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Effect of Coil Collapse on Photon-Harvesting Polymers with Phenanthrene Chromophores

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ABSTRACT: Fluorescence measurements were used to explore the effect of solvent-induced polymer coil collapse on electronic energy transport for both methacrylate and methacrylic acid copolymers with pendant phenanthrene chromophores. Changes in the quantum yield and efficiency of excitation transport show that the efficiency of electronic energy transport to a covalently bound anthracene trap increases with coil contraction, although this increase is part of a complex chain of events in which phenanthrene−phenanthrene self-quenching plays an important role even though classical excimer formation is negligible. Room temperature solution and 77 K matrices display qualitatively similar behavior. Measurements for polymethacrylic acid-*co/alt*-poly(vinylphenanthrene) polymers in aqueous solution at room temperature and at 77 K illustrate analogous behavior as a function of pH.

Introduction

In a previous paper,[1] we described the results of fluorescence measurements for carbazole copolymers in a good solvent (THF) and the changes that occurred when a nonsolvent (water) was added to effect coil collapse. The results showed that as the polymer coil is collapsed, the efficiency of electronic energy transport (EET) to the anthryl trap increases. However as the coil contracts, self-quenching also increases presumably via a "non emitting excimer state"[2,3] a result of diminished chromophore−chromophore separations.

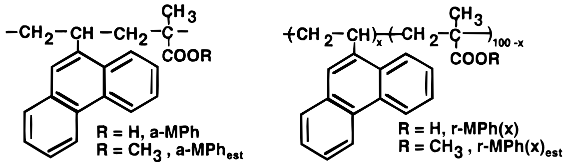
In this paper, the results of fluorescence measurements are described for copolymers of vinylphenanthrene and methacrylic acid or methacrylate, for solvent compositions ranging from good (pure THF) to poor (63 vol % water added), as a function of pH, and in solid matrices. The trends for the phenanthrene methacrylate polymers are similar to those observed for carbazole polymers, although some differences are observed. In general we find that the extent of excited state quenching resulting from intracoil contacts is significant in spite of the fact that phenanthrene has a very small tendency to form excimers. Similar conclusions hold for the analogous methacrylic acid polymers in water as a function of pH.

Experimental Section

Solvents. THF used for sample preparation was prepared immediately before use by distillation over $LiAlH_4$. Water was deionized by successively passing it through three ion exchange resin columns. The background fluorescence of the solvents was undetectable under our normal excitation conditions for both steady-state and time-dependent experiments.

Phenanthrene Polymers. The phenanthrene polymers (Chart 1) are those reported earlier.[3] For the random copolymer the mole fraction of vinylphenanthrene is 0.42. Anthracene traps are covalently bound by direct esterification of 9-anthracenemethanol to the polyacid. Methylation of acid polymers was performed by the addition of excess diazomethane to protonated polymers with stirring in an enclosed container for 24 h. Excess diazomethane remaining after 24 h was removed from the sample by stirring and/or argon bubbling while open to air.

Chart 1



Diazomethane used for methylation of acid polymers was prepared by the dropwise addition of an ethereal solution of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Aldrich) to a 75 °C stirred ethereal solution of NaOH and 2-(2-ethoxyethoxy)-ethanol. The solution was distilled and the diazomethane/ether mixture collected in a chilled flask. (*Caution*! Do not use ground glass joints in the apparatus used in this procedure.)

Fluorescence Spectroscopy. Lifetime measurements were made by the method of time-correlated single photon counting with an excitation wavelength of 293 nm and emission wavelengths of 360 and 460 nm for phenanthrene and anthracene, respectively. Details concerning the single photon counting system and data treatment have been given previously.[1,4]

Steady-state fluorescence spectra were recorded on a SPEX Fluorolog fluorimeter system described elsewhere[5] and a Photon Technology International LS-100 luminescence spectrophotometer.[1] All spectra were corrected for photomultiplier response. Steady-state emission spectra for phenanthrene polymers were collected with an excitation wavelength of 293 nm and span the range 310−510 nm. In some cases it was necessary to fit a steady-state spectrum to a linear combination of donor and acceptor, which was achieved using a linear regression method.[6]

Sample Preparation. All fluorescence measurements were made for deoxygenated samples using a specially designed cuvette with a greaseless stopcock described previously.[1] Solutions remained deaerated for times far in excess of the longest experimental times, and no oxygen quenching was observed 24 h after deaeration. Fluorescence quantum yields were computed by comparison to phenanthrene.[7] For each addition of water, the refractive index was estimated for the appropriate ratio of THF and water. Absorbance measurements for polymers in mixed solvents used the corresponding ratio of THF:H_2O as a reference.

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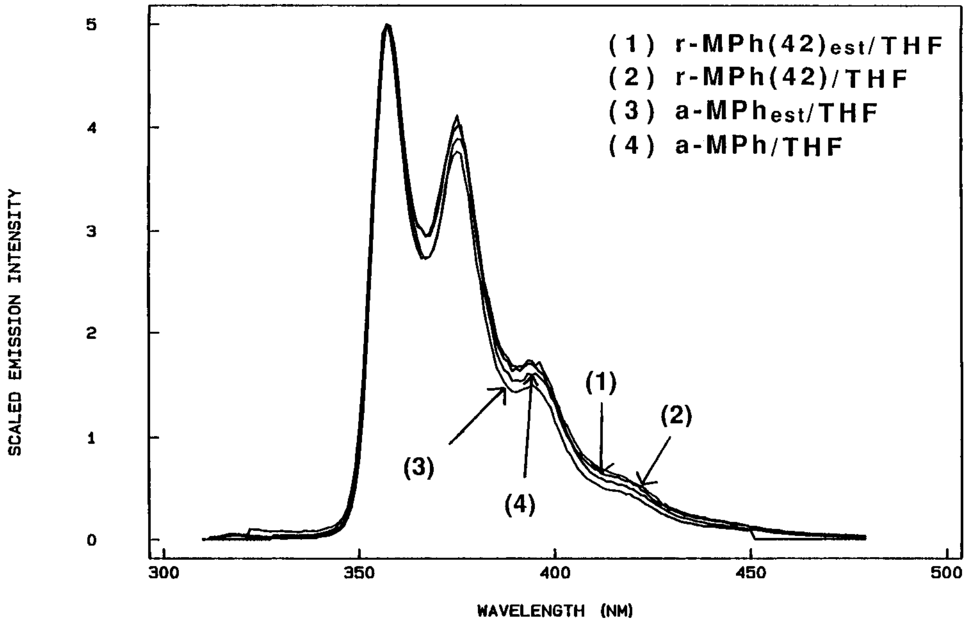

Figure 1. Steady-state spectra for (1) r-MPh(42)$_{est}$, (2) r-MPh(42), (3) a-MPh$_{est}$, and (4) a-MPh, all in pure THF. Excitation: 293 nm.

Results and Discussion

1. Overview. We consider eight polymer samples. Much of our attention will be focused on the alternating polymer of methacrylic acid with vinyl phenanthrene and this same polymer with a small mol % (0.6) of anthracene added by a direct esterification reaction. The methyl ester of these polymers is formed by reaction of the acid with diazomethane as discussed in the experimental section. The polymers are denoted a-MPh, a-MPh-A(0.6), a-MPh$_{est}$, and a-MPh-A(0.6)$_{est}$, the latter two being the ester. The corresponding random copolymer with 42 mol % vinylphenanthrene is denoted r-MPh(42), with analogous notations for the tagged polymer and the ester. These polymers were characterized in earlier work[3] and the GPC molecular weights are *ca.* 3×10^5 and 4×10^4 (based on polystyrene standards) for a-MPh and r-MPh(42), respectively. We also have model polymers r-MPh(3) and r-MPh(3)$_{est}$ with 3 mol % phenanthrene for comparison.

THF appears to be a good solvent for all these polymers while cyclohexane is not. Neither water nor methanol is expected to be a good solvent for the phenanthrene portion of the polymer, although it is possible to dissolve the polyacids in water. Thus we expect cyclohexane, methanol, or water to act as a precipitant when added to THF with the latter two solvents likely to act as a selective precipitant for the hydrophobic segments.

Addition of methanol or cyclohexane to THF solutions produced such small changes in the steady state spectra that we do not present them here. Changes in the fluorescence decays are also negligible except in the case of large additions (more than 60 vol % methanol or cyclohexane is required to show the same magnitude of change as 10 vol % water). This illustrates the fact that a strong precipitant for the phenanthrene groups is required before self-quenching is important (see below). This further implies that quenching interactions occur at points of phenanthrene—phenanthrene contact, which is similar to the idea of "excimer forming sites".[8] This is an important "negative result" because it demonstrates that a very strong precipitant is required to markedly increase the density of these contacts. Thus we conclude that EET experiments of the type described herein are much more sensitive to local polymer structure than hydrodynamic or scattering characterization.

While phenanthrene does not exhibit an obvious excimer fluorescence, we have observed a spectral broadening of fluorescence as a function of phenanthrene loading for random and alternating polymers[3] in poor solvents that can be interpreted as a "weakly bound excimer". The fluorescence yield also drops with chromophore loading or with the addition of precipitant (see later), which suggests a strong degree of self-quenching. Self-quenching implies that the collision of a ground state phenanthrene and excited state phenanthrene yields a radiationless deactivation pathway. This is kinetically equivalent to excimer formation with a very low quantum yield of excimer fluorescence. A similar result was observed for carbazole chromophores.[1]

2. Phenanthrene Polymers in THF:H$_2$O Solution. Untagged Polymers at Room Temperature. In Figure 1 we combine the steady state fluorescence spectra for a-MPh, a-MPh$_{est}$, r-MPh(42), and r-MPh(42)$_{est}$ in pure THF. The spectrum of the model polymer r-MPh(3)$_{est}$ (not shown) is identical in shape to those shown and does not change with the addition of water. These results are similar to previous work, including the fact that no classical excimer is observed.[3] Spectral broadening is most noticeable for r-MPh(42), slightly less so for r-MPh(42)$_{est}$ and a-MPh, and almost undetectable for a-MPh$_{est}$. This can be rationalized as a consequence of the fraction of chromophores in close proximity for random polymers. The minimal spectral broadening observed in Figure 1 indicates just how unfavorable excimer formation is for pendant phenanthrene chromophores. Although the addition of water does not change the fluorescence spectrum appreciably, it does lead to a decrease in fluorescence intensity (Table 1 a).

In Figure 2 the decay curves for a-MPh$_{est}$ as a function of vol % water are shown. This data is representative of the systematic shortening of the ^{1}Ph* lifetime for all polymers except r-MPh(3)$_{est}$ and r-MPh(42). The fluorescence decay for r-MPh(3)$_{est}$ for each addition of water is unchanging and indistinguishable from that of a-

Table 1

(a) Fluorescence Quantum Yields for Untagged Polymers as a Function of vol % H_2O

sample	vol % H_2O	$\phi_D{}^a$	sample	vol % H_2O	ϕ_D
r-MPh(42)$_{est}$	0	0.094	r-MPh(42)	0	0.11
r-MPh(42)$_{est}$	13	0.099	r-MPh(42)	13	0.10
r-MPh(42)$_{est}$	31	0.067	r-MPh(42)	31	0.097
r-MPh(42)$_{est}$	48	0.056	r-MPh(42)	48	0.071
r-MPh(42)$_{est}$	63	0.046	r-MPh(42)	63	0.044
a-MPh$_{est}$	0	0.12	a-MPh	0	0.12
a-MPh$_{est}$	13	0.15	a-MPh	13	0.12
a-MPh$_{est}$	31	0.11	a-MPh	31	0.084
a-MPh$_{est}$	48	0.095	a-MPh	48	0.050
a-MPh$_{est}$	63	0.084	a-MPh	63	0.032
r-MPh(3)$_{est}$	0	0.22			
r-MPh(3)$_{est}$	13	0.21			
r-MPh(3)$_{est}$	31	(precipitation)^b			

(b) Fluorescence Quantum Yields and Efficiency of Energy Transfer for Tagged Polymers as a Function of vol % H_2O

sample	vol % H_2O	$\phi^{fl\ c}$	$\phi_D{}^d$	$\phi_{anth}{}^e$	$\chi_{SS}{}^{[T]f}$	$\chi_\tau{}^g$
rMPh(42)A(1.7)$_{est}$	0	0.103	0.054	0.049	0.43	0.30
rMPh(42)A(1.7)$_{est}$	13	0.113	0.052	0.060	0.48	0.33
rMPh(42)A(1.7)$_{est}$	31	0.090	0.022	0.067	0.67	
rMPh(42)A(1.7)$_{est}$	38					0.76
rMPh(42)A(1.7)$_{est}$	48	0.069	0.012	0.056	0.79	
rMPh(42)A(1.7)$_{est}$	58					0.85
rMPh(42)A(1.7)$_{est}$	63	0.035	0.006	0.028	0.87	
rMPh(42)A(1.7)$_{est}$	74					0.87
aMPhA(0.6)$_{est}$	0	0.078	0.043	0.032	0.63	0.51
aMPhA(0.6)$_{est}$	13	0.086	0.049	0.034	0.66	0.54
aMPhA(0.6)$_{est}$	31	0.073	0.029	0.040	0.72	
aMPhA(0.6)$_{est}$	38					0.80
aMPhA(0.6)$_{est}$	48	0.056	0.016	0.036	0.83	
aMPhA(0.6)$_{est}$	58					0.86
aMPhA(0.6)$_{est}$	63	0.055	0.013	0.036	0.84	
aMPhA(0.6)$_{est}$	74					0.87
aMPhA(0.6)	0	0.088	0.050	0.037	0.59	0.47
aMPhA(0.6)	13	0.082	0.045	0.036	0.63	0.43
aMPhA(0.6)	31	0.066	0.031	0.034	0.63	
aMPhA(0.6)	38					0.33
aMPhA(0.6)	48	0.046	0.017	0.027	0.65	
aMPhA(0.6)	58					0.20
aMPhA(0.6)	63	0.030	0.010	0.020	0.69	
aMPhA(0.6)	74					0.27
rMPh(42)A(1.7)	0	0.120	0.056	0.062	0.49	0.36
rMPh(42)A(1.7)	13	0.121	0.058	0.060	0.43	0.38
rMPh(42)A(1.7)	31	0.115	0.042	0.070	0.57	
rMPh(42)A(1.7)	38					0.76
rMPh(42)A(1.7)	48	0.094	0.016	0.076	0.77	
rMPh(42)A(1.7)	58					0.89
rMPh(42)A(1.7)	63	0.072	0.009	0.060	0.78	
rMPh(42)A(1.7)	74					0.78

[a] ϕ_D is the fluorescence quantum yield of the donor, phenanthrene. [b] In order to achieve a similar OD, the concentration of r-MPh(3)$_{est}$ is necessarily much greater than that of the other polymers (which do not precipitate). [c] ϕ^{fl} is the total fluorescence. [d] ϕ_D is the fluorescence quantum yield of the donor, phenanthrene. [e] ϕ_{anth} is the fluorescence quantum yield of the acceptor, anthracene. The sum of ϕ_D and ϕ_{anth} is not always precisely equal to ϕ^{fl} because of inaccuracies in the deconvolution of the total spectrum into a sum of components. [f] $\chi_{SS}{}^{[T]}$ is the efficiency of energy transfer for the tagged polymer (see ref 1). The error in $\chi_{SS}{}^{[T]}$ depends strongly on the absolute magnitude of $\phi_D{}^{(T)}$ (tagged polymer), which can be in error by ±15% after convolution of the total spectrum, and $\phi_D{}^{(0)}$ (untagged polymer), which can be in error by ±10%. This tends to produce a larger uncertainty in $\chi_{SS}{}^{[T]}$ when both $\phi_D{}^{(T)}$ and $\phi_D{}^{(0)}$ are large than when they are small, since $\chi_{SS}{}^{[T]}$ is bounded by unity. [g] χ_τ is the efficiency of energy tranfer computed using the lifetime of the donor in the presence and absence of the energy trap, anthracene (see ref 1).

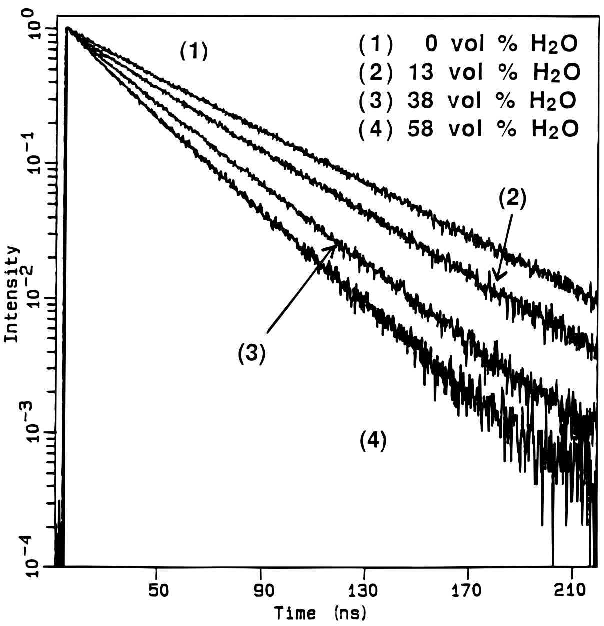

Figure 2. Fluorescence decays for a-MPh$_{est}$ for vol % water indicated. Excitation: 293 nm. Emission: 360 nm.

MPh$_{est}$ in pure THF, analogous to the steady-state spectra. This leads us to conclude that lifetime shortening is the result of self-quenching and not solvent polarity or crowding of neighboring ester groups around the phenanthrene moiety. This is not to say that the environment of the ^{1}Ph* is homogeneous because the fluorescence decay of r-MPh(3)$_{est}$ requires two exponentials for a satisfactory fit. We also note that the behaviors of the esterified and nonesterified polymers are as different from each other as those found between alternating and random polymers. For example, a decrease in lifetime is observed for r-MPh(42)$_{est}$ with added water similar to that observed for a-MPh$_{est}$ and a-MPh. However the lifetime for r-MPh(42) shows only a small decrease for the same conditions. It is surprising to us that r-MPh(42) is less sensitive to the addition of water than a-MPh. We speculate that the blocks that are richer in phenanthrene have a lower yield of fluorescence such that the fluorescence spectrum and decay is strongly influenced by isolated phenanthrene groups which behave similarly to the r-MPh(3)$_{est}$ model polymer.

The polymer concentrations in this study are very low (*ca.* 1 × 10^{-4} M in chromophore, which corresponds to approximately 0.02 mg/mL). Nevertheless, one cannot discount the possibility of polymer aggregation when adding a strong precipitant. Precipitation was observed for r-MPh(3)$_{est}$ because of the higher polymer concentration required to achieve an equivalent OD for this polymer. However, the presence or absence of turbidity did not have any effect on the fluorescence properties other than yielding more scattering of the excitation light which was easily rejected by the monochromator. Evidently the EET properties of polymers in solution (or even in films[9]) is dominated by intracoil processes. We believe that one would have to encounter a strongly interpenetrating network for this not to be the case.

These results have demonstrated that the collapse of the polymer coil is photophysically complex and self-quenching will have to be taken into account in any detailed analysis. This is an undesired complication but it seems to be unavoidable[1] and is consistent with our earlier studies. On the other hand, simple solvent effects like polarity do not seem to be too important and site inhomogeneity is a relatively minor effect compared

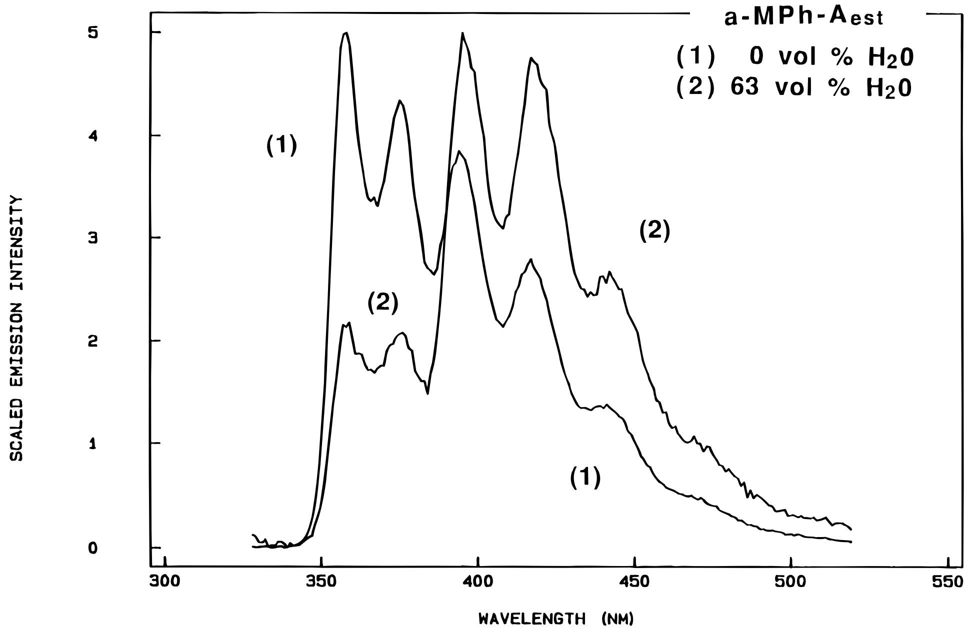

Figure 3. Steady-state spectra for a-MPh-A(0.6)$_{est}$ for 0 and 63 vol % water. Excitation: 293 nm.

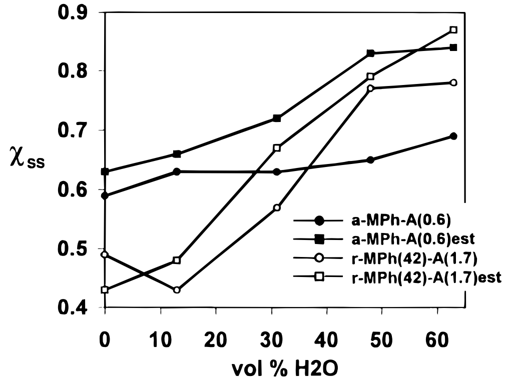

Figure 4. Efficiency of sensitization, χ_{SS}, for phenanthrene polymers as a function of vol % water.

to self-quenching. We now turn to the anthracene-tagged polymers.

Anthracene-Tagged Polymers in Room Temperature Solution. Steady-state spectra show that the effect of adding water to a-MPh-A(0.6)$_{est}$ (Figure 3) is quite dramatic. The spectra in Figure 3 are scaled to equal intensity at the maxima to emphasize the loss of the phenanthrene component with a concomitant gain of the anthracene component. In a good solvent (100% THF), EET is evident and as water is added sensitization of the anthracene increases. When comparing the alternating and random polymer (spectra not shown), we note that there is a greater loss of phenanthrene emission for the random polymer for 63 vol % water. This may indicate more efficient sensitization of anthracene or be the result of greater self-quenching or a combination of both factors. As was the case for the untagged polymers, the total quantum yield decreases with added water (Table 1b).

χ_{SS} was computed as described previously.[1] For nearly all the tagged polymers, the value of χ_{SS} is fairly high, varying from 0.43 to 0.87 (Figure 4 and Table 1b).[10] The random ester polymer has the highest χ_{SS} value, which may be a consequence of the higher anthracene loading (1.7 mol % compared to 0.6 for the alternating copolymers) in addition to potential effects due to polymer architecture. a-MPh-A(0.6) shows the smallest increase in χ_{SS}. There may be diminished coil collapse in this case because of the presence of hydrophilic methacrylic acid groups alternating along the polymer chain which could serve to offset the hydrophobic interactions between the phenanthrene and water. In all cases, the ester polymer has a slightly higher χ_{SS} value, suggesting that they are more compact. We note that there is sufficient inherent error in determining χ_{SS} that differences of less than 0.1 are not significant (see Table 1b, footnote *f*).

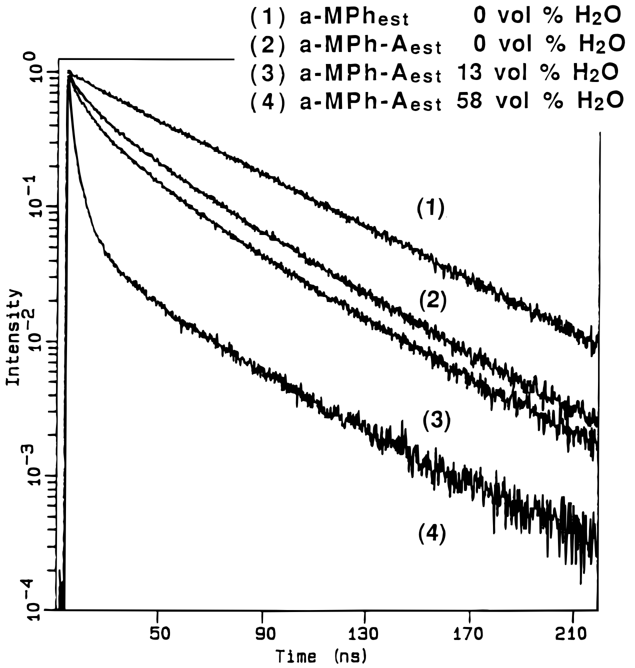

Figure 5. Fluorescence decays for a-MPh$_{est}$ (curve 1) at 0 vol % water and a-MPh-A(0.6)$_{est}$ at vol % water indicated (curves 2–4). Excitation: 293 nm. Emission: 360 nm.

The fluorescence decay reflects EET in a straightforward way. In Figure 5, we plot the decay of a-MPh$_{est}$ in pure THF which overlaps the model polymer r-MPh-(3)$_{est}$ perfectly (not shown), along with a-MPh-A(0.6)$_{est}$ for several vol % of water. The shortening of the phenanthrene lifetime for a-MPh-A(0.6)$_{est}$ compared to a-MPh$_{est}$ is obvious both in pure THF and with added water. Since the phenanthrene lifetime of the model polymer r-MPh(3)$_{est}$ is not affected by solvent composition (see earlier discussion), we ascribe the increased rate of decay to sensitization of the anthryl trap and self-quenching. Any detailed analysis of EET results of this type will also have to take into account EET to self-quenching sites in addition to the trap.[11] At longer times, the decay of a-MPh-A(0.6)$_{est}$ approximately parallels that of a-MPh$_{est}$, which illustrates that a significant fraction of phenanthrene groups do not participate in EET.[12]

The time-dependent anthracene fluorescence at 460 nm was obtained for all tagged polymers (data not shown). The buildup typically observed for energy transfer (or excimer formation) was clearly evident, with buildup times for all four samples in the range 0.93–1.26 ns in pure THF. This relatively small range of values is an interesting result which seems to indicate that the minimum time between excitation and sensitization is nearly the same for these four different samples when the coils are expanded, even though there are differences in steady-state spectra, time-dependent decays of the phenanthrene fluorescence, and χ_{SS}. At 74 vol % of water, the buildup times all decrease within the range 200–300 ps, implying that these polymers behave similarly even if the coils are collapsed to nearly the point of precipitation. Because of the uncertainties of fitting the rising edge of a fluorescence decay, a detailed discussion of these values will not be carried out here.[13]

Tagged and Untagged Phenanthrene Polymethacrylates in 77 K Frozen THF Matrices. The computer simulations of EET we have carried out neglects the effect of polymer motions[14] so we were motivated to examine the fluorescence decays in THF matrices at 77 K. The samples were rapidly frozen to prevent polymer precipitation and are strongly scattering. This scattering does not present any experimental difficulty for time-dependent measurements because of double monochromator detection. Rapidly frozen THF glasses have a more slowly decaying fluorescence than at room temperature, but not by a very large factor (compare curve 2 of Figure 6 with curve 1 of Figure 2). The major component for a-MPh$_{est}$ is essentially identical to the model polymer r-MPh(3)$_{est}$, implying there is no self-quenching. a-MPh-A(0.6)$_{est}$ has a strongly nonexponential decay that is qualitatively similar to the decay at room temperature. The long time component for all three polymers at 77 K is very similar which indicates that there are intrachain energy transfer "barriers" (see the discussion in our earlier paper[1]). The curvature for the fluorescence decay of a-MPh-A(0.6)$_{est}$ is more pronounced for the frozen matrix. We believe this is because thermal motions in room temperature solution tend to average out the highly nonexponential curves predicted from a static lattice model.

3. Phenanthrene Polyacids in Aqueous Solution at Room Temperature and 77 K. The polyacids in this series can be dissolved in water by being predissolved in DMF and then added to basic water (pH ~10) with vigorous stirring. The final pH is obtained by very slow addition of HCl. At a pH below 4 there is a very strong tendency for the polymer to aggregate, even at these very low concentrations.

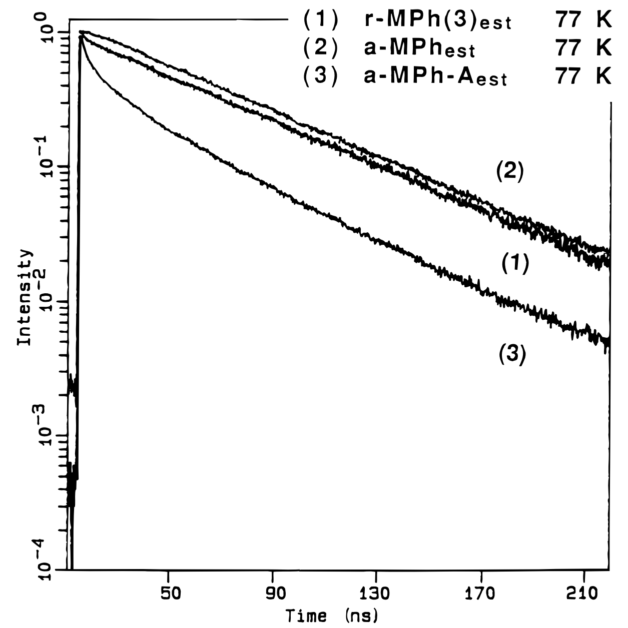

Figure 6. Fluorescence decays for (1) r-MPh(3)$_{est}$, (2) a-MPh$_{est}$, and (3) a-MPh-A(0.6)$_{est}$, all in THF at 77 K. Excitation: 293 nm, emission: 360 nm.

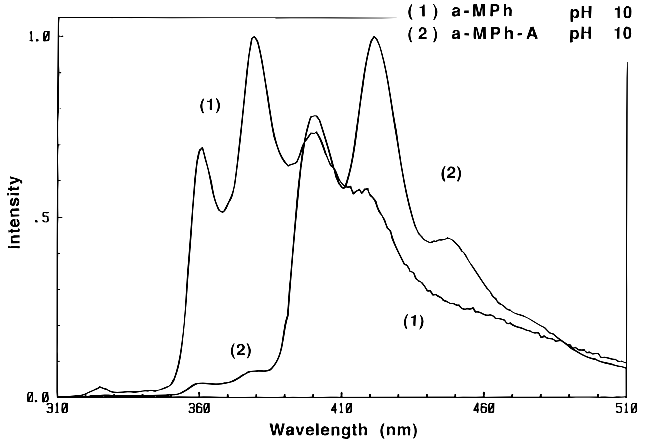

Figure 7. Steady-state fluorescence spectra for a-MPh (curve 1) and a-MPh-A(0.6) (curve 2), both at pH 10. Excitation: 293 nm.

The steady state spectra of a-MPh (Figure 7) and r-MPh(42) (spectrum not shown) in water are similar to the analogous ester samples in THF:H$_2$O. A slight broadening of the spectra is evident at pH 10, and there is only a small difference between a-MPh and r-MPh(42). These changes are typical of other amphiphilic polymers. There is, however, a significant difference when comparing the steady-state spectra of the anthracene-tagged acid polymers in pure water to the ester polymers in THF and with added water. For the anthracene-tagged poly(methacrylic acid-*co*/*alt*-vinylphenanthrene) polymers, the phenanthrene component is almost totally quenched and replaced by anthracene fluorescence (compare Figure 7 and Figure 3) for all pH values in the range 4 –10. For a-MPh-A(0.6), there is only a slight pH effect on the spectrum, and there is essentially no pH effect on r-MPh(42)-A(1.7) (not shown). The spectra are similar to amphiphilic copolymers of vinylnaphthalene with anthracene traps reported previously.[15]

The fluorescence decay of phenanthrene is highly nonexponential in these aqueous solutions and is much shorter than the decays previously described in THF: H$_2$O solutions. The anthryl-tagged polymers always exhibit a shortened phenanthrene lifetime, as expected. Despite the near absence of a pH effect on the steady

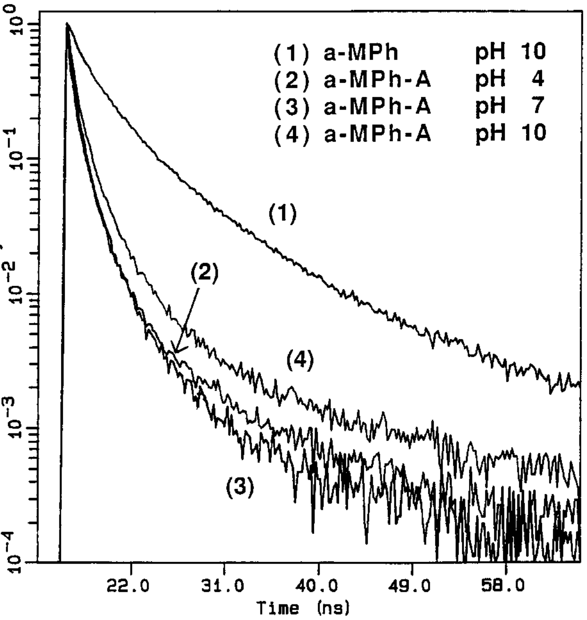

Figure 8. Fluorescence decays for a-MPh (curve 1) and a-MPh-A(0.6) (curves 2−4) at pH indicated, all at room temperature. Excitation: 293 nm. Emission: 360 nm.

state spectra, a clear pH effect on the decay curves is observed for times greater than *ca.* 10 ns for a-MPh and a-MPh-A(0.6) (Figure 8). These results are similar to those observed for the analogous polymers in THF:H_2O (Figure 5). It is important to note that, for the untagged polymer, pH 4 and 7 have similar decays, while at pH 10 the decay is distinctly slower, although still highly nonexponential. We believe that at pH 10 the polyacid is completely deprotonated such that the phenanthrene−phenanthrene contacts are diminished, which in turn reduces self-quenching. As was observed for the tagged polymers in THF:H_2O, the decays are much faster for a collapsed coil because of the effect of EET to the anthryl traps and to self-quenching sites. Clearly these amphiphilic polymers experience considerable phenanthrene−phenanthrene interaction and must assume a relatively collapsed configuration for all pHs.

These solutions were also studied at liquid nitrogen temperature to provide a comparison to THF:H_2O at 77K. The fluorescence decay is much slower at 77 K, although still nonexponential for a-MPh and with a slight pH dependence (decays not shown). For r-MPh-(3) the fluorescence decay is almost a single exponential with a very small pH dependence. The fluorescence decay for a-MPh-A(0.6) is much faster than that of the other two polymers, with the decays at pH 4 and 7 being identical and distinctly faster than the decay at pH 10. Thus it seems that there is some "memory" of the room temperature conformation in the flash-frozen samples. It is evident that the more open polymer structure achieved at a higher pH is less efficient in self-quenching and trapping the phenanthrene excitation.

Qualitatively the situation for r-MPh(42) and r-MPh-(42)-A(1.7) is similar, but in the interest of space, we do not present the data here.[13] The decay for r-MPh-(42) is faster and more nonexponential than for a-MPh, as one might expect from enhanced self-quenching by the interaction of neighboring phenanthrene groups. The decay of r-MPh(42)-A(1.7) is slower than for a-MPh-A(0.6), which we believe is the result of EET "bottlenecks" created by sequences without phenanthrene groups. The qualitative pH dependence for both random polymers is similar to the alternating case.

Conclusions

This paper presents a study of phenanthrene-containing polymers that is a companion of the earlier study of carbazole polymers.[1] Qualitatively the same effects are observed: for both types of polymers, as a nonsolvent is added, self-quenching occurs (resulting in a reduction in phenanthrene quantum yield in the range 30% to 75%), and for the case of anthracene-tagged polymers, the sensitization efficiency increases. Coil collapse brings the chromophores closer together, which enhances the rate of energy transfer, but also creates more sites for self-quenching. The fluorescence of phenanthrene is known to be relatively insensitive to environment, and only rarely have phenanthrene excimers been reported,[3,16] but evidently self-quenching is quite facile.

The dynamics of self-quenching and/or sensitization are complex and any modeling of this process would have to take into account many factors that are difficult to account for *a priori* or to extract from fits to experimental data,[11] although Levitsky has made excellent progress in this area with respect to the quenching of triplet excitons in biopolymers by the Tb^{3+} ion.[17]

Perhaps the most surprising results of this study and our previous work is the minor effect of polymer sequence distribution. While it is true that alternating polymers tend to have a more systematic variation with solvent quality compared to the random polymer, by and large the difference between these polymers is minor. Thus from the point of view of the design of photon-harvesting polymers the lesson emerges that it is the chromophore itself that must be considered first. If high efficiency of sensitization is sought, then not only should the chromophore−chromophore Förster radius be as large as possible, but self-quenching and/or excimer formation must be repressed. This latter can often be achieved with appropriate steric modification of the chromophore.

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Supporting Information Available: Tables of fluorescence decay fitting parameters (a_i, τ_i, see ref 1 for equation) for excitation at 293 nm and emission at 360 nm (phenanthrene) or 460 nm (anthracene) (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Kiserow, D. J.; Itoh, Y.; Webber, S. E. *Macromolecules* **1996**, *29*, 7847.
(2) Kamioka, K.; Webber, S. E.; Morishima, Y. *Macromolecules* **1988**, *21*, 972.
(3) Itoh, Y.; Webber, S. E.; Rodgers, M. A. J. *Macromolecules* **1989**, *22*, 2766.
(4) Prochazka, K.; Kiserow, D. J.; Ramireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. *Macromolecules* **1992**, *25*, 454.
(5) Sturtevant, J. L.; Webber, S. E. *Macromolecules* **1989**, *22*, 3564.
(6) Program by Dr. J. D. Byers, unpublished results.
(7) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.
(8) Semerak, S. N.; Frank, C. W. *Adv. Polym. Sci.* **1983**, *54*, 33.
(9) Kim, N.; Webber, S. E. *Macromolecules* **1980**, *13*, 1233.
(10) These values tend to be ca. 10−15% higher than reported in our earlier work (see ref 3). This may be because we are using

phenanthrene quenching as a measure of χ_{SS}, or because there was some hydrolytic loss of the anthryl group in the sample used previously.

(11) Parsons, W. S. Ph.D. Dissertation, The University of Texas at Austin, 1994.

(12) This corresponds to a low value of f_{EET} in ref. 1.

(13) Photophysical Studies of Copolymers and Copolymer Micelles in Aqueous and Organic Media. D. J. Kiserow, Ph.D. Dissertation, The University of Texas at Austin, 1992.

(14) (a) Byers, J. D.; Friedrichs, M.; Friesner, R. A.; Webber, S. E. *Macromolecules* **1988**, *21*, 3402. (b) Byers, J. D.; Friedrichs, M.; Friesner, R. A.; Webber, S. E. In *Molecular Dynamics in Restricted Geometries*; Klafter, J., Drake, J. M., Eds.; John Wiley and Sons, Inc.: New York, NY, 1989; p 99. (c) Byers, J. D.; Parsons, W. S.; Friesner, R. A.; Webber, S. E. *Macromolecules* **1990**, *23*, 4835. (d) Byers, J. D.; Parsons, W. S.; Webber, S. E. *Macromolecules* **1992**, *25*, 5935. (e) Dean, K. R.; Webber, S. E. Photophysics of Polymers at Interfaces. In *Physics of Polymer Surfaces and Interfaces*; Sanchez, I., Ed.; Manning Publications: Greenwich, CT, 1992; pp 285−304.

(15) Bai, F.; Chang, C-H.; Webber, S. E. *Photophysics of Polymers*; Hoyle, C. E., Torkelson, J. M. Eds.; ACS Symposium Series 358; American Chemical Society: Washington, DC, **1987**; p 384.

(16) Zachariasse, K. A.; Busse, R.; Schrader, U.; Kühnle, W. *Chem. Phys. Lett.* **1982**, *89*, 303.

(17) Levitsky, I. A. *Phys. Rev. B* **1994**, *49*, 15594.

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