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Photon Harvesting Vinylphenanthrene–Methacrylic Acid Polymers: Singlet-State Migration and Trapping

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ABSTRACT: Random and alternating copolymers of 9-vinylphenanthrene and methacrylic acid have been prepared. These polymers have been doped with low mole fractions of anthryl energy traps. The photophysics of these polymers with and without these traps have been studied as a function of phenanthryl content in tetrahydrofuran (THF) and water. The fluorescence properties of the alternating polymers indicate an absence of excimer-forming sites in THF but not in water. Significant singlet energy migration has been implicated by fluorescence quenching methods. The quantum efficiency of anthracene sensitization has been found to be ca. 0.4 for the alternating polymer in THF and water. There is a very strong dependence of the photophysical properties of the random copolymers on pH, which is reflected in the energy-transfer efficiency.

Introduction

As part of our continuing interest in electronic energy-transfer (EET) phenomena in vinyl aromatic polymers we have recently published several papers dealing with alternating naphthalenic polymers.[1-4] These studies served to illustrate some of the advantages of alternating polymer structures with respect to singlet-energy migration, primarily because naphthalene excimer formation is repressed. Also these polymers were water soluble under conditions that the corresponding random polymers were not. However we still do not have a clear model for the conformation of these polymers in the solution phase and the effect this structure has on the polymer photophysics.

The present paper deals with alternating and random copolymers containing 9-vinylphenanthrene and methacrylic acid (a-MPh and r-MPh, respectively). The corresponding methyl methacrylate copolymers have been prepared for studies in organic solvents. The phenanthrene chromophore shares many properties with naphthalene: (1) a relatively long singlet lifetime (57.5 and 59 ns for phenanthrene and 2-methylnaphthalene, respectively[5]), (2) a moderate Förster R_0 for self-transfer[6] ($R_0{}^{\mathrm{Ph}}$ = 0.88 nm, $R_0{}^{\mathrm{2MNap^h}}$ = 1.2 nm), and (3) a fairly large Förster radius for transfer to anthracene[6] ($R_0{}^{\mathrm{Ph-A}}$ = 2.2 nm, $R_0{}^{\mathrm{2MNaph-A}}$ = 2.5 nm). However phenanthrene has a much decreased tendency to form singlet excimers. We find that even in aqueous solutions there is no classical excimer fluorescence although there are some broadening and a spectral feature that can be assigned to a "weakly bound excimer". More importantly in view of our general motivation, both the homopolymer PVPh and r-MPh with reasonably high phenanthrene loadings exhibit an apparent energy migration constant (Λ_S) that compares favorably with a-MPh. This is a completely different finding than for the corresponding naphthalene polymers, in which Λ_S was much larger for the alternating polymer. We ascribe this difference to the almost complete lack of self-trapping for phenanthrene polymers, although there does seem to be significant self-quenching. However the value of Λ_S estimated from quenching studies seems to be a function of the fundamental quenching rate. In the present case the quencher CCl_4 yields $\Lambda_S > 0$ for these polymers while for O_2 $\Lambda_S \cong 0$ is estimated. This will be discussed in more detail elsewhere.[7]

The phenanthrene–methacrylic acid copolymers may have anthracene moieties covalently attached by direct esterification (see the Experimental Section). Anthracene acts as a long-range trap for the phenanthrene singlet (R_0 = 2.2 nm[6]). We find the quantum efficiency for anthracene sensitization (χ) to be reasonably high for a-MPh (ca. 0.4) in organic and aqueous solution. These χ values in THF are similar to alternating naphthalene polymers.[3] On the other hand, the χ values in aqueous solutions are ca. 2× smaller than obtained for alternating naphthalene polymers.[4] Part of this difference may be attributed to self-quenching in phenanthryl polymers even in the absence of obvious excimer formation. Also the general photophysical properties of phenanthrene are more dependent on the environment than naphthalene. Thus elimination of excimer formation is not itself sufficient to ensure efficient photon-harvesting polymers.

Experimental Section

Materials. 9-Vinylphenanthrene (VPhen) and 9-anthrylmethyl methacryrate (AMMA) were synthesized according to the literature.[8,9] Methacrylic acid (MA) (Aldrich) and trimethylsilyl methacrylate (TMSiMA) (Petrarch Systems) were purified by distillation under reduced pressure. 9-Anthracenemethanol (Aldrich) was recrystallized from ethanol. Ethylaluminum sesquichloride ($Et_2AlCl{\cdot}EtAlCl_2$, Aldrich) was used as received. Carbon tetrachloride (spectrophotometric grade, MCB) was

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Table I
Preparation and Characterization of the Copolymers of VPhen and TMSiMA and with MA

run	polym	feed	yield,[a] %	MW[b]	copolym[c]
A-1	a-MPh-1[e]	0.251	6.1	$\sim 2.0 \times 10^5$	0.51
A-2	a-MPh-2	0.401	9.6	$\sim 3.3 \times 10^5$[a]	0.45
A-3	a-MPh-3	0.574	7.5		0.47
A-4	a-MPh-4	0.661	6.7	$\sim 2.8 \times 10^5$	0.51
R-1	r-MPh(3)	0.040	96	2.1×10^5	0.03[d]
R-2	r-MPh(12)	0.101	58	1.2×10^5	0.12[d]
R-3	r-MPh(21)	0.152	58	8.3×10^4	0.21
R-4	r-MPh(42)	0.301	27	3.9×10^4	0.42
R-5	r-MPh(76)	0.698	24	2.2×10^4	0.76
R-6	r-MPh(90)	0.949	30	1.7×10^4	0.90
R-7	PVPh	1.0	28	$\sim 1.0 \times 10^4$	1.0

[a] Determined for the hydrolyzed polymer. [b] Molecular weights determined by GPC for the methyl ester derivatives of the copolymers. [c] From the absorption of the phenanthrene residue in the hydrolyzed polymer (ϵ = 280 M^{-1} cm^{-1} at 354 nm in THF). [d] Determined in methanol. [e] Hydrolyzed polymer was designated a-MPh.

distilled immediately before use. Diazomethane was prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald, Aldrich). Toluene and THF were dried over sodium and distilled. *N*,*N*-Dimethylformamide (DMF) was dried over KOH and distilled. Water was deionized by passing successively through three ion-exchange resin columns.

Alternating Copolymers. The alternating copolymers (a-MPh) were prepared by a method similar to that for P(2VN-*alt*-MA).[1] A solution of Et_2AlCl (7.5 mmol) in 7.5 mL of toluene was added to 7.5 mmol of outgassed TMSiMA at liquid N_2 temperature and then degassed three more times. After stirring for 5 min at 0 °C, the desired amount of VPhen in 4 mL of toluene that had been bubbled with N_2 was added at 0 °C. This solution was degassed twice, sealed, and then stirred at 0 °C for 15 h. The resulting mixture was poured into a large excess of CH_3OH containing 3% (v/v) HCl. The polymer was further purified by precipitating from THF into CH_3OH. Complete hydrolysis of poly(VPhen-*alt*-TMSiMA) was carried out by refluxing in 1:10:1 (v/v) CH_3OH–THF–1% NaOH for 15 h. After neutralization with HCl, the mixture was refluxed for another 2 h. A white precipitate formed and was washed with H_2O. The polymer was further purified by three precipitations from THF into CH_3OH and then dried under vacuum.

Esterification of the hydrolyzed copolymer with diazomethane was carried out in the same manner as reported previously.[2]

Random Copolymers. VPhen and MA were copolymerized in the presence of 0.4 mol % of azobis(isobutyronitrile) (AIBN) on the basis of the total monomers in DMF. The polymerization was carried out in a vacuum-sealed tube at 60 °C for 12–27 h. All polymers were purified by precipitation into a large excess of ether followed by two more precipitations from THF (or DMF) into *n*-hexane (or ether).

The copolymer was esterified with diazomethane as above.

Anthracene-Loaded Polymers. Alternating and random copolymers were esterified with 9-anthracenemethanol. To 50 mg of polymer and a desired amount of 9-anthracenemethanol in 2:1 (v/v) DMF–toluene solution was added a few drops of H_2SO_4, and the solution was refluxed for 24 h. The polymer was precipitated by an excess of ether and purified by reprecipitating from THF (or DMF) into *n*-hexane (or ether) twice. Poly(VPhen-*co*-AMMA) with 1.0 mol % of AMMA (r-MPh(99)–A(1.0)) was prepared by radical polymerization of VPhen and AMMA in THF. The polymer was purified in the same manner as mentioned in the preceding subsection.

Characterization of Copolymers. Composition of the copolymers was determined primarily by using absorption spectra. Polymerization conditions and copolymer compositions are summarized in Table I. The copolymer compositions for all a-MPh samples are nearly equimolar over a wide range of the VPhen mole fraction in the monomer feed, indicating that these polymers are alternating. The mole percentages of anthracene (Anth) in the copolymer were also estimated by absorption spectra.

The molecular weight of the copolymers in the methyl ester form was estimated by using a Waters HPLC and microstyragel GPC columns. Monodisperse polystyrene samples were used as standards (Table I).

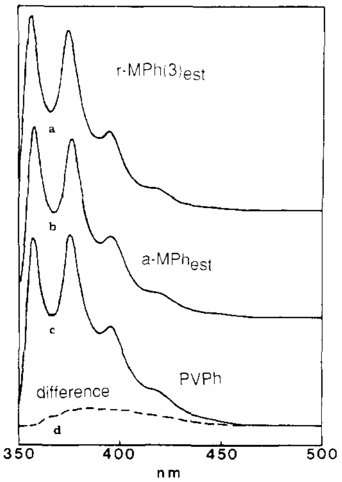

Figure 1. *Steady-state fluorescence spectra measured in THF at room temperature:* (a) r-MPh$(3)_{est}$; (b) a-MPh$_{est}$; (c) PVPh; (d) *difference spectrum obtained by subtracting spectrum* a *(normalized with spectrum* c *at 356 nm) from spectrum* c*; excitation wavelength 304 nm.*

Fluorescence Spectroscopy. Steady-state fluorescence spectra were recorded on a SPEX Fluorolog fluorimeter (Model 1902). All organic solutions were deaerated by bubbling with N_2 for 15 min. For the fluorescence quenching by oxygen, the polymer solutions in THF were purged with nitrogen, air, and oxygen gases for 15 min.

The fluorescence spectra in aqueous solutions were measured without deaeration. In the case of r-MPh(3) the polymer was first dissolved in water at pH 10, and then the pH was adjusted downward by addition of HCl. For the other polymers in aqueous stock solution was prepared by injecting 0.2 mL of DMF solution (ca. 1×10^{-6} mol with respect to Phen) into ca. 20 mL of pH 10 water with rapid stirring. Afterward the pH was adjusted with HCl. The final aqueous solution contained less than 1 vol % DMF. The concentration of the Phen residue was confirmed by measuring the optical density.

The fluorescence quantum yield (Φ_F) for the copolymers was determined by comparing the area under the spectrum with that for chrysene in cyclohexane (Φ_F = 0.0116) as a standard.[10] The Φ_F value for Anth groups in the copolymer was also determined by using 9,10-diphenylanthracene in cyclohexane (Φ_F = 1.00) as a standard.[11]

Fluorescence lifetime measurements were performed on a Photochemical Research Associates correlated single-photon-counting instrument equipped with a Hamamatsu R928 photomultiplier using an excitation wavelength of 316 nm. Details of instrumentation and deconvolution technique have been described.[12] Fluorescence lifetimes for Anth-loaded polymers were measured by using the single-photon-counting system at the Center for Fast Kinetic Research at The University of Texas at Austin, using a mode-locked a Nd:YAG laser, as described previously.[4] Excitation wavelengths of 300 and 380 nm were used to excite the Phen and Anth units exclusively in the copolymer, respectively. Interference filters (360 and 460 nm) were used to isolate the fluorescence spectrum of interest.

Results

1. Organic Solvents. A. Fluorescence Spectroscopy.

The fluorescence spectrum of poly(9-vinylphenanthrene) (PVPh) was compared with that of the random copolymer containing 3 mol % of VPhen groups in the ester form (r-MPh$(3)_{est}$, Figure 1). There is only a slight difference in the fluorescence spectra as the phenanthrene (Phen) loading increases from 3 mol % (r-MPh$(3)_{est}$) to 100 mol % (PVPh). However, a weak, broad emission feature was obtained by subtracting the spectrum of r-MPh$(3)_{est}$ from that of PVPh (Figure 1d), which is consistent with the result of Tamai et al.[13] We also found

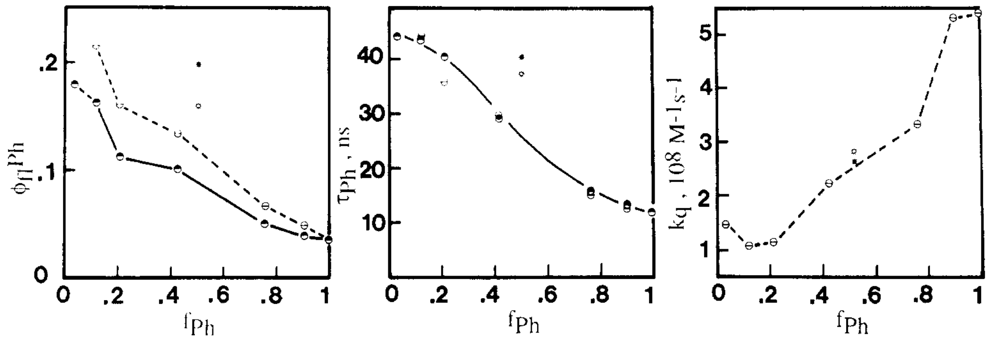

Figure 2. Fluorescence quantum yield (ϕ_{fl}^{Ph}), average lifetime (τ_{Ph}), and CCl_4 quenching rate constants (k_q) for alternating and random copolymers in deaerated THF, as a function of Phen loading (f_{Ph}): ⊖ = r-MPh, ● = r-MPh$_{est}$, ☆ = a-MPh, ★ = a-MPh$_{est}$.

Table II
Fluorescence Quantum Yields (ϕ_{fl}^{Ph}) and Average Lifetime (τ_{Ph}) of Phen Polymers in THF

	ϕ_{fl}^{Ph}		τ_{Ph}, ns		ϕ_{fl}^{Ph}/τ_{Ph}, 10^6 s^{-1}	
polym	acid	ester	acid	ester	acid	ester
r-MPh(3)	0.251[a]	0.180	42.4[a]	44.5	5.92	4.04
r-MPh(12)	0.218	0.163	45.0	43.7	4.84	3.73
r-MPh(21)	0.162	0.111	36.0	40.9	4.50	2.71
r-MPh(42)	0.135	0.103	29.7	29.0	4.55	3.55
r-MPh(76)	0.068	0.049	15.9	16.0	4.28	3.06
r-MPh(90)	0.051	0.043	13.7	13.0	3.72	3.31
PVPh		0.037[b]		11.5[b]		3.22[b]
a-MPh	0.167	0.200	37.7	40.8	4.43	4.90

[a] In DMF. [b] No acid/ester groups in polymer.

that the Phen fluorescence quantum yield (Φ_{fl}^{Ph}) decreases steadily along this series as does the average lifetime (τ_{Ph}) (Figure 2 and Table II). τ_{Ph} is defined by

$$\tau = \sum a_i \tau_i \qquad (1)$$

where a_i is the preexponential factor ($\sum a_i = 1$) and τ_i the lifetime obtained from an unconstrained two- or three-exponential fit to the fluorescence decay. Thus, although no strong excimer emission was observed, it may be concluded that considerable self-quenching occurs as the Phen content (f_{Ph}) increases. It is interesting to note that there is no difference in τ_{Ph} between the random copolymer in the acid form (r-MPh) and the ester form (r-MPh$_{est}$) whereas ϕ_{fl}^{Ph} does differ.

We note that the fluorescence yield is proportional to τ_{Ph} and the constant or proportionality should be the radiative rate of the chromophore. We have calculated the ratio of ϕ_{fl}^{Ph}/τ_{Ph} in Table II. While there is significant scatter, it would seem that this ratio is approximately independent of composition and that the acid has a slightly higher radiative rate than the ester. This effect may represent the effect of polarity on ϕ_{fl}^{Ph}, which will come up again when we discuss these polymers in aqueous solution.

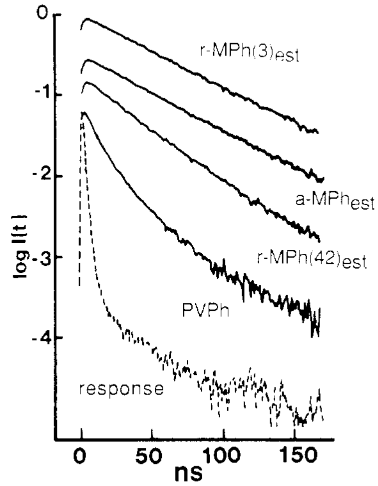

Figure 3. Fluorescence decay for r-MPh(3)$_{est}$, a-MPh$_{est}$, r-MPh(42)$_{est}$, and PVPh at 375 nm in deaerated THF: dashed line, system response function, lamp profile. Curves are offset for ease of comparison.

Table III
Fluorescence Decay Parameters for Phen Polymers in THF[a]

polym	τ_1/a_1	τ_2/a_2	τ_3/a_3	$\langle\tau\rangle$,[b] ns
r-MPh(3)[c]	12.4/0.129	46.9/0.871		45.6
r-MPh(12)	33.5/0.192	47.7/0.808		45.7
r-MPh(21)	21.2/0.222	40.2/0.778		37.7
r-MPh(42)	19.4/0.416	37.0/0.584		32.2
r-MPh(76)	9.2/0.491	21.6/0.489	40.1/0.021	19.1
r-MPh(90)	8.0/0.560	18.8/0.399	41.0/0.041	18.0
a-MPh	20.9/0.230	42.7/0.770		39.9
r-MPh(3)$_{est}$	25.5/0.185	48.8/0.815		46.3
r-MPh(12)$_{est}$	29.7/0.251	48.4/0.749		45.2
r-MPh(21)$_{est}$	27.1/0.295	46.7/0.705		42.9
r-MPh(42)$_{est}$	8.3/0.135	28.4/0.682	46.3/0.183	32.9
r-MPh(76)$_{est}$	9.5/0.477	20.9/0.494	40.6/0.028	19.1
r-MPh(90)$_{est}$	7.6/0.598	19.7/0.368	36.0/0.034	17.0
PVPh	6.9/0.687	18.8/0.279	43.4/0.034	17.0
a-MPh$_{est}$	22.5/0.172	44.6/0.828		39.9

[a] Excitation, 316 nm; emission, 375 nm; in deaerated THF solution; τ_i in nanoseconds. [b] Average lifetime defined by eq 5. For τ_{Ph} see Table II. [c] In DMF.

The spectral features of the alternating polymer (a-MPh$_{est}$) are virtually identical with those of r-MPh(3)$_{est}$ (Figure 1). In addition, ϕ_{fl}^{Ph} and τ_{Ph} of a-MPh$_{est}$ were much larger than those of the corresponding r-MPh$_{est}$ with 42 mol % of VPhen content (r-MPh(42)$_{est}$). The former values were comparable to those of the copolymer with low f_{Ph} (r-MPh(3)$_{est}$). Furthermore, it was found that the decay profile for both a-MPh$_{est}$ and r-MPh(3)$_{est}$ was almost a single exponential (Figure 3). These facts indicate the absence of self-trapping in the alternating copolymer. This is consistent with the previous result[1] that the alternating copolymer of 2-vinylnaphthalene and methyl methacrylate (P(2VN-*alt*-MMA)) shows essentially no excimer fluorescence in THF. Typical examples of fluorescence decay curves (including the best fit) for the alternating and random copolymers are presented in Figure 3. The fitting parameters of fluorescence decay are listed in Table III.

B. Fluorescence Quenching and Singlet Energy Migration. We have often characterized singlet energy migration by the method of comparative quenching. In this method the fluorescence quenching is measured for the polymer of interest and a model polymer, and the following relationship is assumed:[1]

$$(k_q^{polym} - k_q^{model})/k_q^{polym} = \Lambda_S/D_Q \qquad (2)$$

Table IV
Fluorescence Quenching of Phen Polymer by CCl_4 and Energy-Transfer Parameters

polym	K_{SV}, M^{-1}	$\langle\tau\rangle$, ns	k_q, 10^8 M^{-1} s^{-1}	Λ_S/D_{CCl_4}[a]	L_S, Å
r-MPh(3)$_{est}$	6.79	46.3	1.47		
r-MPh(12)$_{est}$	4.81	45.2	1.06	~0	~0
r-MPh(21)$_{est}$	4.92	42.9	1.15	~0	~0
r-MPh(42)$_{est}$	7.25	32.9	2.20	0.497	70
r-MPh(76)$_{est}$	6.25	19.1	3.27	1.22	84
r-MPh(90)$_{est}$	8.93	17.0	5.25	2.57	114
PVPh	9.09	17.0	5.35	2.64	116
a-MPh$_{est}$	11.1	42.5	2.61	0.776	99
a-MPh	11.1	39.9	2.78	0.891	107

[a] $D_{CCl_4} = 1.5 \times 10^{-5}$ cm^2 s^{-1} (ref 1).

where Λ_S is the singlet energy migration coefficient and D_Q is the diffusion constant of the quencher. The quenching rate constant (k_q) could be measured from either lifetime (τ_0/τ) or steady-state quenching (I_0/I). If there is no specific quencher–polymer interaction, one expects a Stern–Volmer relation:

$$I_0/I = 1 + K_{SV}[Q] \qquad (3)$$

For all systems reported herein eq 3 is obeyed. We have used the relation[1]

$$k_q = K_{SV}/\langle\tau\rangle \qquad (4)$$

where

$$\langle\tau\rangle = \sum a_i\tau_i^2/\sum a_i\tau_i \qquad (5)$$

This relationship is appropriate if the polymer fluorescence can be treated as arising from a series of independent emitters, each weighted according to its fluorescence quantum yield. The values of k_q for the quenching by CCl_4 and the resulting Λ_S/D_{CCL_4} ratios are collected in Table IV. For comparison of a variety of photophysical properties k_q is plotted as a function of f_{Ph} in Figure 2 along with ϕ_{fl}^{Ph} and τ_{Ph}. The excitation diffusion length (L_s) can be estimated from the one-dimensional random-walk result:

$$L_S = (2\Lambda_S\langle\tau\rangle)^{1/2} \qquad (6)$$

These results are also presented in Table IV. It is seen that the L_S values are very similar for a-MPh$_{est}$, PVPh, and r-MPh(90)$_{est}$ (ca. 10 nm) and fall off for the random copolymers with lower f_{Ph}. We note that these estimates of L_S are similar to the value reported by Ng and Guillet[14] for poly[(9-phenanthryl)methyl methacrylate] by a completely different analysis ($L_S \cong 12$ nm). Thus on the basis of these results, it would seem that phenanthryl polymers are quite efficient in singlet energy migration despite of the small Förster radius for self-transfer[6] (ca. 0.88 nm). As will be discussed later, we believe that the actual EET rate per elementary step is not so large for these polymers. We also found that the k_q value for a-MPh$_{est}$ is very close to that for the corresponding random copolymer (r-MPh(42)$_{est}$), indicating that the lack of excimer-like trap in a-MPh$_{est}$ does not facilitate the quenching rate. As mentioned in the Introduction, the situation is quite different from 2-vinylnaphthalene polymers, where L_S for the homopolymer (P2VN) has been estimated to be essentially zero by the same method.[15]

There are two important differences in the CCl_4 quenching experiments reported here and the earlier work for 2-vinylnaphthalene polymers: (1) k_q for CCl_4 quenching is much smaller for phenanthryl derivatives than naphthyl ones; (2) for polymers with high f_{Ph}, CCl_4 induces an exciplex (or exterplex[16]) fluorescence (Figure 4). Both these observations tend to support the idea that the mechanism of CCl_4 quenching is different for these two chromophores. For comparison with the steady-state quenching, the lifetime quenching was measured by using a Nd:YAG picosecond laser system and transient digitizer. It was found that the fluorescence was not quenched statically (i.e., the initial fluorescence intensity did not change with added quencher) and that the k_q values determined by both methods are consistent within an overall experimental error (data are not shown). Thus, we have no evidence for the presence of specific interaction between CCl_4 and the polymer with high f_{Ph} except the exciplex emission. However, as we will discuss elsewhere,[7] if the intrinsic quenching rate is small compared to the rate of energy migration, then it is possible that Λ_S is significantly underestimated.

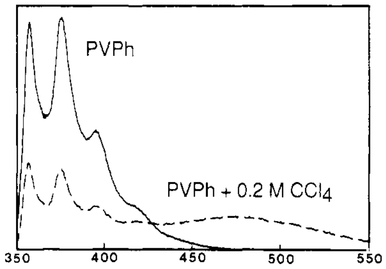

Figure 4. Fluorescence spectra of PVPh in the absence and in the presence of CCl_4 (0.2 M) in deaerated THF: excitation wavelength 304 nm (spectra scaled according to relative intensities).

Table V
Fluorescence Quenching of Phen Polymer by O_2 in THF

polym	K_{SV}, atm^{-1}	$\langle\tau\rangle$, ns	k_q, 10^7 atm^{-1} s^{-1}	Λ_S/D_{O_2}
r-MPh(3)$_{est}$	3.57	46.3	7.70	
r-MPh(42)$_{est}$	2.41	32.5	7.40	~0
PVPh	1.35	17.0	7.94	0.03
a-MPh$_{est}$	3.29	42.5	7.75	0.01

In Table V are summarized the results of fluorescence quenching by oxygen. The k_q values are given in atm^{-1} s^{-1} in place of the more usual M^{-1} s^{-1} because the solubility of oxygen in THF is unknown. However, it is expected that the k_q value would be on the order of 10^{10} M^{-1} s^{-1}. The data of Table V show that there is no difference in the k_q values among the polymers, leading to $\Lambda_S \cong 0$ for PVPh and a-MPh$_{est}$. These results conflict with the CCl_4 quenching in which energy migration is implicated in the polymers with high f_{Ph} and suggest that it is necessary to take into account the difference in the magnitude of k_q to estimate the energy migration rate. It should be also noted that the present result of quenching by O_2 is not consistent with that reported by Holden et al.[17] for poly[(9-phenanthryl)methyl methacrylate] in which it was argued that the k_q was facilitated in the polymer system. However the method used by these authors was somewhat different from that used herein.

C. Singlet Energy Transfer in Anthracene-Loaded Polymers. Alternating and random copolymers have been loaded with small amounts (ca. 1 mol %) of anthracene (Anth) by direct esterification with 9-anthracenemethanol. Typical fluorescence spectra of Anth-loaded polymers in THF excited at 304 nm are shown in Figure 5. Clearly energy transfer from Phen to Anth is occurring. From the spectra this effect is especially pronounced in the copolymers with higher f_{Ph}. However, for a more precise discussion it is necessary to consider several different factors: (1) The Phen fluorescence intensity decreasing

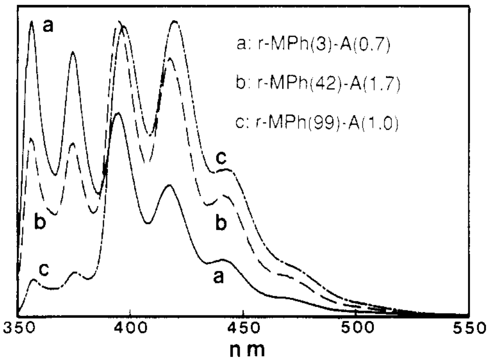

Figure 5. Fluorescence spectra of r-MPh(3)–A(0.7) (a) in deaerated DMF, and r-MPh(42)–A(1.7) (b) and r-MPh(99)–A(1.0) (c) in deaerated THF: excitation wavelength 304 nm.

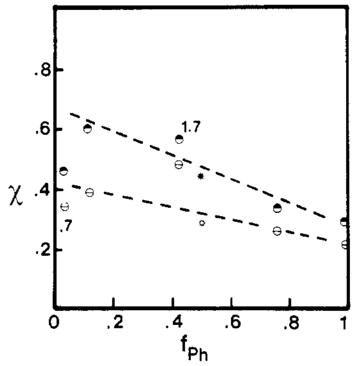

Figure 6. Energy-transfer efficiency (χ) for Anth-loaded random copolymers determined by method A (●) and method B (⊖) in THF. Anthracene loading 1 mol % except for the two samples indicated. χ for a-MPh–A(1.0) determined by method A (★) and B (☆) in THF.

with increasing f_{Ph} in the copolymer (see Figure 2). (2) The efficiency of energy transfer depends on the relative numbers of Phen and Anth per coil such that there may be an effect of molecular weight, i.e., for a degree of polymerization (DP) of 100 and 1 mol % Anth loading there is a significant probability that some Phen polymers will not contain an Anth group. (3) The copolymer may exert an environmental effect on the Anth fluorescence. We note that the Anth fluorescence is 3 nm red-shifted for r-MPh(99)–A(1.0) compared to the other copolymers.

The efficiency of energy transfer (χ) can be quantified by[9]

$$\chi/(1-\chi) = (I_A/I_{Ph})(\Phi_{Ph}/\Phi_A) \tag{7}$$

where I_A and I_{Ph} are the areas of the corrected fluorescence spectra of Anth and Phen, respectively, and Φ_A and Φ_{Ph} are the corresponding fluorescence quantum yields (method A). In addition, we have proposed an alternative method to determine the χ value (method B):[3]

$$\chi = [(I_A(\lambda)/I_A(\lambda_A))f_A(\lambda_A) - f_A(\lambda)]/f_D(\lambda) \tag{8}$$

where $I_A(\lambda)$ and $I_A(\lambda_A)$ are the fluorescence intensities of the acceptor excited at a wavelength (λ) where the donor absorbs light and at the wavelength (λ_A) where only the acceptor absorbs, respectively. I_A is measured at an emission wavelength of the acceptor. f_A and f_D are the fractions of incident light absorbed by the acceptor and donor, respectively. As described previously,[3] the latter method has the advantage that one does not have to measure quantum yields of fluorescence.

In Figure 6, the χ values calculated by both methods are plotted against f_{Ph} in the copolymer. There is a similar tendency for both methods, but the χ values derived by method A are always larger than by method B. The χ value for the copolymer containing about 1 mol % of Anth decreases almost linearly with f_{Ph}. Since direct energy transfer (single step) from Phen to Anth must occur exclusively in r-MPh with low f_{Ph}, this result indicates that the direct energy transfer to the trap is the dominant EET process in these polymers. We also note that the χ value for a-MPh, which has no excimer-like trap, is not enhanced compared to the corresponding r-MPh, which does have excimer-like traps. This is consistent with the similarity of the L_S values for these polymers (Table IV). We will return to this point in the Discussion.

Table VI
Fluorescence Decay Parameters for Anth-Loaded Polymers in THF

	λ_{exc} = 300 nm					λ_{exc} = 380 nm
	Phen (360 nm)[a]			Anth (460 nm)[b]		Anth (460 nm)[b]
polym	a_i	τ_i, ns	τ_{Ph}, ns	a_i	τ_i, ns	τ_A, ns[c]
r-MPh(3)–A(0.7)	0.053	2.0	34.7	−0.989	1.9	7.8
	0.193	9.9		1.325	11.1	
	0.754	43.4		0.665	30.0	
r-MPh(12)–A(1.0)	0.106	2.2	28.2	−1.064	1.2	6.5
	0.357	15.7		1.198	8.6	
	0.537	41.6		0.866	23.1	
r-MPh(42)–A(1.7)	0.285	3.2	19.2	−0.648	1.1	8.2
	0.411	17.0		1.579	13.3	
	0.305	36.9		0.069	50.9	
r-MPh(76)–A(1.1)	0.275	4.4	17.2	−0.979	1.6	10.2
	0.574	17.6		1.934	12.5	
	0.151	39.2		0.045	41.3	
r-MPh(99)–A(1.0)	0.408	3.1	12.0	−3.038	1.3	9.6
	0.505	14.2		3.451	10.7	
	0.087	40.7		0.587	19.1	
a-MPh–A(1.0)	0.288	3.9	20.0	−1.961	1.2	7.1
	0.435	17.9		2.829	11.8	
	0.277	40.2		0.132	39.4	

[a] 200-ns time scale. [b] 100-ns time scale. [c] Averaged lifetime of Anth fluorescence defined by eq 1.

Concerning the discrepancy between χ values obtained by methods A and B, we may consider the following: (1) The direct excitation of Anth at 304 nm cannot be neglected for r-MPh with low f_{Ph} (e.g., ca. 2% of incident light at 304 nm was absorbed by the Anth unit in r-MPh(3)–A(0.7)). In such a case, I_{Ph} in eq 7 is underestimated and I_A is overestimated, and thus χ by method A is overestimated. (2) It is possible that at high Anth loadings the density of excimer-forming sites is diminished, presumably as a result of conformation changes induced by the relatively bulky Anth groups. We note that the average lifetimes of Phen fluorescence for r-MPh(76)–A(1.1) and r-MPh(99)–A(1.0) are essentially equal to those for r-MPh(76) and PVPh, respectively, despite the presence of an energy trap in the former (cf. Tables II and VI). This effect would be expected to increase ϕ_{fl}^{Ph} such that Φ_{Ph} in eq 7 is underestimated, and hence method A underestimates χ for r-MPh with higher Phen and Anth contents. (3) Under the present experimental conditions, the optical density of Anth was extremely small compared to that of Phen in the case of r-MPhs with high f_{Ph}. This decreases the accuracy of Φ_A in eq 7 and $f_A(\lambda_A)$ in eq 8, and thus the χ values are subject to error. However, the difference of the experimental χ values determined by both methods is still larger than our estimates of these correction factors.

The fluorescence decay curve for Anth-loaded polymers was obtained by exciting at 300 nm (primarily Phen absorption) and observing at 360 nm (Phen fluorescence) and 460 nm (Anth fluorescence). The decay profiles for a-MPh–A(1.0) are presented in Figure 7. The decay parameters for the alternating and random copolymers are given in Table VI. The Phen fluorescence decay curve for

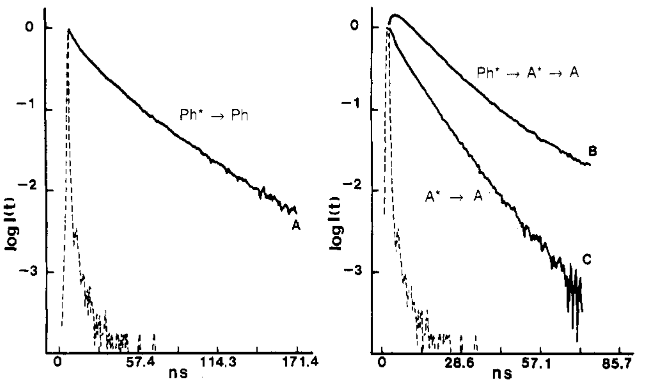

Figure 7. Fluorescence decay for a-MPh–A(1.0) in deaerated THF: (A) excitation at 300 nm, emission at 360 nm; (B) excitation at 300 nm, emission at 460 nm; (C) excitation at 380 nm, emission at 460 nm.

all the Anth-loaded polymers has a rapidly decaying component (τ = 2–4 ns), which we believe is the result of energy transfer from Phen to Anth.[18] However, the decays at longer times for a-MPh–A(1.0) and r-MPh–A with high f_{Ph} are very similar to the corresponding unloaded polymers (cf. Tables III and VI). If the energy transfer from Phen to Anth occurs exclusively via the Förster dipole–dipole mechanism, excited Phen groups sufficiently distant from an Anth group will decay with their own characteristic lifetime. Ng and Guillet[14] have argued that if excited energy transfers via an intermediate mechanism (i.e., combined Förster and diffusion), the long-lifetime component for the acceptor-loaded polymer decays faster than that for the corresponding unloaded polymer. Thus from our data it seems likely that single-step EET to the Anth trap is the dominant mechanism of photon harvesting, even for the alternating copolymers.[19] However the sensitivity of the fits to this long-lived component is not high such that small changes are not detected reliably.

The sensitized Anth fluorescence lifetime for all the Anth-loaded polymer has a rising component (τ = 1–2 ns) (Figure 7B and Table VI). Furthermore, the decreasing component decays more slowly than that for the directly excited Anth. These results are expected from the long lifetime of the Phen donor state. In particular, the sensitized Anth long-lifetime component for a-MPh–A and r-MPh–A with high f_{Ph} are very close to those for the corresponding unloaded polymers. However, it should be noted that the fraction of this component is relatively small and that the fitting function in this region is effectively a two-exponential function because one component of the three-exponential function is required to fit the rising portion of the curve. Consequently the accuracy of the fit is decreased at long times.

2. Aqueous Solution. A. Fluorescence Spectroscopy. In these studies we compare a-MPh with r-MPh(x) for $x < 76$ because r-MPh(76) is not water soluble. The steady-state fluorescence spectra are presented in Figure 8 for r-MPh(3), r-MPh(42), and a-MPh. The fluorescence spectrum of the former is very similar to that in THF (cf. Figure 1) and is essentially unchanged by pH (although ϕ_{fl}^{Ph} is, see below). The spectrum of r-MPh(42) is much broader and relatively pH dependent. Such phenomena have been reported for amphiphilic phenanthryl polymers.[8,20] It was suggested that there is stacking of Phen groups due to hydrophobic interactions and this enhances the weak excimer-like emission that is observed in organic solvent. We also found that for the a-MPh there is a slight increase of the relative intensity for $\lambda > 410$ nm. Comparison of these spectra clearly demonstrates some "excimer component" in a-MPh that was not present in organic solvent (see Figure 1). We note that the alternating naphthalene polymers analogous to a-MPh exhibit strong excimer fluorescence in aqueous solutions at all pH's.[2,4] This further demonstrates the higher proclivity of the naphthalene chromophore to form excimers relative to phenanthrene.

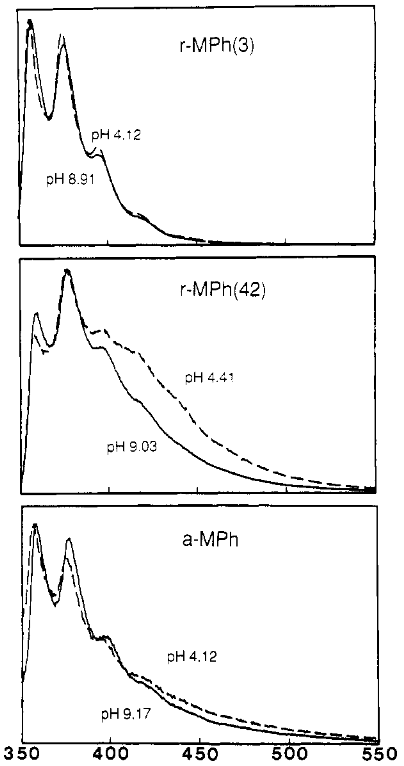

Figure 8. Steady-state fluorescence spectra of r-MPh(3), r-MPh(42), and a-MPh in aqueous solution at pH indicated: excitation wavelength 304 nm.

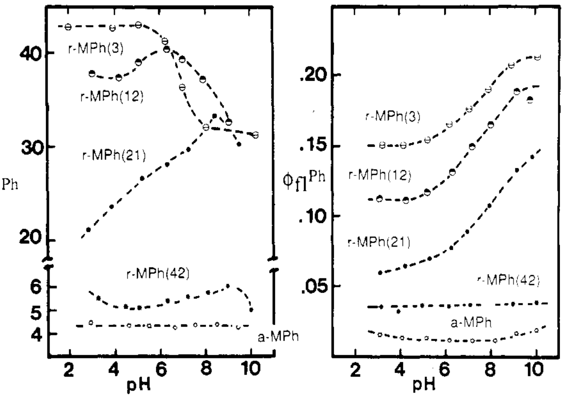

Figure 9. pH dependence of fluorescence quantum yields (ϕ_{fl}^{Ph}) and average lifetimes (τ_{Ph}) of alternating and random copolymers in aqueous solution.

While the fluorescence spectrum of r-MPh(3) is not pH dependent, both the fluorescence yield (ϕ_{fl}^{Ph}) and average lifetime (τ_{Ph}; given by eq 1) vary systematically (Figure 9; for fitting parameters see Table VII). The ϕ_{fl}^{Ph} variation for the random copolymers are similar to each other for Phen loadings below 42 mol %, while r-MPh(42) and a-MPh are very similar to each other and much less sensitive to pH. We note that ϕ_{fl}^{Ph} is much lower in aqueous solution than in THF. The variation of τ_{Ph} with pH is very peculiar for the random copolymers (Figure 9, left), with a complete reversal of character as one goes from r-MPh(3) to r-MPh(42). For the former ϕ_{fl}^{Ph} increases with pH while τ_{Ph} decreases. One is forced to conclude that the singlet-state transition dipole moment is a function of the

Table VII
Fluorescence Decay Parameters for Phen Copolymers in H_2O[a]

pH	τ_1/a_1	τ_2/a_2	τ_3/a_3	τ_{Ph}, ns	$\langle\tau\rangle$,[b] ns
		r-MPh(3)			
10.22	35.1/0.796	16.0/0.204		31.2	33.1
9.13	36.5/0.732	21.8/0.268		32.6	33.9
8.04	36.1/0.831	12.3/0.169		32.1	34.6
6.99	38.9/0.880	17.3/0.120		36.3	37.7
6.26	44.3/0.889	17.3/0.111		41.3	43.0
5.08	45.7/0.900	20.1/0.100		43.1	44.5
3.89	45.5/0.910	13.2/0.090		42.6	44.6
2.00	44.7/0.939	11.5/0.061		42.7	44.2
		r-MPh(12)			
9.07	36.1/0.849	13.9/0.151		32.7	34.7
7.88	42.7/0.752	20.6/0.248		37.2	39.0
7.03	43.9/0.837	16.4/0.163		39.4	42.0
6.32	44.9/0.826	18.9/0.174		40.4	42.8
5.10	44.5/0.808	15.8/0.192		39.0	42.3
4.22	43.9/0.782	14.3/0.218		37.4	41.4
3.05	43.9/0.778	17.0/0.222		37.9	41.2
		r-MPh(21)			
9.50	35.5/0.818	6.0/0.182		30.1	34.4
8.42	38.7/0.803	11.2/0.197		33.3	36.9
7.30	41.5/0.658	7.0/0.342		29.7	38.7
6.35	41.1/0.614	7.4/0.386		28.1	37.7
5.24	40.5/0.580	7.5/0.420		26.6	36.6
3.91	39.6/0.498	7.7/0.502		23.6	34.4
2.83	39.7/0.343	15.2/0.315	7.8/0.342	21.1	30.1
		r-MPh(42)			
10.02	25.8/0.059	7.6/0.341	1.5/0.600	5.0	12.0
8.99	26.8/0.063	8.1/0.323	2.8/0.614	6.0	11.8
8.09	29.5/0.045	8.8/0.309	2.6/0.646	5.7	11.8
7.25	26.5/0.042	9.6/0.255	2.8/0.703	5.5	10.6
6.33	23.7/0.032	9.7/0.236	3.1/0.773	5.4	8.9
5.09	14.7/0.108	6.6/0.236	3.0/0.657	5.1	7.7
4.43	17.0/0.067	8.0/0.246	3.1/0.687	5.2	8.0
3.30	17.1/0.066	8.4/0.274	3.1/0.660	5.5	8.2
		a-MPh			
9.47	14.2/0.053	5.3/0.460	2.0/0.487	4.2	6.1
8.50	16.4/0.037	5.8/0.402	2.6/0.561	4.4	6.2
7.58	16.9/0.033	5.9/0.341	2.8/0.626	4.3	6.1
6.67	16.4/0.033	6.4/0.251	2.9/0.717	4.2	6.0
5.53	20.0/0.017	7.2/0.232	3.1/0.751	4.3	6.0
4.64	18.4/0.021	7.5/0.213	3.2/0.766	4.4	6.1
2.95	16.7/0.034	6.6/0.245	3.2/0.720	4.5	6.1

[a] Excitation 316 nm; emission 378 nm; τ_i in nanoseconds. [b] Average lifetime defined by eq 5.

local polarity. For r-MPh(12) and r-MPh(21) there is a distinct decrease in τ_{Ph} at low pH that we ascribe to Phen–Phen self-quenching. This apparently overwhelms any tendency toward lengthening τ_{Ph} as a result of the hydrophobic environment. Neither r-MPh(42) nor a-MPh display very much variation of ϕ_{fl}^{Ph} or τ_{Ph} with pH. This implies that there is very little change in the exposure of the Phen moiety to water or each other as the acid groups are deprotonated. We also note that a-MPh has the lowest values of ϕ_{fl}^{Ph} and τ_{Ph} in aqueous solution. This is surprising because only a few excimer-like traps in a-MPh are expected to be formed on the basis of the fluorescence spectrum. We conclude that it is self-quenching that dominates the photophysics of these polymers rather than excimer formation.

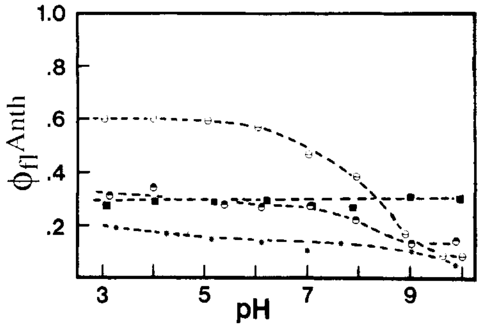

Figure 10. Fluorescence quantum yields of Anth groups (ϕ_{fl}^{Anth}) in Anth-loaded polymers in aqueous solution: ⊖, r-MPh(3)–A(0.7); ◒, r-MPh(12)–A(1.0); ★, r-MPh(42)–A(1.7); ■, a-MPh–A(1.0); excitation wavelength 370 nm.

Some of these same environmental effects are observed for directly excited covalently bound anthracene. While the spectrum is not changed as a function of pH the fluorescence yield changes dramatically (Figure 10). For r-MPh(3) ϕ_{fl}^{Anth} decreases with pH in a manner commensurate with the titration of poly(methacrylic acid) and the exposure of the aromatic chromophore to the solvent. This kind of behavior has been observed for several other aromatics.[21] (In fact the results for r-MPh(x), $x < 42$, in Figure 9, right, are unusual in that ϕ_{fl}^{Ph} increases with pH.) For the higher loadings of Phen ϕ_{fl}^{Anth} is much less pH sensitive. It is reasonable to suppose that this is the result of a smaller change in the local polarity experienced by the Anth as the acid deprotonates. The lifetime data for directly excited Anth are less systematic. The fluorescence decay is highly nonexponential and τ_{Anth} or $\langle\tau_{Anth}\rangle$ do not uniformly change with pH (Table VIII).

B. Singlet Energy Transfer to Covalently-Bound Anthracene Groups. The anthracene-tagged copolymers that were discussed in subsection 1C were dissolved in water (see the Experimental Section), and the steady-state fluorescence spectra were measured (Figure 11). The apparent anthryl component increases with f_{Ph} and decreases with pH for r-MPh(3)–A(0.7) and r-MPh(12)–A(1.0). However for r-MPh(42)–A(1.7) and a-MPh–A(1.0) the spectra are essentially independent of pH.

The dependence of the spectra on f_{Ph} and pH is much simpler than on χ because of the complex ϕ_{fl}^{Ph} dependencies. In Figure 12 the pH dependence of χ calculated by method B (eq 8) for different polymerxs is plotted. For the lowest Phen loading χ decreases as the polyacid is deprotonated but then increases at the highest pH. For r-MPh(12)–A(1.0) χ changes rapidly near the deprotona-

Table VIII
Fluorescence Decay Parameters for Anth-Loaded Polymers in H_2O: Direct Excitation of Anth Groups[a]

polym	pH	τ_1/a_1	τ_2/a_2	τ_3/a_3	τ_{Anth}, ns	$\langle\tau\rangle_{Anth}$, ns
r-MPh(3)–A(0.7)	9.21	3.6/0.460	9.3/0.358	18.7/0.182	8.4	12.0
	4.56	4.9/0.309	13.3/0.0658	41.4/0.032	11.6	15.4
r-MPh(12)–A(1.0)	9.14	1.2/0.361	5.6/0.481	18.8/0.158	6.1	11.7
	4.73	2.2/0.569	7.4/0.155	11.9/0.276	5.7	8.9
r-MPh(42)–A(1.7)[b]	8.98	0.3/0.520	2.5/0.408	10.3/0.072	1.9	5.3
	4.91	0.2/0.480	2.5/0.422	10.8/0.098	2.2	6.4
a-MPh–A(1.0)	9.06	2.3/0.458	6.7/0.433	16.8/0.108	5.8	9.1
	4.76	2.9/0.469	7.0/0.420	18.0/0.111	6.3	9.6

[a] Excitation 375 nm; emission 460 ns; τ_i in nanoseconds. [b] Measured by using a PRA single-photon-counting system: excitation 358 nm; emission 460 nm.

Table IX
Fluorescence Decay Parameters for Anth-Loaded Polymers

Phen Emission (360 nm)[a]

polym	pH	τ_1/a_1	τ_2/a_2	τ_3/a_3	τ_{Ph}, ns	$\langle\tau\rangle$, ns
r-MPh(3)–A(0.7)	8.96	2.6/0.174	26.7/0.570	39.9/0.256	25.9	31.4
	4.89	4.2/0.414	21.4/0.261	43.2/0.325	21.4	34.3
r-MPh(12)–A(1.0)	9.00	5.8/0.273	18.7/0.314	33.1/0.413	21.1	27.1
	4.66	1.0/0.611	6.2/0.287	32.8/0.102	5.7	21.2
r-MPh(42)–A(1.7)	9.10	too short to analyze				
	4.85	too short to analyze				
a-MPh–A(1.0)	9.01	too short to analyze				
	4.87	too short to analyze				

Sensitized Anth Emission (460 nm)[b]

polym	pH	τ_1/a_1	τ_2/a_2	τ_3/a_3
r-MPh(3)–A(0.7)	8.96	0.2/–0.991	5.9/1.373	24.1/0.619
	4.89	0.5/–1.786	12.3/2.303	32.3/0.483
r-MPh(12)–A(1.0)	8.97[c]	0.1/–2.630	4.6/2.490	26.8/1.140
	4.87[c]	0.1/–2.406	7.2/1.994	28.6/1.412
r-MPh(42)–A(1.7)	9.10[c]	0.08/–5.120	2.4/5.250	22.0/0.870
	4.85[c]	0.09/–4.997	2.4/5.249	20.9/0.749
a-MPh–A(1.0)	8.85	0.3/–2.081	5.0/2.528	16.8/0.553
	4.60	0.2/–5.961	4.3/6.440	16.7/0.520

[a] Excitation 300 nm; emission 360 nm; τ_i in nanoseconds. [b] Excitation 380 nm; emission 460 nm; τ_i in nanoseconds. [c] Measured by using a PRA single-photon-counting system: excitation 297 nm; emission 460 nm.

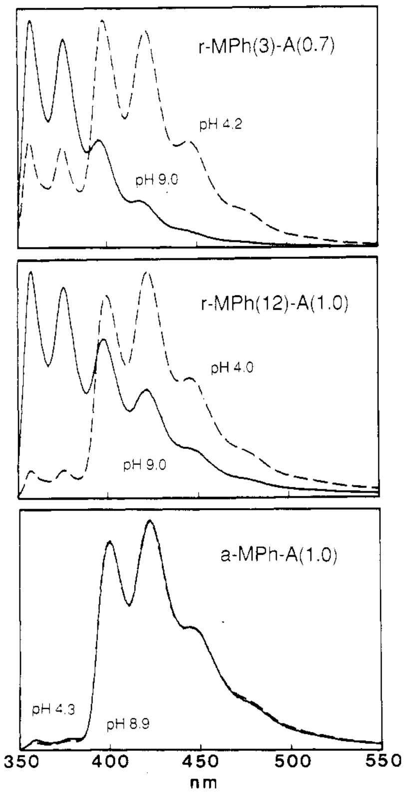

Figure 11. Fluorescence spectra of r-MPh(3)–A(0.7), r-MPh-(12)–A(1.0), and a-MPh–A(1.0) in aqueous solution at indicated pH (excitation wavelength 304 nm).

tion point but is increasing as the pH changes from 3 to 6, while for r-MPh(42)–A(1.7) there is a slight increase over the whole pH range. χ for a-MPh–A(1.0) is essentially independent of pH. Such diverse dependences are difficult to rationalize adequately. However, we note that τ_{Ph} exhibits similar behavior (see Figure 9, left). The increase of χ in r-MPh(3)–A(0.7) and r-MPh(12)–A(1.7) near the deprotonation point is consistent with a polymer structure in which the average Phen–Anth separation is diminished, which enhances direct energy transfer. The decrease of χ in r-MPh(12)–A(1.7) at low pH corresponds to the decrease of τ_{Ph} and ϕ_{fl}^{Ph}. Furthermore, introducing Anth groups into the polymer chain may facilitate intracoil

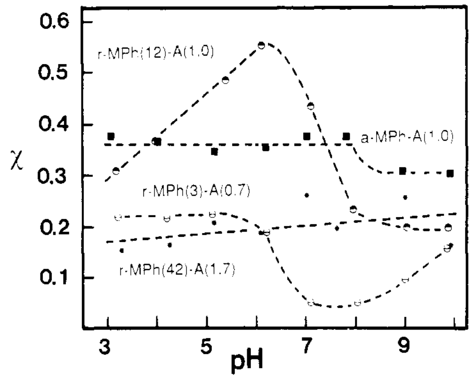

Figure 12. Energy-transfer efficiency (χ) for Anth-loaded polymers in aqueous solution: ⊖, r-MPh(3)–A(0.7); ●, r-MPh-(12)–A(1.0); ★, r-MPh(42)–A(1.7); ■, a-MPh–A(1.0).

hydrophobic aggregation, leading to a further decrease of τ_{Ph} and ϕ_{fl}^{Ph} through self-quenching and excimer formation. This decreases the χ values. On the other hand, it should be noted that a-MPh–A(1.0) has relatively large χ values in spite of the lowest ϕ_{fl}^{Ph} and τ_{Ph}.

The fluorescence decays of Phen and sensitized Anth were highly nonexponential. The fitting parameters of a three-exponential fit are collected in Table IX for low (ca. 4.6–4.9) and high (ca. 8.9–9.1) pH's. We note that τ_{Ph} is always shortened by the presence of the Anth, and the sensitized Anth fluorescence always contains a very fast rise time. Unfortunately the lifetime shortening in the case of high f_{Ph} is so extreme that we are unable to obtain a valid deconvolution. A meaningful discussion of the time dependence of these photon-harvesting polymers in aqueous solution will require data with better time resolution than we presently have available.

As was discussed in the previous section, the fluorescence decay of directly excited Anth is not exponential (Table VIII). While there is scatter in these data, τ_{Anth} tends to be slightly shorter than the singlet lifetime for Anth observed in THF (see Table VI). For the alternating copolymer τ_{Anth} is essentially the same at high and low pH. The changes in τ_{Anth} do not mirror the ϕ_{fl}^{Anth} dependence on pH (see Figure 10). It seems to us that the main point demonstrated by these data is the heterogeneity experienced by the anthryl groups as a function of Phen loading or polymer type.

Discussion

1. **Organic Solvents.** The spectral features of r-MPh$_{est}$ and PVPh in THF are qualitatively in agreement with the results of Tamai et al.[13] Tamai et al.[13] and Zachariasse et al.[22] have discussed the geometrical structure of the excimer and concluded that only the sandwich type of structure is suitable for the singlet excimer stabilization. By analogy with many other vinyl aromatic polymers one would expect a variety of Phen–Phen interactions, including this sandwich structure. Very little excimer fluorescence is observed (Figure 1), and the spectral shift of this feature is small compared to the naphthalene excimer. Furthermore there is a very systematic decrease in ϕ_{fl}^{Ph} with f_{Ph} (see Figure 2). This self-quenching may be interpreted as the formation of a weakly bound excimer that has a low quantum yield and that may thermally dissociate to the normal Phen singlet state. This is an important difference between the phenanthrene polymers of the present study and the previously reported naphthalene polymers[1-4] Thus we propose that for phenanthrene polymers many of the nearest-neighbor EET steps are accompanied by self-quenching. In part this is the result of the smaller R_0 for Phen–Phen transfer, which requires a closer approach of the chromophores compared to the corresponding naphthalene polymers. Thus while these phenanthrene polymers have the desirable feature that excimer traps are largely eliminated, they suffer from this self-quenching that inevitably accompanies EET.

The fluorescence quenching by CCl_4 is facilitated with increasing f_{Ph} in the random copolymer, and the k_q value for a-MPh$_{est}$ is smaller than that for PVPh. These results are reasonable because singlet migration is expected to be strongly dependent on the distance between Phen groups in the copolymer. If we use the Förster expression, the migration rate constant (k_{mig}) is given by

$$k_{mig} \cong 1/\tau^0{}_{Ph}(R_0/R')^6 \qquad (9)$$

where $\tau^0{}_{Ph}$ is the unperturbed lifetime of Phen, R_0 is the Förster radius for Phen self-transfer (ca. 0.88 nm[6]), and R' is the average Phen–Phen separation. Since the probability that more than two methyl methacrylate groups intervene between Phen groups (thus $R' > R_0$) increases in r-MPh$_{est}$ with less than 50 mol % of VPhen content, long-range energy migration does not occur. On the other hand, facile energy migration appears to occur in PVPh, which has no spacer groups, on the basis of the k_q value for CCl_4. These quenching results also imply that the rate of energy migration to the quenching site (collision site with CCl_4 molecules) can compete with that to the excimer-like traps in PVPh. This is plausible because the fraction of excimer sites in the polymer is believed to be low ($\leq 10^{-2}$).[23] It is also possible that PVPh has shallow excimer-like traps that permit thermal detrapping. This is supported by the fact that there is a small spectral shift of the excimer emission (Figure 1d).

On the basis of eq 9, the migration rate for a-MPh$_{est}$ would be expected to be much smaller than that for PVPh (a factor of 10^{-2}–10^{-3}) because the R' values are estimated to differ by a factor of approximately 2. However, facile energy migration does occur in a-MPh$_{est}$. This can be explained as follows: Although the k_{mig} value is small in a-MPh$_{est}$, the excited energy can migrate over a large fraction of the polymer chain because there are no excimer-like traps. Thus the average k_{mig} value may be close to that for the elementary migration step. On the other hand, PVPh and r-MPhs have excimer-like traps and/or isolated Phen sequences with limited lengths. In the latter case the excited energy migrates within the Phen sequences containing no traps with the rate constant of k_{mig}. However once the ends of the sequence are reached, no further new sites are visited and the apparent k_{mig} value is diminished. These effects tend to compensate each other, leading to the comparable migration constant (Λ_S; the small difference in χ values for these polymers may be ascribed in part to this effect). In this connection, the energy-hopping time (τ_h = 1/migration rate) can be roughly estimated from[1]

$$\Lambda_S = \langle R' \rangle^2 / 2\tau_h \qquad (10)$$

If we estimate $\langle R' \rangle$ = 0.3–0.4 nm for PVPh and 0.6–0.8 mm for a-MPh$_{est}$, then $\tau_h \simeq$ 0.01–0.02 ns and $\tau_h \simeq$ 0.15–0.3 ns respectively are obtained (using Λ_S values in Table IV). Although these values are very approximate, as may be expected from the small R_0 value the migration rate for Phen polymer is estimated not to be so high. In any event, the alternating copolymer has not only the highest K_{SV} value but also the highest overall quenching efficiency. We ascribe this to efficient energy migration (leading to the higher k_q) and the absence of excimer-like traps (leading to the higher ϕ_{fl}^{Ph} and τ_{Ph}). We found that a-MPh$_{est}$ and r-MPh$_{est}$ with high f_{Ph} facilitated CCl_4 quenching but not O_2 quenching. It is reasonable that if the energy migration rate is slow compared to the diffusion-controlled reaction, energy migration no longer enhances the diffusion-controlled quenching reaction. We believe this is the case for the O_2 quenching. On the other hand, the energy migration in Phen polymers can still facilitate the CCl_4 quenching because the quenching rate constant for CCl_4 is the order of 10^8 M^{-1} s^{-1}. This points to a difficulty of investigating the energy migration processes by the comparative quenching method, which will be discussed in a separate paper.[7] We note that poly[(9-phenanthryl)methyl methacrylate] has been reported to facilitate O_2 quenching.[17] This type of polymer has the following advantages compared to the present case: (1) There are no excimer traps (like a-MPh). (2) The Phen–Phen distance is shorter than a-MPh. Thus the difference in the O_2 quenching results for these two polymers may be that poly[(9-phenanthryl)methyl methacrylate] has a higher energy migration rate than our polymers, which enables it to facilitate the diffusion-controlled O_2 quenching.

2. **Aqueous Solution.** It is well-known that amphiphilic polymers have a compact conformation in aqueous solution due to hydrophobic interaction[4,24] and that the strong interaction of nearest-neighbor chromophore groups is diminished in alternating polymers.[1,3] Thus in aqueous solution one may expect that amphiphilic alternating polymers permit facile intrachain energy migration without necessarily containing a high density of excimer-forming sites. In fact, alternating methacrylic acid–naphthalene[4] and phenanthrene (present results) polymers show less excimer emission than the corresponding random copolymers. This is not the case for a maleic acid–vinylnaphthalene polymer[2] in which the nearest-neighbor naphthalene groups can achieve the required orientation for excimer formation. Although the Phen groups in a-MPh cannot necessarily obtain the orientation for excimer formation,[22] there still exists an interaction between the Phen groups that may act to self-quench the singlet exciton. Furthermore, as expected from eq 9, the compact conformation in aqueous solution causes a decrease in the R' value and thus enhances the energy migration rate. Therefore, it may be supposed that the excited energy is efficiently captured by a few self-quenching sites via energy migration. This leads to the observed strong decrease of ϕ_{fl}^{Ph} and τ_{Ph} in aqueous solution.

The photophysical properties of Phen and Anth in the present polymers were found to be strongly dependent on the microenvironment. This dependence makes it very difficult to interpret the energy-transfer process in aqueous solution. However we can point out some of the important factors that affect sensitization:

(1) The average separation between Phen and Anth groups will be affected by the pH as the polymer deprotonates (e.g., the results for r-MPh(3)–A(0.7) and r-MPh(12)–A(1.0)). Intracoil hydrophobic aggregation between Phen and Anth groups also decreases this separation (e.g., r-MPh(42)–A(1.7) and a-MPh–A(1.0)). At the present time we do not have a persuasive model for the conformation of these high-loading amphiphilic polymers in aqueous solution. This is the object of continuing effort in our laboratory.

(2) The density of excimer-like or self-quenching sites is lower in the alternating polymer. Thus the χ value is larger for a-MPh–A(1.0) than for r-MPh(42)–A(1.7).

(3) The singlet-state lifetime is much shorter in the Phen polymers than the corresponding naphthalene polymers, and these latter polymers obtain much higher Anth sensitization efficiencies (0.9–1.0)[4] with similar Anth loading. We believe this is because EET in phenanthrene polymers is accompanied by self-quenching, $R_0{}^{\mathrm{Ph}}$ for self-transfer is relatively small (ca. 0.7 of that for naphthalene), and $R_0{}^{\mathrm{Ph-A}}$ is slightly smaller (cf. 2.2 and 2.5 nm). These factors serve to diminish the efficiency of these polymers with respect to photon harvesting in water.

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Registry No. (MA)(VPhen) (copolymer 9-anthracenemethanol ester), 119454-67-0; CCl_4, 56-23-5; O_2, 7782-44-7.

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