-2; III, 88315-89-3; methacryloyl chloride, 920-46-7; 9-anthrylmethyl 2-methylpropanoate, 88315-77-9; 9-anthracenemethanol, 1468-95-7; isobutyryl chloride, 79-30-1; 10-phenyl-9-anthrylmethanol, 24451-26-1; (10-phenyl-9-anthryl)methyl methacrylate, 85702-19-8; (10-phenyl-9-anthryl)methyl 2-methylpropanoate, 88315-78-0; 9-anthrylmethyl ethyl ether, 86170-50-5; bromoethane, 74-96-4.

## References and Notes

(1) Holden, D. A.; Guillet, J. E. *Macromolecules* **1980**, *13*, 289.
(2) Campaigne, E.; Archer, W. L. *J. Am. Chem. Soc.* **1953**, *75*, 989.
(3) Stewart, F. H. C. *Aust. J. Chem.* **1960**, *13*, 478.
(4) Skorokhodov, S. S.; Anufrieva, E. V.; Koltsov, A. I.; Lushchik, V. B.; Pautov, V. D.; Stepanov, V. V. *J. Polym. Sci., Polym. Symp.* **1973**, *No. 42*, 1583.
(5) Johnstone, R. A. W.; Rose, M. E. *Tetrahedron* **1979**, *35*, 2169.
(6) Shelekhov, N. S.; Krakovyak, M. G.; Klenin, S. I.; Lashkov, G. I.; Kozel, S. P.; Skorokhodov, S. S. *Vysokomol. Soedin, Ser. A* **1977**, *A19*, 1586.
(7) The molecular weights we obtain are comparable to those of pyrene or naphthyl ethers. See: Yoshimoto, S.; Okamoto, K.; Hirata, H.; Kusabayashi, S.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 358.
(8) Weissberger, A., Ed. "Techniques of Organic Chemistry"; Interscience: New York, 1970; Vol. VII.
(9) Plesch, P. L., Ed. "The Chemistry of Cationic Polymerization"; Macmillan: New York, 1963.
(10) Webber, S. E.; Avots-Avotins, P. E.; Deumie, M. *Macromolecules* **1981**, *14*, 105.
(11) Baum, E. J. in "Excited State Chemistry"; Pitts, J. N., Jr., Ed.; Gordon and Breach: New York, 1970.
(12) Hayashi, T.; Mataga, N.; Sakata, Y.; Misumi, S.; Morita, M.; Tanaka, J. *J. Am. Chem. Soc.* **1976**, *98*, 5910.
(13) De Schryver, F. C.; Boens, N.; Huybrechts, J.; Daemen, J.; De Brackeleire, M. *Pure Appl. Chem.* **1977**, *49*, 237.
(14) Birks, J. "Organic Molecular Photophysics"; Wiley: New York, 1973.
(15) Chandross, E. A.; Ferguson, J. *J. Chem. Phys.* **1966**, *45*, 3554.
(16) (a) Suzuki, Y.; Tazuke, S. *Macromolecules* **1981**, *14*, 1742. (b) Tazuke, S.; Banba, F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2463.
(17) (a) Abuin, E. A.; Lissi, E. A.; Gargallo, L.; Radic, D. *Eur. Polym. J.* **1979**, *15*, 373. (b) Ishii, T.; Handa, T.; Matsunaga, S. *Macromolecules* **1978**, *11*, 40.
(18) (a) Voltz, R.; Laustriat, G.; Coche, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1966**, *63*, 1253. (b) Heisel, F.; Laustrait, H. *Ibid.* **1965**, *66*, 895.
(19) However, Nakahira et al. have demonstrated that reducing excimer formation in naphthalenic polymers does not necessarily enhance $\Lambda_p$. see: (a) Nakahira, T.; Sakuma, T.; Iwabuchi, S.; Kojima, K. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1863. (b) Nakahira, T.; Sasaoka, T.; Iwabuchi, S.; Kojima, K. *Makromol. Chem.* **1982**, *183*, 1239.
(20) Bowen, E. J.; Metcalf, W. S. *Proc. R. Soc. London, Ser. A* **1951**, *206*, 437.
(21) Ware, W. R.; Novros, J. S. *J. Phys. Chem.* **1966**, *70*, 3246.
(22) Keizer, J. *J. Am. Chem. Soc.* **1983**, *105*, 1494.
(23) (a) Masuhara, H.; Mataga, N. *J. Lumin.* **1981**, *24/25*, 511. (b) Masuhara, H.; Shioyama, H.; Mataga, N.; Inoue, T.; Kitamura, N.; Tanabe, T.; Tazuki, S. *Macromolecules* **1981**, *14*, 1738. (c) Masuhara, H.; Tamai, N.; Inoue, K.; Mataga, N. *Chem. Phys. Lett.* **1982**, *91*, 109.
(24) In an earlier synthesis of PAMMA (ref 6) loss of solubility even during purification was noted.
(25) (a) Lashkov, G. I.; Krakovyak, M. G.; Shelekhov, N. S.; Shatseva, L. S.; Skorokhodov, S. S. *Dokl. Akad. Nauk SSSR* **1974**, *214*, 850. (b) Kozel, S. P.; Lashkov, G. I. *Opt. Spectrosk.* **1980**, *45*, 607.
(26) Bowen, E. J. "Advances in Photochemistry"; Interscience: New York, 1963; Vol. 1, p 23.
(27) Ranby, B.; Rabek, J. F. "Photodegradation, Photo-oxidation and Photostabilization of Polymers"; Wiley: New York, 1975.

# Nitrile Function as a Probe of Cis/Trans Stereochemistry: $^{13}C$ NMR Studies of Poly(bicyclobutane-1-carbonitrile) and Related Model Compounds

**Michael Barfield,* Lung-fa Kao, H. K. Hall, Jr.,* and L. Glen Snow**

*Department of Chemistry, University of Arizona, Tucson, Arizona 85721.*
*Received June 10, 1983*

ABSTRACT: To better understand the stereochemistry of poly(bicyclobutane-1-carbonitrile) (PBBC), $^{13}C$ NMR studies were performed for a series of 3-substituted cyclobutanes. Of particular interest were the syntheses and NMR assignments for the two dimers (*cis*- and *trans*-3-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile) and the four trimers. In all of the molecules studied, substituents at C3, which were cis to the nitrile, led to $^{13}C$ NMR shifts of the nitrile that were 1–1.5 ppm to high field of those for the trans isomer; therefore the nitrile chemical shift is a very useful probe of cis/trans stereochemistry in cyclobutanecarbonitriles. Using data for cyclobutanecarbonitrile and the two dimers, we obtained additivity relationships; the calculated $^{13}C$ resonances of the four possible trimers are in very good agreement with the experimental values for the trimers. Furthermore, the shifts of the central cyclobutanecarbonitrile moieties of the four trimers are completely consistent with the nitrile resonances and account for most of the features of the ring carbon resonances of PBBC. As a consequence, the approximate 1:3 ratio of the intensities of the low-field to high-field CN resonances for the anionic-initiated PBBC indicates that about 75% of the rings are trans fused.

The stereochemistry of polymers based on vinyl and diene monomers and possessing all-carbon backbones have been extensively investigated by proton and $^{13}C$ NMR methods. It has been shown that bridgehead-substituted bicyclobutanes are a new family of highly reactive monomers which also yield polymers with all-carbon backbones upon polymerization.[1-3] These monomers polymerize by opening the bond between the C1–C3 bridge, yielding

0024-9297/84/2217-0240$01.50/0 