continuous rearrangements occur on a local scale.

Experimental Section

Polymer samples, obtained by radical initiation, were prepared and purified as previously reported.[1] Poly(*trans*-4-vinylstilbene) (poly-VS) was also prepared by cationic polymerization (CH sample) under dry nitrogen at -40 °C in CH_2Cl_2 solution using $BF_3{\cdot}Et_2O$ as initiator (molar ratio $VS/BF_3{\cdot}Et_2O = 30$). The polymerization was stopped by pouring the reaction mixture into a large excess of methanol. The coagulated polymer was dissolved in $CHCl_3$ and reprecipitated into methanol several times in the dark. After drying, the polymer samples were stored in the dark at -30 °C.

trans-4-Methylstilbene (MS), mp 132 °C, was prepared as previously reported.[1] UV spectra in the range of 400-250 nm were performed at 25 °C in $CHCl_3$ solution with a Cary 219 or a Jasco UVIDEC-710 spectrophotometer. Concentrations in the range $(3-5) \times 10^{-5}$ mol L^{-1} of stilbene chromophores and a cell path length of 1 cm were used. The molar extinction coefficient (ϵ) in the polymeric samples is referred to one VS monomeric unit and is expressed as L mol^{-1} cm^{-1}. CD spectra in the range of 400-250 nm were recorded at 25 °C in $CHCl_3$ solution by a Jasco J500B dichrograph using a cell path length of 1.0 cm. In the case of all-trans samples concentrations in the range of $(3-5) \times 10^{-5}$ mol L^{-1} of VS units were employed, whereas for irradiated samples concentrations in the range $(1-2) \times 10^{-4}$ mol L^{-1} of VS units were generally used. The molar differential dichroic absorption coefficient ($\Delta\epsilon$), expressed as L mol^{-1} cm^{-1}, is referred to one VS monomeric unit and has been calculated as $\Delta\epsilon = (Es)/(3300cl)$ where E is the measured elongation in centimeters, s is the sensitivity in mdeg cm^{-1}, c is the chromophore concentration in dmol L^{-1}, and l is the cell path length in centimeters. Fluorescence emission and excitation spectra were recorded with a Perkin-Elmer MPF3 spectrofluorimeter for $CHCl_3$ solutions of the samples having absorbance lower than 0.4. In the case of emission spectra a 280-nm excitation wavelength was used. Experimental spectra were corrected for detector response. The degree of fluorescence polarization (p) was measured at 360 nm by using an excitation wavelength of 280 nm. Irradiation experiments were carried out on $CHCl_3$ solutions having absorbance at 330 nm lower than 0.1 with a 25-W Zn Osram lamp equipped with suitable cutoff filters to select the emission at 334-328 nm. Photoisomerization reactions were followed by measuring the absorbance of the sample at 313 nm at different irradiation times.

Registry No. Poly(MtA-*co*-VS) (copolymer), 90168-61-9; MS, 1860-17-9; poly(*trans*-4-vinylstilbene) (homopolymer), 25067-52-1.

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Water-Soluble Photon-Harvesting Polymers: Intracoil Energy Transfer in Anthryl- and Fluorescein-Tagged Poly(vinylpyrrolidinone)

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ABSTRACT: Poly(vinylpyrrolidinone) containing small mole fractions of pendent 9,10-diphenylanthracene (DPA) and fluorescein (F) was prepared. These copolymers are soluble in polar solvents such as methanol and water. Absorption of light by DPA results in efficient intracoil sensitization of the $^1(F)^*$ state. The quantum efficiency (χ) of this process was determined to be 0.4 in methanol and 0.8 in water. It is demonstrated that this increase in χ corresponds to a decrease in polymer coil size in water. Analysis of the fluorescence decay also demonstrates (1) the intracoil energy-transfer process is essentially a static process and (2) anthryl aggregation can result in nonexponential fluorescence decay, which is interpreted as a dynamic equilibrium between $^1(DPA)^*$ and a nonfluorescent dimer state. Fluorescence quenching demonstrates that these polymers are not homogeneous and apparently self-organize into hydrophobic and hydrophilic regions.

Introduction

In polymer photophysics it has been recognized that there are at least two "polymer effects" that differentiate this field from small-molecule photophysics: (1) solvent effects on both the polymer-bound chromophore and the polymer coil itself and (2) intracoil energy transfer and/or excited-state annihilation. In the former case the polymer can be used to direct photochemical processes via hydrophobic or electrostatic interactions (i.e., polyelectrolytes). In the latter case the polymer can be used as a photon-harvesting agent, either providing for intracoil multiphoton processes or extending the "action spectrum" of some polymer-bound energy trap.[1] The present study has an element of both of these features. Copolymers have been prepared in which water-soluble poly(vinylpyrrolidinone)

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Table I
Properties of PVP–DPA and PVP–DPA–FTC Polymers

				MeOH[c]		H_2O[c]	
	VP/DPA[a]	DPA/FTC[b]	M_v	$[\eta]$	$\langle r\rangle$ or $\{\chi\}$	$[\eta]$	$\langle r\rangle$ or $\{\chi\}$
PVP–DPA-a	95 (10)		1.05×10^5	0.42	(26)	0.22	(21)
PVP–DPA-b	2×10^3 (<1)						
PVP–DPA–FTC	40 (15)	8 (2)	6.5×10^4	0.31	{0.40}	0.18	{0.80}

[a] Mole ratio of pyrrolidinone/DPA in purified polymer. The monomer feed ratios were 105 for both PVP–DPA-a and PVP–DPA–FTC. The values in parentheses are estimates of the number of DPA chromophores/coil based on M_v and the absorption spectrum (see text). [b] Like *a*. Monomer feed ratio was 1. It is estimated that there are an average of two fluoescein chromophores/coil. The DPA/FTC ratio is estimated from the absorption spectrum (see text). [c] Intrinsic viscosity at 25 °C in the indicated solvent (dL/g). The values in parentheses are coil diameter (in nm) estimated from the Flory–Fox equation or light scattering (see text) (PVP–DPA-a only). The values in braces are the χ values (see text) (PVP–DPA–FTC only).

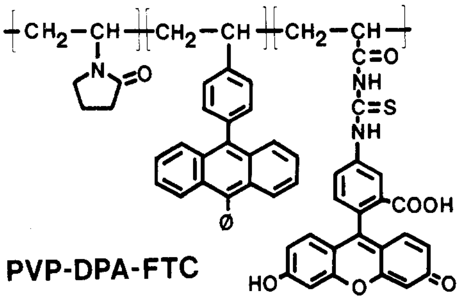
(PVP) contains pendent 9,10-diphenylanthracene (DPA) and fluorescein moieties. The former is sufficiently hydrophobic that in the present study one may assess the photophysics of DPA in aqueous solution. Since PVP is uncharged the present study may be distinguished from those in which the hydrophobic moiety is bound to a polyelectrolyte.[2,3] As will be shown there is a strong tendency for the DPA to segregate into a presumably hydrophobic region of the polymer coil and to be partially screened from solution species.

Energy transfer from the singlet state of DPA to fluorescein is quite efficient (~80% in H_2O) and is shown to depend on the solvent by virtue of the solvent-induced change in polymer coil density. This is similar to earlier observations on very different polymer systems.[4,5] It will also be shown that this energy-transfer process is essentially equivalent to static quenching since the fluorescence lifetime of $^1(DPA)^*$ is only slightly decreased.

Experimental Section

Polymer Preparation. Fluorescein isothiocyanate (FITC, Aldrich) (0.165 g (4.2×10^{-4} M)) and acrylamide (Gold Label, Aldrich) (0.06 g (8.5×10^{-4} M)) were dissolved in 5 mL of dimethyl sulfoxide (Me_2SO) that had been freshly distilled after refluxing over calcium hydride for 24 h. This solution was stirred at room temperature for 4 h, effecting the following coupling reaction: $F\text{–}NCS + H_2N\text{–}R \rightarrow F\text{–}NH\text{–}CS\text{–}NH\text{–}R$. This solution was added to 15 mL of acetone containing 5 g (4.4×10^{-2} M) of *N*-vinyl-2-pyrrolidinone (VP, Aldrich), 0.15 g (4.2×10^{-4} M) of 9-(*p*-ethenylphenyl)-10-phenylanthracene (VDPA),[1] and 1% by weight azobis(isobutyronitrile) (AIBN, Aldrich). The solution was placed in a polymerization tube, degassed by three freeze–pump–thaw cycles, and polymerized at 60 °C for 24 h. Both FITC and acrylamide were used as received. Vinylpyrrolidinone was chromatographed on an activated alumina column prior to use and stored at 0 °C.

The term FTC instead of FITC is more appropriate because the isothiocyanate group is transformed into the thiocarbamyl radical.[6] Polymers containing diphenylanthracene and fluorescein will thus be given the acronym PVP–DPA–FTC. Fluorescein attached to the chain is thus FTC, while small molecular fluorescein used in the quenching studies will be denoted as F, to avoid ambiguity.



PVP–DPA–FTC was partially purified by three precipitations of a methanol solution into ether. Excess FITC was removed by dialysis (Spectrapor membrane tubing, molecular weight cutoff 6000–8000) for 7 days against water. The polymer may be recovered by precipitation into acetonitrile. As a final precaution the polymer was further purified by gel filtration using a Sephadex column (Sigma, G-10-120) with water as the eluent. A polymer containing no fluorescein, PVP–DPA-a, was also prepared by using the same mole ratios of VP and VDPA as for PVP–DPA–FTC. A second fluorescein-free polymer with a very low mole fraction of VDPA was also prepared (PVP–DPA-b). The properties of these polymers are collected in Table I. The polymers are readily soluble in methanol but vigorous stirring overnight is required to dissolve PVP–DPA-a and PVP–DPA–FTC in water. In order to ease the use of the latter as a solvent, the polymers were first dissolved in a minimum amount of methanol, followed by addition of a large excess of water such that the percentage volume of methanol was less than 1%. No turbidity nor precipitation could be detected. We note that PVP–DPA-b was readily soluble in water.

The molecular weight of these polymers was estimated from viscosity measurements in methanol by using the Mark–Houwink parameters for PVP.[7] The intrinsic viscosity was also measured for buffered (pH 8) aqueous solutions. As expected for a thermodynamically poorer solvent, $[\eta]$ is decreased significantly. These results are presented in Table I. One may estimate the mean-square end-to-end distance ($\langle r^2\rangle$) from the Flory–Fox equation[8]

$$[\eta] = (\langle r^2\rangle^{3/2}/M)\phi \qquad (1)$$

where M is the molecular weight and ϕ is a constant (2.5×10^{23} in cgsu). The hydrodynamic radius of PVP–DPA could be obtained by photon correlation spectroscopy.[9] When this hydrodynamic radius is compared to the average end-to-end distance the agreement is exact between the two methods. Hence there is no doubt that there is a major decrease in polymer coil size in going from methanol to water solutions.

Fluorescence Spectroscopy. Because the spectral properties of FTC are strongly pH dependent,[10] all measurements on the polymer, whether in water or in methanol, were carried out under basic conditions. A 0.02 M sodium hydroxide solution or a borax buffer (pH 8) was used.

Methanol (MCB spectrograde) was used as received. Water was deionized by passing successively through six ion-exchange resin columns. 1,4-Diazabicyclo[2.2.2]octane (Dabco, Aldrich) was sublimed and methylviologen hydrochloride (MV^{2+}, Aldrich) was recrystallized twice from ethanol before use.

Fluorescence emission, lifetime, and quantum yield measurements have been described elsewhere.[2,5] Fluorescence quenching was monitored at 440 nm for DPA and at 525 and 570 nm for directly excited and sensitized FTC fluorescence, respectively (there is a finite DPA fluorescence contribution out to 560 nm). No change in the spectral distribution of either DPA or FTC was observed with addition of quenchers used here, except for DPA solubilized in water by PVP and quenched by MV^{2+} (see Results).

Results

(a) Absorption, Steady-State Fluorescence, and Energy-Transfer Efficiencies. Figure 1 shows the absorption spectrum of PVP–DPA–FTC in water. The relative intensities of the maxima are virtually identical in methanol (0.02 M NaOH). It can be seen that for wavelengths below ~380 nm, DPA absorbs most of the

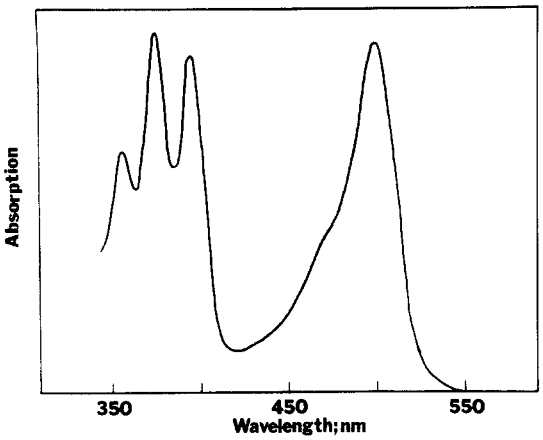


Figure 1. Absorption spectrum of PVP–DPA–FTC in water (0.02 M NaOH).

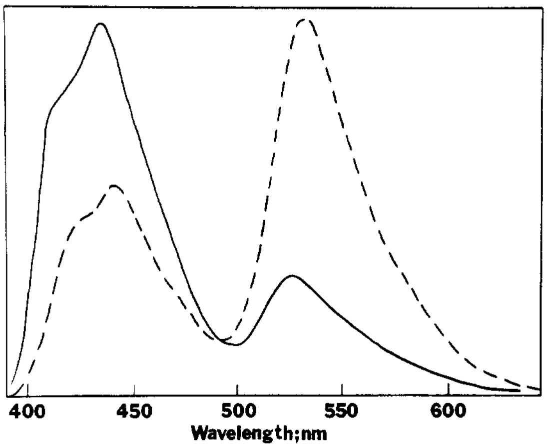


Figure 2. Fluorescence spectra of PVP–DPA–FTC in methanol (solid line) and in water (dashed line) (both 0.02 M NaOH). Normalized at emission maxima.

exciting light. The extinction coefficient (ϵ) at 378 nm of polymerized DPA in methylene chloride has been given as 10 500 M^{-1} cm^{-1}.[11] The optical density of PVP–DPA in water is lowered by approximately 10% compared to an equal weight/volume solution of the polymer in methanol. Assuming that ϵ in CH_2Cl_2 and CH_3OH is the same, this gives an estimate for ϵ at 378 nm for PVP–DPA in water of 9500 M^{-1} cm^{-1}.

The exact value of ϵ for FTC is in doubt because there is a slight broadening of the absorption spectrum and a red shift of approximately 5 nm for the polymer-bound dye ($\lambda_{\max}^{\text{water}}$ = 496 nm) relative to the free dye in solution. A red shift of the same magnitude has been found for FTC bound to protein molecules,[6,12] accompanied by a decrease in the value of ϵ of approximately 25% relative to fluorescein. Assuming that this is the case here, an estimate of ϵ for FTC in basic aqueous solution at 496 nm is 7×10^4 M^{-1} cm^{-1}. From Figure 1, for PVP–DPA–FTC, there is therefore one molecule for FTC for every eight molecules of DPA.

The red shift and broadening of the absorption spectrum of FTC may also be the result of hydrophobic binding of the dye to the polymer backbone. Such spectral shifts have been found, for instance, in neutral solutions of Rose Bengal and PVP.[13] However, addition of FITC to a 0.02 M alkaline solution containing 0.5% by weight off PVP showed no change in optical density or $\lambda_{\max}$ when compared to a polymer-free solution. We presume, therefore, that differences in the absorption spectrum of FTC are due solely to its being bound covalently to the amide.

The fluorescence spectra of PVP–DPA–FTC in water and in methanol are shown in Figure 2. The small dimensions of the polymer coil and the close proximity of DPA and FTC chromophores make energy transfer from DPA to FTC very probable. The quantum efficiency of singlet energy transfer (χ) is defined as the fraction of photons absorbed by DPA that are transferred to FTC. This quantity was measured in two ways:

Method 1: $\chi/(1-\chi) = (\phi_D/\phi_A)(I_A/I_D)$. Here, ϕ_D is the fluorescence quantum yield of donor in the absence of acceptor. ϕ_A is the fluorescence quantum yield of directly excited acceptor, and I_D and I_A are the relative areas of donor and acceptor fluorescence, respectively, in the emission spectrum.

Method 2: $\chi = 1 - (I_Q/I_0)$. Here, I_0 and I_Q are the fluorescence intensities of the donor chromophore of optically matched solutions of PVP–DPA-a and PVP–DPA–FTC, respectively.

In methanol (0.02 M NaOH) ϕ_f for PVP–DPA-a was measured as 0.8 and for FTC, as 0.45. The latter value agrees well with published values of protein-attached FTC in neutral aqueous solutions.[12] Both methods 1 and 2 give χ as 0.4.

In water both methods also agree within experimental error (~±5%), yielding a χ value of 0.8. The increase in χ is a reflection of the diminished coil size of the polymer in water relative to methanol. We note that ϕ_f for PVP–DPA in water has decreased to 0.43, almost half that in methanol and for methacrylic acid–diphenylanthracene copolymers (PMA–DPA) in water.[2] For the latter, however, the chains do not contain as many DPAs as PVP–DPA. Thus it would seem that there is a large degree of self-quenching of PVP–DPA in water solutions. This was further confirmed by measuring ϕ_f for PVP–DPA-b: 0.82 in methanol and 0.95 in water.[14]

Similarly, ϕ_f for FTC has been lowered, in this instance to 0.15. The ϕ_f of FITC is very dependent on pH, especially between pH 6 and pH 8.[10,12] A value of 0.5 is usually quoted for ϕ_f of FITC bound to proteins above pH 9.[12] A lowering of ϕ_f for protein FTC has also been noted with increasing dye/protein content,[12] although not so dramatically as here. The fluorescence lifetime of FTC was found to be 4.1 ns (see next subsection), in agreement with protein FTC. In FTC/protein systems the lifetime of FTC also did not vary with increasing FTC/protein ratios although ϕ_f decreased. It was therefore proposed that static self-quenching was responsible for the lowering of ϕ_f for protein-bound FTC.[12] It is unlikely that this is the case for our system for several reasons: (1) low doping of FTC; (2) χ agrees well by both methods (method 1 measures χ only of fluorescent species, and aggregates of fluorescein are nonfluorescent[15]); (3) the spectral shape and $\lambda_{\max}$ of both FTC absorption and emission spectra are similar to proteins containing only one FTC chromophore.[12] The changes exhibited by extensive aggregation, as shown for instance by fluorescein,[15,16] are not apparent in our system.

The decrease of ϕ_f for FTC may be an environmental effect. The polymer in water acts as a heterogeneous system, as will be discussed later. Solvents of different polarity are known to dramatically affect the ϕ_f of fluorescein, albeit with spectral changes not observed in this system.[17] We speculate that the ionized carboxylic acid group on FTC may be electrostatically attracted to one of the small mole fraction of positively charged nitrogen atoms of the pyrrolidinone groups.[18] Although no such process appears to occur for free fluorescein in alkaline solutions of PVP, perhaps because of the salt effect, this may not be so unreasonable in the copolymer because of the close proximity of FTC and PVP. If this were so, then

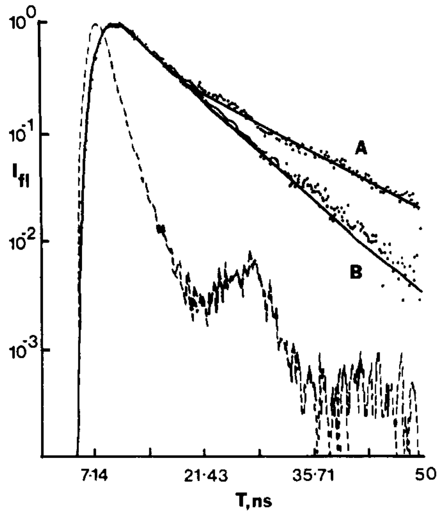


Figure 3. Fluorescence decay curves for PVP–DPA-a (A) and PVP–DPA-b (B) in H_2O (0.02 M NaOH).

Table II
Fluorescence Lifetimes[a,b]

	τ_1, ns	A_1	τ_2, ns	A_2
(a) λ_{obsn} = 440 nm				
PVP–DPA-a, MeOH	7.3	0.84	13.9	0.16
PVP–DPA-b, MeOH	6.8			
PVP–DPA-a, H_2O	3.8	0.61	12.6	0.39
PVP–DPA-b, H_2O	6.0			
PVP–DPA–FTC, MeOH	5.4	0.77	10.7	0.29
PVP–DPA–FTC, H_2O	2.7	0.69	11.0	0.31
PVP–DPA, film	<3.0	0.98	13.5	0.02
DPA, MeOH[c]	9.2			
DPA, H_2O[d]	1.9	0.68	12.3	0.32
DPA, crystal	2.5			
(b) λ_{obsn} = 570 nm				
PVP–DPA–FTC, MeOH	5.4			
PVP–DPA–FTC, H_2O	4.1			

[a] Deaerated by N_2 bubbling. [b] All excited at 381 nm. [c] Reference 2. [d] DPA solubilized in water by PVP.

the FTC chromophore would resemble 6-hydroxy-9-phenylfluorone (HPF).[17] No significant spectral changes are observed between fluorescein and HPF in water, apart from a dramatic lowering of ϕ_f for the latter compound.[17]

The low ϕ_f of FTC in water may therefore be explained by a combination of one or more of the following factors: pH, environment, electrostatic binding, and static quenching.

The important point in this section is that an increase in static quenching efficiency of DPA by FTC by a factor of 2 in water relative to methanol is observed. This is consistent with the decrease in coil size in the former solvent. Further, the large differences in ϕ_f for both DPA and FTC in water when compared to those in methanol show that the macromolecular environment changes molecular properties in a way that is very different from simple changes in solvent. This will be confirmed by the quenching studies discussed in section c.

(b) Fluorescence Lifetime Measurements. The fluorescence decay of DPA in deaerated methanol is monoexponential with a lifetime in agreement with reported values.[2] The same is true for the PVP–DPA-b polymer (with a low loading of DPA) in methanol and water. For the polymers highly doped with DPA the decay curves (monitored at 440 nm) could only be fit satisfactorily with a biexponential decay function (see Figure 3) regardless of solvent or presence of FTC. Table II lists the various fluorescence lifetimes and preexponential values for the polymers. For the PVP–DPA in methanol there is a short (~7 ns) and a long (~13 ns) component. The former is reduced and its preexponential value decreased in water. DPA, solubilized by PVP into water, also displays an analogous biexponentiality. The fluorescence decay of a DPA crystal could be fit satisfactorily to a single exponential. For a PVP–DPA film it was possible to extract a minor component with a long lifetime (Table II).

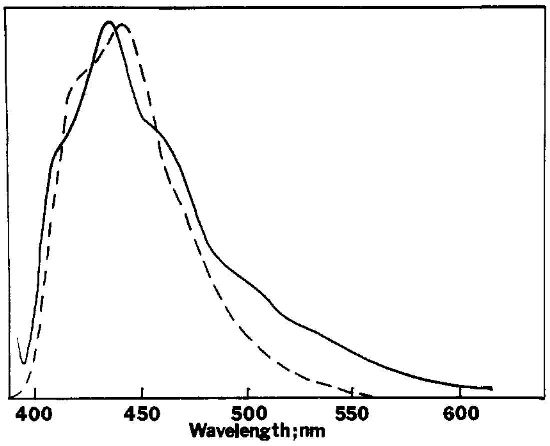


Figure 4. Fluorescence spectra of PVP–DPA-a in water (dashed line) and DPA (solid line) solubilized in water by PVP.

Hence, as the coil density increases and the DPA molecules become closer together, the short-lived component decays faster. Thus there appears to be a large degree of self-quenching. This self-quenching at high loading has been reported for DPA molecules solubilized into micelles, although if there is only one DPA/micelle, there is no difference between τ_f and ϕ_f for micellar solutions and pure solvent.[19]

There is no obvious excimeric component in the fluorescence spectrum of PVP–DPA-a in solution (nor in film). Furthermore all spectra are very similar to the lightly doped PVP–DPA-b in water. There is, however, some low-energy emission that occurs when DPA is solubilized in water by PVP (Figure 4). The excitation spectrum of this latter emission is identical with the absorption spectrum. Hence this long-wavelength emission is not from ground-state dimers. We assume that there must exist a region of the polymer coil that is relatively nonpolar and crowded with DPA molecules. As we will discuss later, PVP solubilized DPA does not seem to be equivalent to polymer-bound DPA.

We speculate that the long-lived component of the fluorescence decay results from excited monomer regenerated by rapid back-dissociation of a weakly bound and almost nonfluorescent dimer. This idea will be discussed in more detail in the Discussion. We note that DPA is generally regarded as being among that class of molecule that does not readily form excimers.[20] This class includes phenanthrene, and in fact a recent study by Ng and Guillet[21] on poly(phenanthryl methacrylate) suggests that very efficient singlet energy migration can occur in phenanthryl polymers because there is no self-trapping at excimer-forming sites. On the other hand, poly(9-vinylphenanthrene) has been shown recently to form excimers,[22] although not very efficiently. We note in Figure 4 that there is a distinct broadening and red shift of the PVP-solubilized DPA fluorescence spectrum in water relative to PVP–DPA in the same solvent.[23] We would expect the former system to accentuate aggregation by virtue of the extreme hydrophobicity of DPA and the absence of covalent bonding to the PVP (i.e., the DPA moieties can arrange themselves anywhere along the polymer coil).

Table III
Quenching of Polymer-Bound DPA by Dabco

	solvent	K_{SV}, M^{-1}	τ_f,[c] ns	k_q, M^{-1} s^{-1}
PVP–DPA-a	water	1.4	7.2	2.1×10^8
PVP–DPA–FTC	water	1.6	5.3	3×10^8
PVP–DPA-a	methanol	4.7	8.4	5.6×10^8
PVP–DPA–FTC	methanol	4.4	6.9	6.4×10^8
DPA[a]	methanol	16.6	9.2	1.8×10^9
PMA–DPA[a]	water[b]			1.1×10^9

[a] Reference 2. [b] Basic solution: pH 11.1. [c] Weighted average lifetime except for those from ref 2.

Table IV
Quenching of Polymer-Bound FTC by Dabco

	solvent[a]	λ_{ex},[b] nm	K_{SV}, M^{-1}	τ_f, ns	k_q, M^{-1} s^{-1}
PVP–DPA–FTC	water	380	0.72	4.1	1.75×10^8
PVP–DPA–FTC	water	480	2.71	4.1	6.6×10^8
PVP–DPA–FTC	methanol	380	1.17	5.4	2.2×10^8
PVP–DPA–FTC	methanol	480	1.17	5.4	2.2×10^8
fluorescein	water	480	8.9	4.0	2.2×10^9
fluorescein	methanol	480	1.58	4.1	3.85×10^8

[a] 0.02 M NaOH solution. [b] λ_{ex} = 380 nm for sensitized emission; λ_{ex} = 480 nm for directly excited emission.

Table V
Quenching of Polymer-Bound DPA and FTC by MV^{2+}

	solvent	K_{SV}, M^{-1}	k_q,[a] M^{-1} s^{-1}
(a) DPA Quenching			
PVP–DPA-a	water	21.3	3.0×10^9
	methanol	43.5	5.2×10^9
PVP–DPA–FTC	water	10	1.9×10^9
	methanol	70	1.0×10^{10}[b]
DPA	methanol		1.35×10^{10}[a]
PMA–DPA (pH < 6)	water		2.7×10^9[c]
(b) FTC Quenching			
PVP–DPA–FTC (λ_{ex} = 380 nm)	water	47	1.14×10^9
PVP–DPA–FTC (λ_{ex} = 480 nm)	water	100	2.4×10^{10}

[a] Lifetimes used given in Tables III and IV. [b] MV^{2+}–FTC complexation. [c] From ref 2.

Thus the polymer environment may permit excimer or excited-state dimer formation even if absent in the homogeneous solution phase.

There is no evidence for any exciplex interaction between the backbone of the polymer and DPA. For example, (1) the fluorescence spectrum and decay of PVP–DPA-b are essentially like that of monomeric DPA and (2) addition of monomeric VP to a solution of DPA does not quench DPA fluorescence or change the shape of the emission spectrum. Similarly, no ground-state perturbation is observed. The low photon flux used in the single-photon-counting technique allows us to rule out any interaction between two excited states, such as T–T annihilation (for which it would be expected that the long component would have a much longer lifetime)[24] or the formation of radical or ionic species. Indeed, laser flash photolysis of DPA and PVP–DPA-a in methanol and water yields the same transient absorption spectrum, notwithstanding the much higher photon flux used in this experiment.

From Table II it is seen that the $^1(DPA)^*$ lifetime is only slightly shortened by the presence of FTC (i.e., each component of the biexponential fit is shorter), despite the fact that the measured χ values are quite large. This demonstrates that the energy-transfer process is essentially equivalent to static quenching, similar to what has been observed in our earlier work.[5]

The fluorescence lifetime of sensitized fluorescein emission is very similar to protein-bound or free fluorescein. For the methanol solvent the polymer-bound fluorescein lifetime is slightly longer than free fluorescein lifetime in methanol. However, the difference is no more than might be expected from differences in the local polarity.[25]

(c) Fluorescence Quenching. Quenching of Polymer-Bound DPA by Dabco. Quenching of the excited DPA chromophore on PVP–DPA or PVP–DPA–FTC by Dabco yields linear Stern–Volmer plots in both methanol and water (Table III).

In methanol, quenching rate constants (k_q) for DPA and a copolymer of methacrylic acid and DPA (PMA–DMA) by Dabco have been reported as 1.8×10^9 and 1.1×10^9 M^{-1} s^{-1}, respectively.[2] These two values are in agreement with each other considering that diffusion of the polymer coil can be neglected. Yet k_q for DPA on PVP–DPA or PVP–DPA–FTC, although approximately the same, is about 50% that reported for the above polymer. Thus in methanol there is some screening of the DPA from the quencher by the polymer coil, although the effect is not unduly large. There is no evidence for singlet energy migration between DPA chromophores, as shown by the low value of k_q.

In water the quenching rates are noticeably reduced. The polymer coil is much more compact and provides a greater barrier to quenching in water than in methanol.

One point is in order here. The value of τ_f used to estimate k_q is a weighted average of the two lifetimes shown by the polymer. Any subtle differences in k_q between PVP–DPA and PVP–DPA–FTC for the same solvent should therefore be treated with caution.

Quenching of Polymer-Bound FTC by Dabco. K_{SV} and k_q constants are shown in Table IV. In water quenching of fluorescein (F) is an order of magnitude larger than quenching of sensitized FTC and 3 times that of directly excited FTC. Obviously FTC is shielded to a large extent by the backbone. The low value of k_q for sensitized compared to directly excited FTC suggests that, at least in water, most of the former reside in the more hydrophobic, inaccessible regions of the coil, close to where DPA would be found.

In methanol, no such difference could be detected. The Stern–Volmer quenching constant is the same whether the exciting wavelength is 380 or 480 nm. For the polymer, k_q is half that found for F, as expected based on diffusion constants. Thus, these results suggest that in methanol the acceptor fluorophore is easily accessible.

Quenching of Polymer-Bound DPA by MV^{2+}. Similar to Dabco quenching, DPA fluorescence quenching by MV^{2+} obeyed the Stern–Volmer equation with quenching constants given in Table V. As was found for PMA–DPA,[2] MV^{2+} is a much more efficient quencher than Dabco, presumably because it is easier to reduce. For PVP–DPA-a, k_q is slightly higher in methanol than water, as was the case for Dabco. We ascribe this to the improved accessibility of the MV^{2+} to DPA moieties in the better solvent. This situation is accentuated for PVP–DPA–FTC, by a factor of 5. As will be discussed in the next subsection, there is complexation of MV^{2+} with FTC in methanol. Thus in this solvent the concentration of MV^{2+} within the coil is increased, leading to efficient DPA quenching. We have no explanation for the slight increase of k_q for PVP–DPA-a relative to PVP–DPA–FTC in water.[26]

We note the close agreement of k_q for PVP–DPA-a with PMA–DPA in acid solution and that both are much lower than DPA in methanol. We ascribe this decrease to a polymer screening effect, similar to that observed for

Dabco (Table III). We have not included any quenching results for PVP-solubilized DPA in water because the MV^{2+} induced an exciplex-type emission. Qualitatively MV^{2+} was not an efficient quencher in this case ($k_q \sim 10^8$ M^{-1} s^{-1}).

Quenching of Polymer-Bound FTC by MV^{2+} in Water. MV^{2+} will strongly complex with FTC or F in methanol, invalidating the Stern–Volmer equation. Consequently the results in Table V are only for water (pH 8). There is apparently weak complexation in this solvent as there is a very slight broadening and red shift of the FTC absorption spectrum. It will be noted that k_q is quite large for directly excited FTC, i.e., near the diffusion-controlled limit with no evidence for polymer screening. Undoubtedly electrostatic attraction between MV^{2+} and the partially ionized FTC enhances the quenching efficiency.

It is interesting that sensitized FTC (λ_{ex} = 380 nm) is quenched ca. 10 times less efficiently than directly excited FTC (λ_{ex} = 480 nm). The former must be located reasonably near the hydrophobic region that contains the DPA moieties and apparently is screened from the MV^{2+}. Thus these results clearly demonstrate that there exists heterogeneity in amphiphilic polymers of this type.

Discussion

There are three main results that follow from the experiments presented herein:

(1) The quantum efficiency (χ) of every transfer from ^{1}(DPA)* to FTC is fairly high and dependent on the coil density which in turn is a function of solvent; the fluorescent decay implies that the energy transfer is essentially a static process.

(2) The fluorescence decay of ^{1}(DPA)* associated with PVP is nonexponential in the case of relatively high DPA loading. One component of the biexponential fit to the fluorescence decay has a longer lifetime than PVP with low DPA content.

(3) The polymer environment generally seems to hinder the approach of quencher species to the DPA and FTC moieties except in the case of complexation (FTC:MV^{2+}:methanol). Directly excited ^{1}(FTC)* is always quenched more efficiently than sensitized ^{1}(FTC)*, which demonstrates that those FTCs that are capable of being sensitized are in a hydrophobic environment primarily occupied by DPAs and for which the approach by the quencher is especially hindered.

We will now discuss each of these in turn.

Energy-Transfer Efficiency. We assume the mechanism of energy transfer from ^{1}(DPA)* to be that due to Förster, for which the energy-transfer rate is given by[27]

$$k_{ET}(r) = k^0_{DPA}(R_0/r)^6 \tag{2}$$

where k^0_{DPA} is the normal decay rate of ^{1}(DPA)* in the absence of energy transfer, r is the DPA–FTC separation, and R_0 is a parameter that can be derived from the fluorescence and absorption spectra; i.e.

$$R_0 = \frac{(9000 \ln 10)\kappa^2}{128\pi^2\eta^4 N}\int_0^\infty \frac{F_{DPA}(\bar{\nu})\epsilon_{FTC}(\bar{\nu})\,d\bar{\nu}}{\bar{\nu}^4} \tag{3}$$

In most applications the value of κ^2 is taken to be 2/3, corresponding to an average over random orientations of the donor and acceptor. For ^{1}(DPA)* and fluorescein R_0 has been estimated as 41 Å.[28] As was noted in the Results, ϵ_{FTC} seems to be diminished by ~25% when polymer bound, and likewise the quantum yield of fluorescence of ^{1}(DPA)* is decreased, which affects eq 3 because

$$\phi_F^{DPA} = \int_0^\infty F_{DPA}(\bar{\nu})\,d\bar{\nu} \tag{4}$$

Thus R_0 for PVP–DPA–FTC in water may be as low as ca. 15 Å.

For a DPA–FTC pair separated by r the quantum yield of energy transfer from eq 2 would be given by

$$\begin{aligned}\chi(r) &= k_{ET}(r)/(k_{ET}(r) + k^0_{DPA}) \\ &= [1 + (r/R_0)^6]^{-1}\end{aligned} \tag{5}$$

If we associate our measured χ with an average r value ($\bar{r}$), then

$$\bar{r}/R_0 = (1/\chi - 1)^{1/6} \tag{6}$$

The quantity $\bar{r}/R_0$ has the value 1.07 and 0.79 for methanol and water, respectively. The ratio of these values is 1.35, on the order of the ratio of the coil diameter in Table I (1.24). Thus if one assumes that R_0 is unchanged in these two environments, the increase of χ in going from methanol to water can be rationalized as the result of a uniform shrinkage of all internal coil dimensions. If the maximum decrease of R_0 is taken into account, then one would estimate $\bar{r}$(methanol)/$\bar{r}$(H_2O) ≈ (41/15)(1.24) = 3.69, which corresponds to an "aggregation" of the DPA and FTC groups within the polymer coil. On the basis of the quenching results, we believe this is a correct assessment of the physical situation, despite the crudeness of these estimates.

We note that there is only a very small decrease in τ_f for ^{1}(DPA)* in PVP–DPA–FTC (Table II), implying that a significant fraction of the energy transfer can be thought of as "static". It would be very interesting to obtain these decay curves with better time resolution than we have available at present. In such a case one could test statistical models of DPA–FTC separation ($g(r)$) by averaging $\chi(r)$ in eq 5 and the fluorescence decay function for ^{1}(DPA)*:[29]

$$I_f(t) = \int g(r) \exp\{-k^0_{DPA}t(1 + (R_0/r)^6)\} \tag{7}$$

Nonexponential Decay of DPA Fluorescence. It is not surprising in a microheterogeneous environment that the fluorescence of a probe species would be nonexponential, since there may be various quenching sites available. However, in such a case one expects one lifetime component to be shorter and one to be the same as the unquenched species. Our data demonstrate the existence of a *longer* component in the fluorescence decay. This observation cannot be the result of an anthryl–pyrrolidinone interaction because it is not observed for PVP–DPA-b. It would appear to be an effect of anthryl aggregation only since the same phenomenon is observed for DPA solubilized in PVP.

In the polymer photophysical literature there are many examples of a dynamic equilibrium existing between a monomer and excimer species,[30] i.e.

$$^1M^* + M \leftrightarrow {}^1D^* \tag{8}$$

in which case the fluorescence decay of $^1M^*$ will be biexponential and there may be a long-lived component that corresponds to the lifetime of the $^1D^*$ state. However, in the present case there is no evidence for the $^1D^*$ state in the emission spectrum, nor is formation of a $^1D^*$ state expected for DPA.[31] Thus, in order to use a kinetic scheme like eq 8 to rationalize our data one has to postulate that either $^1D^*$ is nonfluorescent or has a fluorescence spectrum that corresponds exactly to $^1M^*$. The latter model certainly does not correspond to the usual properties of an excimer. The former model is strengthened by the observation that the quantum yield of fluorescence is lower for PVP–DPA-a in water than that of PVP–DPA-b.

We note that in the exciton-resonance theory of excimer stabilization, eq 8 can be treated as a valence-bond stabilization[32]

$$ {}^1M_1^* + M_2 \leftrightarrow M_1 + {}^1M_2^* \tag{9} $$

with states

$$ \phi_\pm = (1/2^{1/2})(\phi_{M_1}{}^*\phi_{M_2} \pm \phi_{M_1}\phi_{M_2}{}^*) \tag{10} $$

with energies

$$ E_\pm = E_M{}^* \pm M^2/r^3 \tag{11} $$

where $E_M{}^*$ is the normal excited-state energy of M and M^2/r^3 is the dipolar interaction between these states (M = transition dipole and r the intermolecular separation). If the transition dipoles of M_1 and M_2 are parallel, then the lower energy state (ϕ_-) has zero transition moment to the ground state. This kind of treatment corresponds to a weak interaction treatment of excimer formation, and while it is not an adequate explanation of normally observed excimers, we suggest that such a situation may arise here. In the case of DPA there may be sufficient steric hindrance to prevent all but the longest range "excimer coupling" mechanism, which corresponds to the terms indicated above.

Of course, there is no good reason for the DPA species to be perfectly aligned, as is required for the ϕ_- state to have zero transition dipole moment. However, there may be adequate pairwise interactions between DPA molecules as to produce an ensemble of excited dimers with very different radiative rates, resulting in a nonexponential fluorescence decay with a long-lived component.[33]

Quenching Results. In general, DPA is always quenched more efficiently in methanol than in water and the polymer-bound DPA is always quenched less efficiently than monomeric DPA. (In the case of MV^{2+} as a quencher and methanol solvent, the FTC further enhances the former effect by complexingg with the quencher, which presumably raises its local concentration.) We ascribe this solvent effect to the aggregation of DPA moieties to form a hydrophobic region which is partially protected from the solvent by the polymer coil. On the basis of earlier work on PMA–DPA[2] we do not believe this is a universal effect but is due to the properties of the pyrrolidinone backbone.

The same solvent effect is not observed for FTC where, for example, Dabco quenching is more efficient in water than methanol for direct excitation (Table IV). We assume that this implies that the FTC is not confined exclusively to hydrophobic regions. However, sensitized ${}^1(\mathrm{FTC})^*$ is always quenched less efficiently in water than directly excited FTC. Thus there seems to be some partitioning of the FTC between "accessible" and "less accessible" regions of the polymer coil, with the latter corresponding to the DPA-rich region. This kind of observation might be expected to be a general technique for assessing the homogeneity of a polymer system via fluorescence probe–energy-transfer techniques.

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Registry No. (*N*-vinyl-2-pyrrolidinone)·(9-(*p*-ethenylphenyl)-10-phenylanthrace)·(*N*-(5-fluorescein-*N*′-(1-*oxo*-2-propenyl)thiourea) (copolymer), 95070-20-5.

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