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Photophysics of Diphenylanthracene Polymers: Fluorescence and Singlet Energy Migration

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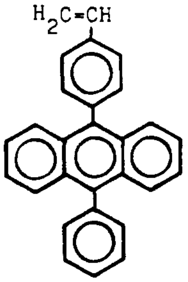
ABSTRACT: The fluorescence and energy-transfer properties of polymers containing pendent 9,10-diphenylanthracene chromophores is discussed (monomer: 9-(*p*-ethenylphenyl)-10-phenylanthracene (1)). The fluorescence for solutions and films of the homopolymer is slightly red-shifted relative to 9,10-diphenylanthracene, unlike copolymers of 1 with styrene (PDPA-*co*-PS) (maximum mole fraction of anthracene groups 0.08). On the basis of comparative quenching results we tentatively conclude that no singlet energy migration between anthryl groups occurs in these copolymers in fluid solution. However, in polystyrene films doped with PDPA-*co*-PS there is clear evidence for energy migration (based on Förster energy transfer to tetrabromo-*o*-benzoquinone). These results are compared to previous results with phenylanthracene-containing polymers (*Macromolecules* **1983**, *16*, 1017; **1984**, *17*, 235).

Introduction

In several recent publications we have reported studies on polymers containing pendent anthracene groups.[1,2] These polymers were either homopolymers or copolymers with styrene, in the latter case with the objective of improving compatability with polystyrene host matrices. Our overall objectives in these studies are (1) to understand the effect of the polymer environment on the photophysics of pendent chromophores and (2) to understand the factors that influence down-chain energy migration in either the singlet or triplet state. In principle, this latter phenomenon can be exploited in the use of polymeric photon collection "antennas" in photochemical transformations.

The present study is concerned with pendent diphenylanthracene (DPA) groups, produced by polymerization of 9-(*p*-ethenylphenyl)-10-phenylanthracene (1)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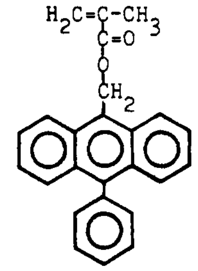
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either alone or with styrene (referred to as PDPA or PDPA-*co*-PS hereafter). There are several reasons for this choice of pendent chromophore: (1) the fluorescence quantum yield is close to unity[3] such that fluorescence is very easy to observe and complex photophysical pathways are avoided (i.e., singlet–triplet annihilation); (2) the Förster R_0 value for self-transfer is fairly large,[4] which should act to enhance singlet energy transfer; (3) because of extensive steric hindrance, DPA does not exhibit singlet excimer formation, photodimerization, or concentration quenching,[5] which suggests that one might expect tht the polymer excimer trapping of intracoil singlet excitons should be unimportant; and (4) photostability. Our previous studies[1] on anthracene-containing polymers show that the methacrylate bond is highly susceptible to photodegradation. Irradiation of PDPA, under conditions identical with those of either PAMMA (poly(9-anthrylmethyl methacrylate)) or PPA (poly[9-(10-phenylanthryl)methyl methacrylate]), does not produce any detectable photodegradation products. This is in direct contrast to these latter two polymers.

However, polymers containing DPA moieties are not so well-behaved as expected. In the solution-phase PDPA, the fluorescence of PDPA is red shifted relative to monomeric DPA to a greater extent than observed in polymers of 9-(10-phenylanthryl)methyl methacrylate[1] (2) (PPA). This red shift may be interpreted as arising from anthryl "self-polarization" (which is equivalent to a weakly bound excimer state[6]). For reasons to be discussed later we have not attempted to characterize singlet energy migration in PDPA as yet but we have not observed this phenomenon either in PDPA-*co*-PS or in the corresponding copolymers of 2 (PPA-*co*-PS) in solution. On the other hand, Förster quenching of anthracene fluorescence by tetrabromo-*o*-quinone (TBBQ) for these copolymers in polystyrene (PS) films does imply energy migration between anthracene groups, although in this case the transfer need not be confined to a given polymer coil. In the case of PDPA-*co*-PS/PS films there is no improvement in the apparent energy migration rate relative to the small-molecule model, DPA/PS, unlike the previously reported case of PPA-*co*-PS/PS.[2] On the other hand, the present results do demonstrate that polymer-bound chromophores can be used in preparing doped thin films, and in general this technique might be expected to be advantageous with respect to film quality and resistance to chromophore loss.

Experimental Section

1. Preparation of Monomers, Polymers, and Samples. **9-Hydroxy-9-phenylanthrone** was prepared by the oxidation of 9-phenylanthracene using sodium dichromate in acetic acid by the method of Blicke.[7] It was recrystallized from toluene to give a yield of 75%; mp 213–214 °C (lit.[8] mp 213–214 °C).

9-(*p*-Ethenylphenyl)-10-phenylanthracene (1) was synthesized via the action of (*p*-vinylphenyl)magnesium bromide[9] on 9-hydroxy-9-phenylanthrone and subsequent reduction of the quinol by KI and sodium hypophosphite as described by Meyer.[10] It was purified by column chromatography: mp 216 °C (lit.[10] mp 216 °C); NMR ($CDCl_3$) δ 5.2–5.4 (d, 1 H), 5.7–6.0 (d, 1 H), 6.7–7 (q, 1 H), 7.1–7.9 (m, 17 H).

9-(10-Phenylanthryl)methyl Methacrylate (2). This monomer was synthesized and purified as previously described.[1]

9-(10-Phenylanthryl) 2-Methylpropanoate (PA). This too was prepared as previously described.[1]

The above monomers were polymerized with styrene (PDPA-*co*-PS and PPA-*co*-PS for 1 and 2, respectively) or in the absence of styrene (PDPA and PPA for 1 and 2, respectively). The polymerizations were carried out in thoroughly degassed benzene solutions containing 1% by weight of AIBN (2,2′-azobis(isobutyronitrile)) as initiator at 60 °C for 24 h in sealed tubes. Polymerization for 60 h was carried out for PDPA-*co*-PS5 and PDPA-*co*-PS6 (see Table I for description of polymer samples).

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Table I
Properties of PDPA-*co*-PS

compd	mol fraction[a]	mol wt × 10^{-3} (PD)[b] (P)[c]	τ_f,[d] ns	τ_f,[e] ns
DPA (mdl compd)				~7.0
PDPA-*co*-PS1	0.0026	17.9 (1.35) (170)	6.5	6.5
PDPA-*co*-PS2	0.0085	17.9 (1.35) (170)	6.5	6.5
PDPA-*co*-PS3	0.009	17.9 (1.35) (170)	6.2	6.4
PDPA-*co*-PS4	0.012	17.9 (1.35) (170)	5.9	6.3
PDPA-*co*-PS5	0.038	43.1 (1.86) (410)	4.7	6.2
PDPA-*co*-PS6	0.08	32.7 (1.51) (310)	3.3	6.2
PDPA	1.0	48.5 (2.54) (136)	biexp	7.2

[a] Mole fraction of diphenylanthracene units in the copolymers. [b] Value in parentheses is polydispersity. [c] Degree of polymerization calculated with a monomer molecular weight of 104 for the copolymers and 356 for the PDPA. [d] Fluorescence lifetimes of neat films (±10%). [e] Fluorescence lifetimes in degassed benzene solution (±10%). For DPA in PS films, values used for τ_S were those given by Faulkner.[12]

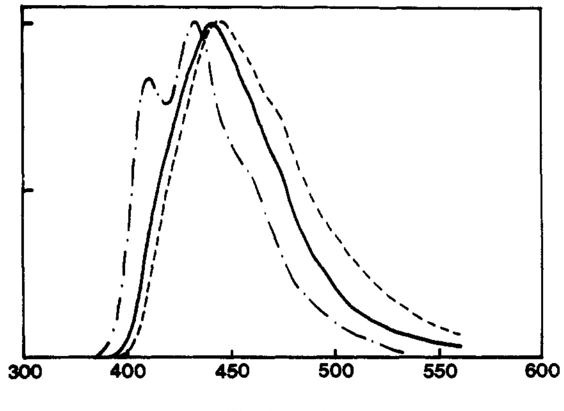

Figure 1. (-·-) DPA in CH_2Cl_2; (—) PDPA in CH_2Cl_2; (---) PDPA in 1:1 (v/v) CH_2Cl_2–ethanol. OD at excitation wavelength <0.1 for all spectra. Spectra scaled to equal maximum intensity.

All polymers were purified by repeated reprecipitations of benzene solutions by methanol. In certain cases, polymer solutions were further purified by collection of the material after it passed through a Waters HPLC chromatograph (with Waters μ-Styragel columns, 500-, 10^3-, 10^4-, and 10^5-Å pore size and CH_2Cl_2 mobile phase). This latter technique also enabled the molecular weights of the polymers to be determined, using a polystyrene calibration curve as reference. Mole fractions of the anthracene chromophore in the copolymers were determined by visible absorption spectroscopy on a Cary 17D spectrometer, using extinction coefficients given elsewhere.[11]

Styrene (Aldrich) was purified immediately prior to use by column chromatography using activated alumina. Diphenylanthracene (DPA) (Aldrich) was recrystallized several times from ethanol. Tetrabromo-*o*-benzoquinone (TBBQ) (Aldrich) was used as received. Spectrophotometry-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. Benzene (spectrophotometry grade from MCB) was also used as received.

Films were prepared by casting a ~5 wt % toluene solution of the components (polystyrene with polymer or small-molecule model, with or without quencher, in predetermined mole ratios) onto a glass slide rotating at approximately 200 rpm on a Headway Research (Model EC101) spin-casting apparatus. Thin films formed by this method were optically clear on visual inspection. All films from which we report results were prepared in this manner. Rapid atmospheric evaporation of a polymer/quencher solution from the surface of a glass slide resulted in nonhomogeneity of the components. This inhomogeneity could easily be detected visually because of the red color of the quencher. Furthermore, some films formed by this latter method were opaque. Slow evaporation of a casting solution, as for instance from the bottom of a long-necked specimen tube, appeared homogeneous to the naked eye, but inspection of the fluorescence from a film cast by this method and containing DPA showed conclusively that the latter had crystallized out and was thus concentrated in aggregates. The resulting emission spectrum was exactly the same as that obtained from a solid, crystalline DPA sample.[12] Thus the only method we found satisfactory, and therefore used in preparing films, was the spin-casting technique.

Mole ratios of the components in the casting solutions were retained on the slides. This was determined by redissolving the films in benzene. This enabled the absorption maximum of the quencher (TBBQ) to be considerably red shifted with respect to the film state and thus eased the separation of the absorption spectrum into its relative components.

Glass slides (Scientific Products, Inc.) were thoroughly cleaned with soap solution, distilled water, and acetone before being dried for use. Polystyrene of molecular weight 12 000 (Polysciences, Inc.) was thoroughly purified by the reprecipitation technique, described earlier, to remove considerable amounts of fluorescent impurities.

No attempt was made to measure accurately the thickness of the films. Previous workers in this field report that film thickness has no effect on the magnitude of the quantitative data.[12,13] However, the films are always less than 100 μm thick. Thus self-absorption distortion of the fluorescence spectra is essentially absent. Opaque films, which were discarded, do show distortion of the emission spectra.

Optical Measurements. 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 (375 nm) of <0.1 with a 1-cm cell path length. Thus concentrations in anthracene units are less than 1×10^{-5} mol L^{-1}. Excitation spectra of very thin films (OD < 0.05) were identical with those obtained in solution (except for a small environmental shift), which in turn were identical with the visible absorption spectra for wavelengths longer than 320 nm. Fluorescence emission from film samples were taken with front-face illumination.

Fluorescence lifetimes were obtained with a picosecond Nd:YAG laser (FWHM = 40 ps), operated at the third harmonic (355 nm). A filter was placed between the sample and the detector in order to minimize scattered light. A Tektronix 7912 fast digitizer was used to capture the fluorescence waveform, which was transferred to a computer for data analysis. All decay traces, whether from film or solution and with or without quencher, could be fit satisfactorily to a single exponential from the maximum of the decay curve (time $t = 0$) to a time t where the intensity had dropped approximately eightfold from that a $t = 0$.

Solution-phase quenching studies were carried out in aerated dichloromethane using fractionally distilled carbon tetrachloride (CCl_4) as quencher. Fluorescence lifetimes of the same aerated solutions, prior to quenching, were taken and used to determine quencher rate constants.

Results and Discussion

1. Fluorescence of PDPA Homopolymer in the Solution and Solid Phase.

The fluorescence spectra of PDPA and the model compound DPA are compared in Figure 1. As can be seen there is a distinct red shift and loss of structure in the polymer. This is not a self-absorption effect since the OD at the excitation wavelength is less than 0.1. This may be contrasted with our previous results with PPA in which there was only a very slight red shift in going from monomer of polymer.[1] Also displayed in Figure 1 is the red shift and broadening effect on the polymer fluorescence upon addition of a nonsolvent (ethanol). Note that DPA does not demonstrate any significant solvent shifts[3a–b,14] nor are any solvent shifts observed for the PDPA-*co*-PS copolymers. Enhancement of excimer fluorescence in poor solvents is common among polymers that form excimers because of the higher local concentration of pendent chromophores. There is no evidence that the fluorescence spectrum of PDPA is composed of overlapping monomer and excimer peaks since the shape

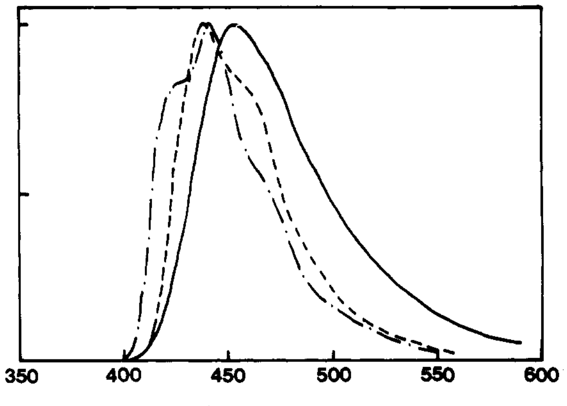

Figure 2. PDPA neat film at room temperature (—) and (- - -) 77 K; (-·-) PDPA) in MTHF glass at 77 K.

of the fluorescence spectrum does not change with CCl_4 quenching nor is the fluorescence decay a function of the observation wavelength. We conclude that the red shift observed in the PDPA solution-phase fluorescence is the result of anthracene–anthracene "self-polarization". This is similar to the mechanism of excimer formtion. However, in the case of PDPA there does not seem to exist a classical monomer–excimer interconversion. Our proposed "self-polarization" mechanism is equivalent to a thermally equilibrated monomer–weakly bound excimer state that behaves spectroscopically as a single state. Likewise there is no evidence for ground-state dimer formation, since the absorption and excitation spectra of the polymers and DPA are essentially identical.

In Figure 2 is presented the fluorescence of a film of PDPA at room temperature and 77 K. The room-temperature film spectrum is to the red of the solution spectrum, while at 77 K the film spectrum is very similar to that of a 77 K MTHF (methyltetrahydrofuran) glass (while not shown, the 77 K spectrum of DPA in MTHF is much more structured than that of PDPA). It is typical of excimer-forming polymers to exhibit strong excimer fluorescence in the film state even at 77 K (but not in a low-temperature glass). The enhanced red shift in the room-temperature film spectrum is consistent with our proposed self-polarization mechanism in the solution phase; i.e., the higher the anthracene density, the more important is this effect. However, the weakening of this red shift in a 77 K film implies that physical movement of anthryl groups is required to achieve the appropriate configuration for this coupling. Unfortunately, we do not have a measure of T_g for this polymer system.

We note that we did not observe these effects in PPA solution or film fluorescence. We speculate that this is a result of the lower flexibility of the methacrylate backbone compared to the polystyrene-like backbone in PDPA. In addition the juxtaposition of neighboring anthryl groups in undoubtedly affected by the linkage to the polymer main chain.

2. Energy Transfer in PDPA and P(DPA-*co*-S). (a) Solution Phase. A series of copolymers of 1 and styrene were prepared and characterized as described in the Experimental Section. The relevant properties of these copolymers are summarized in Table I. The solution-phase spectra of these copolymers are virtually identical with that of DPA, while the fluorescent lifetime is slightly shortened. There is no significant broadening and red shifting in the fluorescence spectrum as the mole fraction of anthracene increases, which is consistent with random copolymers with such low anthracene contents. While there is a trend toward shortening the fluorescence lifetime with increased anthracene content (see Table I), the changes are within experimental error.

Table II
CCl_4 Fluorescence Quenching Constants

compd	$k_q \times 10^{-9}$ (±10%),[b] $M^{-1}\ s^{-1}$
DPA	1.0
PDPA	0.96
PDPA-*co*-PS[a]	1.1

[a] The k_q value was identical for all copolymers. [b] ±10% error estimated because of uncertainty in τ_S (see Table I).

Table III
Properties of PPA-*co*-PS and CCl_4 Quenching Data

compd	mol fraction[a]	τ_f,[b] ns	τ_f,[c] ns	$k_q \times 10^{-9}$,[d] $M^{-1}\ s^{-1}$
PA (mdl compd)			8.6	0.23
PPA-*co*-PS1	0.016	6.9	8.8	0.28
PPA-*co*-PS2	0.021	6.2	8.8	0.28
PPA-*co*-PS3	0.039	5.3	8.8	0.28
PPA-*co*-PS4	0.051	5.2	8.8	0.28
PPA-*co*-PS5	0.07	4.5	8.8	0.28
PPA	1.0	biexp	8.8	0.25

[a] Mole fraction of anthracene in polymer. For PPA-*co*-PS all molecular weights (estimated from GPC) were 13 500 with a polydispersity of 1.5. [b] In neat films at room temperature (±10%). [c] In degassed benzene solution (±10%). [d] CCl_4 fluorescence quenching constant (see eq 1).

In order to assess the rate of energy migration, we used the comparative quenching technique that we[15] and others[16] have employed in the past. In this method of fluorescence quenching of the polymer and a model compound (DPA in the present case) is compared by means of the Stern–Volmer equation:

$$I_0/I_q = 1 + K_{SV}[Q] = 1 + k_q\tau_S[Q] \qquad (1)$$

where k_q is the bimolecular quenching rate constant and τ_S is the lifetime of the unquenched excited singlet state. I_0/I_Q is the ratio of unquenched to quenched fluorescence. The k_q values evaluated by this method are listed in Table II.

The argument we have used in the past with data such as these is that if $k_q^{\text{polym}} > {}^1/_2 k_q^{\text{model}}$, then the energy migration diffusion constant (Λ_S) is greater than zero. Specifically

$$\Lambda_S/\bar{D} = (k_q^{\text{polym}} - {}^1\!/_2 k_q^{\text{model}})/({}^1\!/_2 k_q^{\text{model}}) \qquad (2)$$

where $\bar{D}$ is an average diffusion constant, given in the present case by $\bar{D} = (D_{DPA} + D_{CCl_4})/2$. Thus the data in Table II would imply that $\Lambda_S/\bar{D} \sim 1$ for all polymers, including the copolymers.[17] For this latter group $\Lambda_S/\bar{D}$ is independent of the mole fraction of anthracene. This does not seem physically reasonable since the mole fraction changes by a factor of ~30 through this series of copolymers. A similar set of copolymers of 2 and styrene was examined (see Table III for results). The results were the same: the polymers are quenched as readily as the model compound and independently of the mole fraction of anthracene. We conclude that the results of the chemical quenching method lead to erroneous results in the present case.

It would seem that the proper "model compound" for comparative quenching studies would be a very low mole fraction of the chromophore of interest attached to an "inert" polymer chain such as our PDPA-*co*-PS1 or PPA-*co*-PS1. In such a copolymer the probability of any intracoil energy transfer is very low, such that the assumptions that lead to eq 2 would be valid. There would be two important differences: (1) the factor of ${}^1/_2$ would be re-

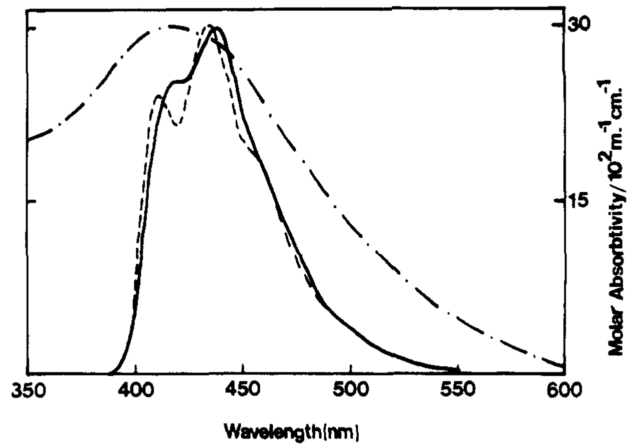

Figure 3. (—) PDPA-*co*-PS5 and (---) PPA-*co*-PS1 fluorescence in doped PS film; (-·-) absorption of TBBQ energy acceptor (see Tables I and III for sample designations).

placed by unity; (2) $\bar{D}$ would be replaced by D_{CCl_4}. With this modification $\Lambda_S \simeq 0$ is calculated. Certainly the use of a copolymer model compound is a better approximation to the effect of steric hindrance. However, there remains the important assumption that the probability of quenching per collision is independent of the density of chromophores along the chain. Since we are observing some perturbation of the fluorescence spectrum in PDPA relative to PDPA-*co*-PS, this assumption may not be justified for these anthryl polymers.[18] Thus the situation with respect to solution-phase singlet energy transfer is clouded for these polymers. On the basis of comparative quenching, we tentatively conclude that Λ_S is not significant with the caveat that the assumptions inherent in the method may not be valid.

(b) Solid Phase (Mixed Films of PDPA-*co*-PS/PS). In a previous paper[2] we used a technique like that of Renschler and Faulkner[12] to assess energy migration between chromophores dispersed in polystyrene (PS) films. The basic idea is to use a Förster quencher, in this case tetrabromo-*o*-benzoquinone (TBBQ), and the theory of Yokota and Tanimoto (Y–T)[19] to separate the effect of a single-step Förster transfer to the quencher from the effect of energy migration between identical chromophores preceding quenching. The Y–T expression is

$$I(t) = I(0)\exp(-t/\tau_S)\exp(-K[Q]t^{1/2}) \tag{3}$$

where

$$K = (4/3)\pi^{3/2}N'\alpha^{1/2}B \tag{4}$$

$$B = [(1 + 10.87x + 15.5x^2)/(1 + 8.743x)]^{3/4} \tag{5}$$

$$\alpha = R_0^6/\tau_S \tag{6}$$

$$x = \Lambda_S\alpha^{-1/3}t^{2/3} \tag{7}$$

In eq 6, R_0 is the critical transfer distance from fluorophore to quencher defined by Förster.[20,21] (N' is 6.023 × 10^{20}, Avogadro's number per millimole, and [Q] is the concentration of the quencher in mol/L). R_0 is evaluated by extrapolating the Förster quenching parameter λ ($\lambda = [Q]/[Q]_0$, where $[Q]_0 = (3/2)(\pi^{3/2}N'R_0^3)^{-1}$) to zero fluorophore concentration for a known TBBQ concentration, where λ is determined from the decay curve of quenched and unquenched DPA.[12] We obtain $R_0 = 28 \pm 1$ Å for DPA–TBBQ, in agreement with Renschler and Faulkner.[12] This large value for R_0 reflects the favorable overlap between the PDPA-*co*-PS fluorescence and TBBQ absorption (see Figure 3). Since the PDPA-*co*-PS fluorescence and DPA fluorescence are virtually identical in PS, we assume that R_0 = 28 Å for both of these. The situation for PDPA/PS or PPA/PS is more complex and will be discussed briefly at the end of this section.

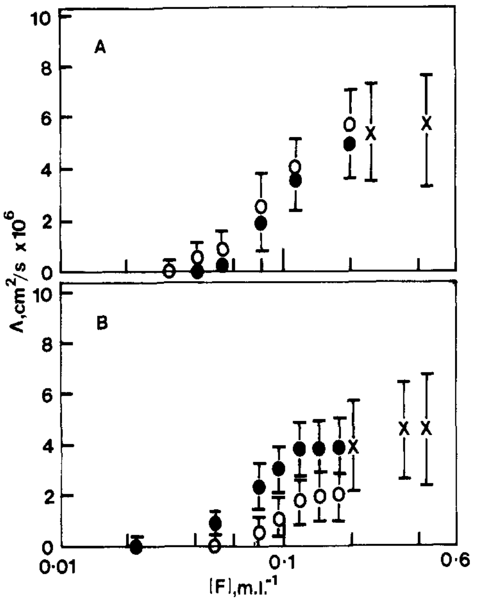

Figure 4. Plot of Λ vs. [F], where [F] is the average concentration of fluorophore. Open and closed circles are for (A) DPA and PDPA-*co*-PS in PS, respectively, and (B) PA and PPA-*co*-PS in PS, respectively. × represents the value of Λ for a neat film of a copolymer in the absence of added PS.

In principle, the time dependence of the fluorescence in the presence of the quencher should be fit to the relatively complex from of eq 3. In practice, a fairly good fit to a single exponential is obtained. Λ_S is obtained by taking the $1/e$ time of this decay curve and inserting into eq 3–7. The value we obtain for DPA is in good overall agreement with Renschler and Faulkner,[12] although with larger error bars, primarily because of the ±10% uncertainty in the τ_S value used.[22] Despite these relatively large uncertainties two conclusions can be drawn: (1) Λ_S does increase with the overall concentration of anthracene to a plateau[23] and (2) Λ_S for the copolymer dispersed in PS is no larger than Λ_S for DPA/PS. This is in contrast with our earlier report[1] on PPA-*co*-PS in which $\Lambda_S^{\text{polym}} \approx 2\Lambda_S^{\text{model}}$. The results for PDPA-*co*-PS/PS and PPA-*co*-PS/PS are compared in Figure 4. In all cases the concentration is the average concentration of the anthracene fluorophore in the film. We note that the limiting Λ_S value for both copolymers is very similar. Hence we interpret the lack of improvement in Λ_S for the copolymer relative to DPA to be the result of the good compatibility of DPA with PS. Conversely we assume that the model compound (9-(10-phenylanthryl) 2-methylpropanoate) (PA) was relatively incompatible with PS, although there was no direct visual or spectral proof of this incompatibility.

While it is reasonable that Λ_S should tend to saturate when the average chromophore separation is less than R_0 for chromophore–chromophore transfer (estimated as 23.4 Å for DPA by Renschler and Faulkner[12] and given as 27.2 Å by Berlman[4]), we note that the mean free path of the singlet exciton migration (i.e., $L_S = (6\Lambda_S\tau_S)^{1/2}$) would be larger if τ_S did not also decrease with fluorophore concentration, especially in the case of neat films of the copolymers (see Table I or the overall plot in Figure 5). This decrease in τ_S could be an inherent self-quenching effect or could reflect quenching impurities in the PS (which of course become more effective as Λ_S increases). We believe the latter is the source of lifetime shortening on the basis of the PDPA-*co*-PS/PS fluorescence spectra as a function

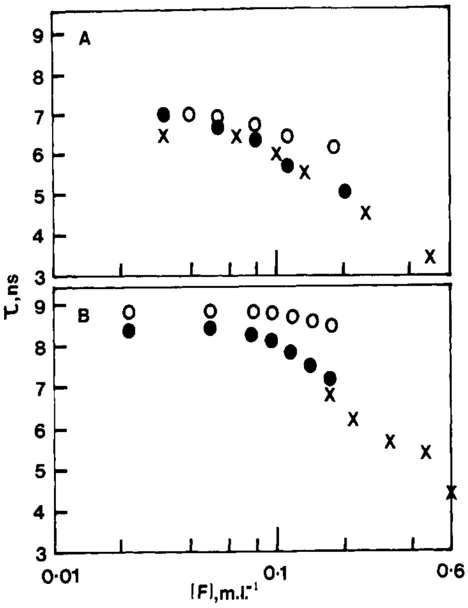

Figure 5. Plot of τ vs. [F], where [F] is the average concentration of the fluorophore. Open and closed circles are for (A) DPA and PDPA-*co*-PS in PS, respectively, and (B) PA and PPA-*co*-PS in PS, respectively. × represents the value of τ for a neat film of a copolymer in the absence of added PS (±10% accuracy in τ).

of overall anthracene concentration. Examination of the fluorescence spectra of either PDPA-*co*-PS/PS as a function of added copolymer or the neat films of the various copolymers reveals less than a +5-nm shift as the anthracene concentration increases over the range of values for which τ_S is plotted in Figure 5. Thus if the lifetime shortening in Figure 5 is the result of anthracene–anthracene coupling, it is not reflected in the fluorescence spectra. Förster coupling and energy migration do not lead to any spectral shifts but do provide a mechanism for "concentration quenching". Thus we speculate that if unknown quenching moieties could be removed from the film, τ_S would not be decreased, and in this case the exciton mean free path for neat films could be as large as for mixed films. If these quenching moieities are bound to the copolymer itself, then standard purification procedures (i.e., precipitation) will be futile.

In this section we have only discussed the experimental results for the copolymers PDPA-*co*-PS and PPA-*co*-PS. The situation for either PDPA/PS or PPA/PS, or the neat films, is complicated by the highly nonexponential fluorescence decay that makes application of Y–T theory extremely difficult and subject to very large errors.[24] In addition, the homopolymers are incompatible with PS films such that doped-film studies are impossible. Studies of energy-transfer phenomena in anthracene homopolymers are planned and will be reported in future publications.

Summary

In this paper we have presented the results of photophysical studies of homopolymers and copolymers with styrene of 9-(*p*-ethenylphenyl)-10-phenylanthracene (**1**). Despite the presence of two phenyl groups to protect the anthracene chromophore, the homopolymer (PDPA) exhibits a slightly red-shifted solution fluorescence while homopolymers, of **2** (9-(10-phenylanthryl)methyl methacrylate) do not display this phenomenon. Similarly, the film fluorescence spectrum of PDPA at room temperature is significantly red shifted. This red shift is assigned to strong resonance coupling between neighboring anthryl groups rather than a classical excimer fluorescence. (This resonance coupling is equivalent to a weakly bound excimer state.)

Copolymers of **1** and **2** with styrene were prepared (PDPA-*co*-PS and PPA-*co*-PS) primarily to study energy transfer in polystyrene (PS) films. While the results for these copolymers in fluid solution are somewhat ambiguous, there seems to be clear evidence for energy migration in doped PS films, presumably by a Förster transfer between identical chromophores. Unlike our earlier work with PPA-*co*-PS, the copolymer does not seem to be more efficient with respect to energy transport than an equivalent concentration of model compound (i.e., 9,10-diphenylanthracene (DPA)). This is attributed to the high compatibility of DPA with PS. The present work demonstrates several important points with respect to polymer photophysics.

(1) One cannot always expect the excited-state properties of a chromophore to be retained when the chromophore is part of a polymer chain (i.e., in solution, DPA does not show excimer formation at all, while a "weakly bound excimer" is found for PDPA).

(2) Copolymers can be used successfully to achieve energy migration in doped films but a copolymer does not necessarily have larger Λ_S values than a polymer film doped with a small molecule.

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Registry No. 1, 6671-65-4; PDPA-*co*-PS, 26742-85-8; PPA-*co*-PS, 85702-20-1; PDPA, 26742-86-9; PPA, 88315-88-2; DPA, 1499-10-1; PA, 91384-76-8; 9-hydroxy-9-phenylanthrone, 5146-30-5; 9-phenylanthracene, 602-55-1; (*p*-vinylphenyl)magnesium bromide, 18120-63-3.

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(22) The calculated value of Λ_S is increased if the $1/e^2$ decay time is used in eq 3–7 instead of the $1/e$ decay time. However, these values agree within the error bars in Figure 4 which are based on the uncertainty in τ_s.

(23) These results were the same for the various copolymers with higher mole fractions (Table I). For the lower anthracene mole fraction copolymers, it is not possible to achieve a sufficiently high anthracene concentration to reach the plateau region of Figure 4.

(24) Analysis of complex fluorescence decay from using a six-bit transient recorder (Tektronix 7912) presents deconvolution difficulties.

Photochemistry in Polymer Solids. 3. Kinetics for Nonexponential Decay of Benzophenone Phosphorescence in Acrylic and Methacrylic Polymers

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ABSTRACT: The laser-pulse-excited phosphorescence of benzophenone molecularly dispersed in poly(methyl methacrylate) (PMMA), poly(isopropyl methacrylate) (PIPMA), and poly(methyl acrylate) (PMA) decays nonexponentially for the temperature range $T_\beta < T < T_g$, while it decays single-exponentially for both $T < T_\beta$ and $T > T_g$ of each polymer. The kinetics for the nonexponential decay of benzophenone triplet in these polymer matrices at 80–433 K are given by using the diffusion-controlled rate coefficient with a time-dependent transition term for the dynamic quenching process of benzophenone triplet by side-chain ester groups of the matrix polymers. The resulting kinetic parameters, namely the reciprocal lifetime ($1/\tau$), a factor characteristic of the deviation from single-exponential decay (C), and the diffusion coefficient of interacting groups (D), reflect molecular motion at the glass transition (T_g) and other secondary transitions ($T_{\alpha'}$ and T_β) of the matrix polymers.

Introduction

The photochemistry and photophysics of chromophores molecularly dispersed in polymer matrices have been studied extensively from both fundamental and practical points of view.[1-3] A typical phenomenon encountered in the study of photoprocesses in polymer solids is that reactions expected to be unimolecular in model systems are frequently not first order[4-7] and that phosphorescence of the chromophores in polymer or organic solids sometimes decays non-single-exponentially.[8-13] The phenomenon has been attributed to several isomeric species,[4,5,9] to heterogeneity of free volume distribution in the matrix,[6] to influence of triplet–triplet (T–T) annihilation,[11] or to the existence of intermolecular energy transfer to acceptor molecule[8,10] or to matrices.[12,13]

The measurement of temperature dependence of these rate processes is very important since the photochemical and photophysical processes are strongly affected by molecular motion, glass transition, and other secondary transition processes of polymer matrices. In our previous papers, the phosphorescence of benzophenone in poly(methyl methacrylate)[12] and in other acrylic polymers[13] has been shown to decay single-exponentially at temperatures, T, both lower than the β-transition temperature, T_β, corresponding to the onset of ester side-group rotation of matrix polymer, and higher than the glass transition temperature, T_g. But the decay curves have markedly deviated from an exponential type in the temperature range between T_β and T_g, and the deviation was suggested to be caused by the intermolecular quenching of the benzophenone triplet by ester groups in the side chain of these polymers.

On the other hand, the concept of diffusion-controlled reaction has been established for many years[14,15] and has been applied to very fast polymer–polymer reactions in solution.[16-19] The influence of a time-dependent term in the expression of diffusion flux expected for the very early stage of reaction where steady-state concentration is not yet attained has been discussed by several authors,[14,20-23] but a clear experimental presentation of the influence of the transient term has not been reported so far for the rate process in dilute solution due to the experimental difficulty of detecting the very early stage of the reaction. Viscous liquid, micellar,[24] and solid systems[25] are supposed to be rather convenient for detection of the transient term.

The present paper is concerned with the kinetics of the nonexponential decay of benzophenone phosphorescence in poly(methyl methacrylate) (PMMA), poly(isopropyl methacrylate) (PIPMA), and poly(methyl acrylate) (PMA) at 80–433 K, based on the application of a concept of a diffusion-controlled reaction with a time-dependent rate coefficient to the dynamic quenching process in solid state.

Experimental Section

Materials. Benzophenone and benzoyl peroxide were purified by recrystallization from ethanol solution. The monomers of methyl methacrylate, isopropyl methacrylate, and methyl acrylate were distilled under reduced pressure and stored in a dark refrigerator.

Sample Preparation. The purge of oxygen is important in the study of triplet lifetimes even in solid matrices. Solutions of benzophenone (2×10^{-3} M) and benzoyl peroxide (1×10^{-3} M) in methyl methacrylate or other monomers were evacuated by several freeze–pump–thaw cycles under a high-vacuum system, sealed in a cylindrical Pyrex cell with a diameter of 10 mm, polymerized at 70 °C for 120 h, and postcured at a temperature above T_g of each polymer for 20 h. In cases of PMMA and PIPMA, the sealed rod samples were annealed by cooling from 130 °C at a rate of 0.2 °C/min. The resulting rod samples in the sealed cell were used for the phosphorescence measurements.

Measurements of Phosphorescence Decay. A pulsed nitrogen laser (Avco C950B) with a pulse width of 10 ns as an exciting light at 337 nm, cryostat (Oxford DN704), monochromator (Jasco CT10), photomultiplier (HTV R1464), transient time

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