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

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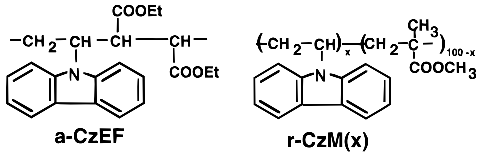
ABSTRACT: Steady-state and time-dependent fluorescence measurements were made for copolymers with pendant carbazole chromophores as a function of polymer coil collapse induced by the addition of a nonsolvent. The results show that although the efficiency of electronic energy transport to a covalently bound trap increases with coil contraction, this increase is part of a complex chain of events, the most important being a decrease in donor quantum yield. It was found that classical excimer formation is small for the polymers studied, while self-quenching is prevalent and competes for donor energy. The result is that, as the efficiency of energy transfer increases, the quantum yield and fluorescence lifetime of the donor decrease while the fluorescence intensity of the acceptor increases. It is quite likely that if self-quenching were eliminated, the efficiency of electronic energy transfer would approach unity for a small degree of coil collapse.

Introduction

The transport of excitation along a polymer chain has been studied actively by a number of authors for more than a decade[1−3] and has been reviewed by one of us.[4] The qualitative features of intrachain energy transport and trapping by a covalently bound species have been clear for some time and we have recently developed a computer simulation method to analyze these processes as a function of chain length, excitation transfer distances, and solvent−polymer (and surface−polymer) interaction energies.[5] Our motivation in these simulations has been to relate the degree of coil expansion and intracoil contacts to the phenomenon of down-chain electronic energy transport (EET). The experiments described in this paper were undertaken to provide the kind of experimental data required for a meaningful test of experiment and theory.

The polymer systems chosen for study were alternating and random copolymers with carbazole chromophores (Chart 1). Alternating polymers were considered to be a good choice for a model system because excimer fluorescence is minimized and we hoped to be able to consider only down-chain EET to the covalently bound anthracene trap.

Chart 1



a-CzEF

r-CzM(x)

The experimental plan was straightforward: the polymers were dissolved in a "good" solvent (THF) at a very low concentration and a precipitant (water) was added. As the coil collapsed the fluorescence was expected to change in a qualitatively predictable way; i.e., a smaller, more compact coil should lead to more efficient sensitization of the anthryl trap unless excimer formation and/or self-quenching prevented long-distance EET. These latter possibilities could be assessed by experiments on the same polymer without the covalently attached anthryl trap. One of our primary diagnostics is the time-dependence of donor fluorescence which we can currently measure with ca. 0.1 ns resolution. It is this time-dependent information that we have considered in our polymer simulation work since this data contains the details required for a molecular level understanding of polymer photophysics.

What we find is that the interplay between solvent and polymer photophysics is quite complex and in this paper we wish to describe our observations in some detail. A more quantitative comparison of our computer simulations and experimental data has been presented elsewhere.[6] A major conclusion of this comparison is that the parameters of self-trapping and/or self-quenching and energy transport to covalent traps depends on the solvent-segment energy interaction in such a complex way that no unique fit of theory and experiment is possible. Nevertheless, the experimental data presented herein illustrates some important photophysical consequences of polymer coil collapse that are of interest in their own right. In broad overview, we find that coil collapse leads to self-quenching *even in the absence of excimer fluorescence*, and this process competes with the process of energy transfer to a covalently attached trap. Thus in the design of "photon-harvesting polymers", the elimination of self-quenching between chromophores must be considered along with the Förster transfer radius and the excited state lifetime.[4]

Experimental Section

Solvents. THF was prepared daily for use by distillation over $LiAlH_4$. Water was deionized by successively passing through three ion exchange resin columns. THF and water were tested for spectral purity at the wavelength of interest by steady-state and time-dependent fluorescence techniques. In both cases the fluorescence intensity was negligible.

Carbazole Polymers. Copolymerizations for the carbazole polymers were performed by adding *N*-vinylcarbazole and

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Table 1. Preparation and Characterization Data for Carbazole Copolymers

polymer	feed %	yield %	MW[a]	f_{Cz} % in polymer	anth/ chain[b]
r-CzM(45)	60	5.6	3.3×10^5	45	
r-CzM(45)-A(0.7)	74.7 (Cz)	12.2	2.5×10^4	51	1.23
a-CzEF	50	3.0	1.0×10^5	52	
a-CzEF-A(0.7)	49.4 (Cz)	5.9	3.2×10^4	51	1.30

[a] Determined by GPC. [b] Average number of anthracene moieties per chain.

either diethyl fumarate or methyl methacrylate in the presence of *N*,*N*-azobis(isobutyronitrile) in benzene at 60 °C for 1−6 h. Polymers were then purified by three precipitations from THF into *n*-hexane. Anthryl energy traps were covalently bound by terpolymerization of 9-anthrylmethyl methacrylate with the two monomers. We have also found that the O-CH_2-Anth group undergoes hydrolysis very rapidly, so one must carefully monitor the time between exposure of the sample to water and the photophysical experiment. Generally the THF:H_2O solution may be stored safely for several days. Tests of samples refrigerated and stored in the dark for 1 week showed that a partial loss of anthracene (as measured by a GPC system coupled to a fluorimeter) can lead to a greatly diminished sensitization efficiency. Consequently only fresh solutions were used for all measurements. Polymer compositions were determined by UV absorption, and molecular weights were determined by GPC. Details are given in Table 1.

Fluorescence Spectroscopy. Steady-state fluorescence spectra were recorded on a SPEX Fluorolog fluorimeter system described elsewhere[7] and a Photon Technology International (PTI) LS-100 luminescence spectrophotometer. The details of the PTI system are as follows: the light source is a 5 kW peak power pulsed Xe lamp. Both the excitation and emission monochromator have 1200 lines/mm, 4 mm/mm dispersion, 0.5 mm/step minimum resolution, and a wavelength range of 200−1000 nm. The grating is blazed at 300 nm for the excitation monochromator and 500 nm for the emission monochromator. The detector is a R928 PMT with a wavelength range of 200−930 nm. Spectra were corrected for photomultiplier response. Steady-state emission spectra for carbazole polymers were generated using 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 the donor and acceptor, which was achieved with a linear regression method.[8]

Lifetime measurements were made by the method of time-correlated single photon counting with an excitation wavelength of 293 nm and emission wavelengths of 350 and 460 nm for carbazole and anthracene, respectively. Details concerning the single photon counting system and data treatment have been given previously.[9]

Sample Preparation. All fluorescence measurements were made for deoxygenated samples using a specially designed cuvette with a greaseless stopcock. Extensive tests were made with this cuvette and it was found that the solutions remained deaerated for times far in excess of the longest experimental times (no oxygen quenching was observed 24 h after outgassing). THF solutions were deaerated by bubbling with argon for 10 min with frequent repositioning of the argon flow to ensure all oxygen was removed. A system of outgassing was used whereby argon is bubbled through a small container of THF. This process minimized the loss of THF during outgassing. The outgassing technique was tested for various times and we found no change in steady-state or time-dependent spectra with outgassing longer than 5 min. The aforementioned times were doubled to 10 min during data collection to insure complete and reproducible outgassing. Solution volumes were measured using an adjustable micropipet accurate to ±1 μL. Fluorescence quantum yields were computed by comparison to phenanthrene.[10] For each addition of water the refractive index was estimated for the appropriate ratio of THF and water. Absorbance measurements for polymers in THF:H_2O solution were made using a reference with the corresponding ratio of THF:H_2O.

Results and Discussion

Overview. In all the experiments discussed herein we will have a donor chromophore, carbazole (Cz), pendant to a polymer coil which may be untagged or may contain a small mole percent of anthracene attached by copolymerization.[11,12] (see Chart 1.) It is always possible that some fraction of the polymers will not contain an anthryl trap, or in what amounts to the same thing, there may be an energy “barrier” along the polymer chain (e.g. a sequence of spacer groups) that prevents the excitation from migrating from a trap-free region to a region that contains a trap. These “bottlenecks” to photon harvesting can lead to a component of donor fluorescence that decays like the untagged polymers.

One of the characteristics of EET from a donor to a trap is more rapid fluorescence decay for the donor. The donor fluorescence is inevitably predicted to be highly nonexponential by any kind of transport model.[5,13] However, in a polymer coil there can also be a variety of local environments each of which have slightly different fluorescence lifetimes and yields.

When EET to traps occurs, the quantum yield of the donor species decreases while the magnitude of fluorescence of the trap increases. If the excitation wavelength is selected such that the trap is not excited directly, the efficiency of trap sensitization for the steady-state case can be derived from the expression of Holden and Guillet[14−16]

$$\frac{I_{\mathrm{A}}^{\mathrm{SS}}}{I_{\mathrm{D}}^{\mathrm{SS}}} = \frac{\phi_{\mathrm{A}}^{\mathrm{fl}}}{\phi_{\mathrm{D}}^{\mathrm{fl}}} \frac{\chi_{\mathrm{SS}}}{1 - \chi_{\mathrm{SS}}} \tag{1}$$

where $I_{\mathrm{A}}^{\mathrm{SS}}$ and $I_{\mathrm{D}}^{\mathrm{SS}}$ are the total integrated fluorescence intensity of the acceptor and donor, respectively, and ϕ^{fl} is the appropriate quantum yield of fluorescence. It is assumed that $\phi_{\mathrm{A}}^{\mathrm{fl}}$ is the same for directly excited or sensitized acceptors.[17]

Alternatively, it can be assumed that the difference between the total fluorescence of the donor with and without a covalently bound trap is the result of EET only. In this case

$$\frac{[I_{\mathrm{D}}^{(\mathrm{T})}]_{\mathrm{SS}}}{[I_{\mathrm{D}}^{(0)}]_{\mathrm{SS}}} = 1 - \chi_{\mathrm{SS}}^{[\mathrm{T}]} \tag{2}$$

where T and 0 superscripts represent the tagged and untagged polymers, respectively. With this expression, the effect of intrinsic traps (including self-quenching) is contained in $[I_{\mathrm{D}}^{(0)}]_{\mathrm{SS}}$, the total fluorescence intensity for the untagged polymers. It is assumed that the presence of a small mole fraction of trap does not affect the conformation of the polymer (this assumption underlies all studies of this type) and hence does not affect the density of excimer forming or self-quenching sites.

The time-dependence of the donor fluorescence should reflect the energy transfer process in a similar way. In any trapping model,[5] the time dependent fluorescence intensity can be related to the survival probability, $S(t)$, by

$$I_{\mathrm{D}}(t) = k_{\mathrm{D}}^{\mathrm{rad}} S(t) \exp(-t/\tau_{\mathrm{D}}^{\mathrm{o}}) \tag{3}$$

where $k_{\mathrm{D}}^{\mathrm{rad}}$ is the donor radiative rate in the particular solvent, $\tau_{\mathrm{D}}^{\mathrm{o}}$ is the intrinsic lifetime of the donor in the solvent in the absence of energy transfer, and $S(t)$ is the survival probability of the donor excited state in the presence of energy transfer to a trap. However, any "site inhomogeneity" that leads to a multiple exponential decay would also be included in $S(t)$ in this representation. It is a fundamental experimental difficulty in work of this type to account for this inhomogeneity properly.

The time dependence can be related to the steady-state fluorescence yield by the following integration[18]

$$I_{\mathrm{D}}^{\mathrm{SS}} \propto \int_{\mathrm{o}}^{\infty} I_{\mathrm{D}}(t)\,\mathrm{d}t = k_{\mathrm{D}}^{\mathrm{rad}} \int_{\mathrm{o}}^{\infty} S(t)\exp(-t/\tau_{\mathrm{D}}^{\mathrm{o}})\,\mathrm{d}t = k_{\mathrm{D}}^{\mathrm{rad}}\langle\tau_{\mathrm{D}}\rangle = k_{\mathrm{D}}^{\mathrm{rad}}\sum_{i=1}^{N} a^{\mathrm{i}}\tau_i \quad (4)$$

where $\langle\tau_{\mathrm{D}}\rangle$ represents the zeroth moment of the function $S(t)\exp(-t/\tau_{\mathrm{D}}^{\mathrm{o}})$. The last form is appropriate for multiexponential fitting.[19] For the multiexponential fitting presented here, N is typically three, although for a few decays, two or four exponentials were used to achieve good fits. The choice of N depends on the complexity of the decay, which is a function of the photophysical processes occurring. (Details of the multiexponential fitting are available as supporting information.) Thus, the value of $\chi^{(\mathrm{T})}$ can be related to the time-dependent data by the following equation (where the T and 0 superscripts have the same meaning as before)

$$\frac{\langle\tau_{\mathrm{D}}\rangle^{(\mathrm{T})}}{\langle\tau_{\mathrm{D}}\rangle^{(0)}} = 1 - \chi_{\tau}^{(\mathrm{T})} \quad (5)$$

We reserve the symbol $\chi_{\tau}^{(\mathrm{T})}$ to describe the efficiency of energy transfer derived in this way. The values of $\chi_{\tau}^{(\mathrm{T})}$ and $\chi_{\mathrm{SS}}^{(\mathrm{T})}$ should agree unless (1) the fluorescing state is not the sole sensitizing state of the donor,[20] (2) there is a very fast component of the donor fluorescence (presumably due to energy transfer to nearby traps) that was not measured and hence is not included in the function used in eq 4,[4] or (3) $\chi_{\mathrm{SS}}^{(\mathrm{T})}$ was overestimated by the use of eq 3 because the trap does perturb the polymer conformation. Despite the fact that we are able to detect fluorescent components with a time resolution of ca. 0.1 ns, we find that $\chi_{\tau} < \chi_{\mathrm{SS}}$ for a number of cases (see later discussion).

It was mentioned earlier that photon-harvesting "bottlenecks" can occur, which lead to some fraction of donor species that decay with their intrinsic lifetimes. $S(t)$ can be thought of as a summation of many exponential terms with the longest lifetimes corresponding to excitations that are created at the largest possible separation from the trap. Thus we can write

$$I_{\mathrm{D}}(t)/k_{\mathrm{D}}^{\mathrm{rad}} = \{f_{\mathrm{EET}}S(t) + (1 - f_{\mathrm{EET}})\}\exp(-t/\tau_{\mathrm{D}}^{\mathrm{o}}) \quad (6a)$$

and

$$\lim t \rightarrow \text{large } I_{\mathrm{D}}(t)/k_{\mathrm{D}}^{\mathrm{rad}} = \{f_{\mathrm{EET}}a_{\mathrm{s}}\,\mathrm{e}^{-t/\tau_{\mathrm{s}}} + (1 - f_{\mathrm{EET}})\}\exp(-t/\tau_{\mathrm{D}}^{\mathrm{o}}) \quad (6b)$$

In eq 6, f_{EET} is the fraction of polymer coils or segments that can participate in EET, and $1 - f_{\mathrm{EET}}$ is the fraction that either is untagged or which possesses a bottleneck. a_{s} and τ_{s} are the preexponential factor and lifetime that corresponds to the slowest rate of EET to the trap.[21,22] As a practical matter, it is not always easy to distinguish these two components, but if we wish to test $S(t)$ against theory, we need to estimate f_{EET}. We do this primarily by examining the decay curve at long times and subtracting the component that decays solely like $\exp(-t/\tau_{\mathrm{D}}^{\mathrm{o}})$. There is a certain degree of arbitrariness to this procedure which implies that $S(t)$ should be compared to theory only over the time range for which its magnitude is much larger than $1 - f_{\mathrm{EET}}$. We estimate f_{EET} to be between 0.95 and 0.99 for all our polymers.

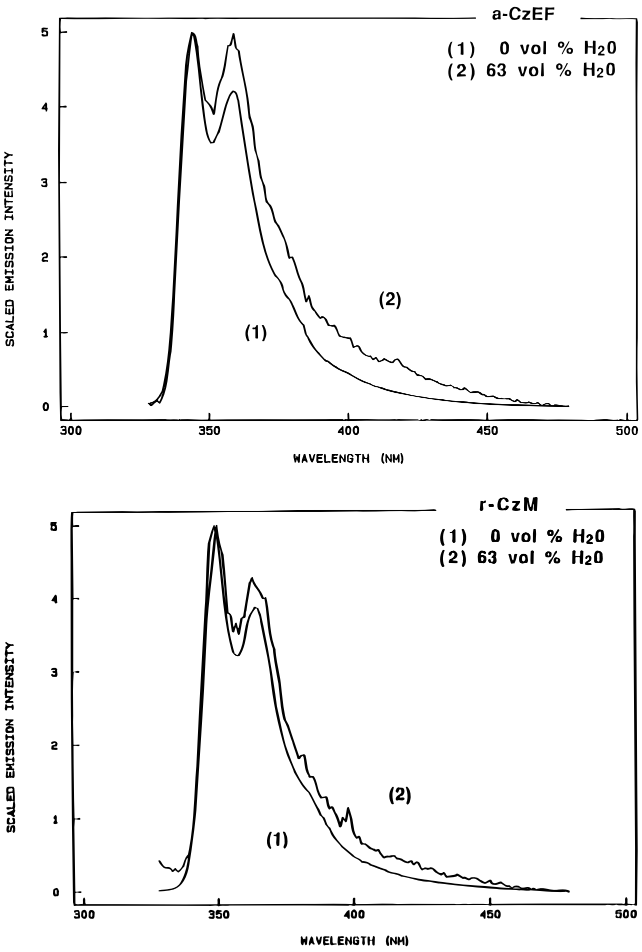

Figure 1. (top) Steady-state fluorescence spectra for aCzEF: (1) 0 vol % and water and (2) 63 vol % water; excitation, 293 nm. (bottom) Steady-state fluorescence spectra for r-CzM-(45): (1) 0 vol % water and (2) 63 vol % water; excitation, 293 nm.

Carbazole Polymers in THF:H$_2$O Solution. The alternating and random polymers a-CzEF and r-CzM-(45) were studied (Chart 1). These were prepared by free radical polymerization in benzene, and the tagged polymers were prepared by a terpolymerization with 9-anthrylmethyl methacrylate and have a lower molecular weight than the untagged polymers in general (Table 1). The mole percentage of anthracene chromophores per coil is approximately 0.7 for both polymers. Neither of these polymers displays significant excimer fluorescence in pure THF or with high volume percentages of water.

Steady-state fluorescence measurements were made for a-CzEF and r-CzM(45) to qualitatively assess the effect of chromophore proximity (Figure 1). All spectra are scaled to a common maximum for ease of comparison, but we note that the intensity of fluorescence declines rapidly with addition of the strong precipitant, water. In a good solvent (pure THF), where the polymer

Table 2. Fluorescence Quantum Yields for Untagged Polymers as a Function of vol % H_2O

a-CzEF		r-CzM(45)	
vol % H_2O	$\phi_D{}^a$	vol % H_2O	ϕ_D
0	0.62	0	0.61
13	0.55	13	0.46
31	0.32	31	0.43
48	0.26	48	0.24
63	0.24	63	0.12

[a] ϕ_D is the fluorescence quantum yield of the donor, carbazole.

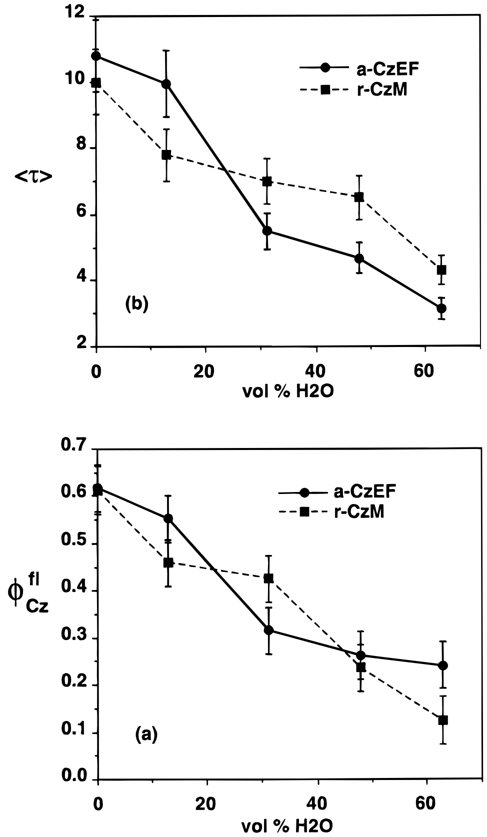

Figure 2. (top) Average lifetime, $\langle\tau\rangle$ (see eq 4), in nanoseconds for a-CzEF and r-CzM(45) as a function of vol % water. (bottom) Quantum yield of carbazole fluorescence, ϕ^{fl}_{Cz}, for a-CzEF and r-CzM(45) as a function of vol % water. The total error in the reported values for $\langle\tau\rangle$ is ±10% and for ϕ^{fl}_{Cz} is ±5%.

conformation is expected to be expanded, thereby minimizing intracoil contacts, the average lifetime and quantum yield for the random and alternating polymers are approximately the same. As the nonsolvent is added there is a steady decrease in lifetime and quantum yield for both polymers (see Table 2, Figure 2). Although a slightly more rapid decrease in quantum yield is measured for r-CzM(45), a-CzEF exhibits slightly more fluorescence broadening with a hint of excimer fluorescence upon addition of water (Figure 1, top). Given the rather strong tendency for *N*-polyvinylcarbazole to form excimers,[23] this may imply that the “random” copolymers are substantially alternating.[24]

Both polymers exhibit a faster fluorescence decay with decreasing average fluorescence lifetimes (eq 4) upon addition of water (Figure 2, top). The fluorescence decays are strongly nonexponential for both polymers, even without the addition of water (decays not shown). Thus it seems that self-quenching and/or site inhomogeneity is significant even in a good solvent, even though excimer formation is minimal. When comparing the average lifetimes and quantum yields plotted in Figure 2 for both polymers and the spectral features shown in Figure 1, it is evident that both the random and alternating polymers exhibit similar behavior as a function of added precipitating solvent. It is also evident that even without an anthryl energy trap present, complex photophysical processes occur as the polymer coil collapses. We believe that self-quenching is kinetically equivalent to excimer formation with a very low quantum yield or excimer fluorescence. Although self-quenching is an undesired complication in any theoretical analysis of photon-harvesting polymers, it is unavoidable, even for the alternating copolymers studied here.

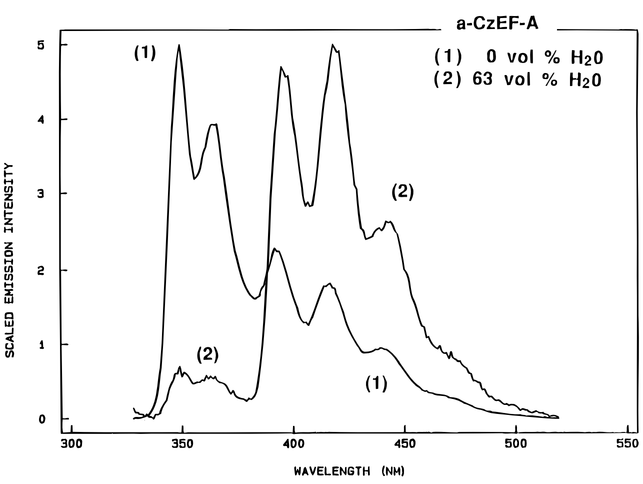

Figure 3. Steady-state fluorescence spectra for a-CzEF-A(0.7) for 0 and 63 vol % water; excitation, 293 nm.

The steady-state fluorescence of the anthracene-tagged polymer a-CzEF-A is very sensitive to the addition of water (see Figure 3). The spectra in Figure 3 are scaled to equal intensity at the maxima to demonstrate the concurrent loss in carbazole emission with the gain in anthracene emission. Even with no precipitant added, significant energy transfer is evident. As water is added, there is a steady increase in anthracene sensitization relative to carbazole fluorescence. Figure 3 shows only the extreme case with 63 vol % water for which carbazole emission is severely diminished relative to anthracene emission. While there is sensitization of anthracene as the polymer coil is collapsed, there must also be significant carbazole–carbazole self-quenching, based on the results for the untagged polymer. The steady-state spectrum for the random polymer is not shown since it is qualitatively indistinguishable from the alternating polymer spectra shown in Figure 3. The similarity is not surprising since we noted previously that the “random” polymers may be nearly alternating.

The lifetime decays are highly sensitive to the addition of the nonsolvent (Figure 4). In pure THF the decays are nonexponential, as might be expected from energy transfer from carbazole to anthracene and/or carbazole–carbazole self-quenching. The nonexponentiality of the fluorescence decay from the anthryl-tagged polymers in pure THF is not strikingly different than for the untagged polymers, but the average lifetime is diminished. The lifetime shortening is very severe as a function of added water from the joint effect of EET and self-quenching.

A more quantitative measure of the effect of coil collapse on EET can be gained by computing $\chi^{[T]}_{SS}$ (Table

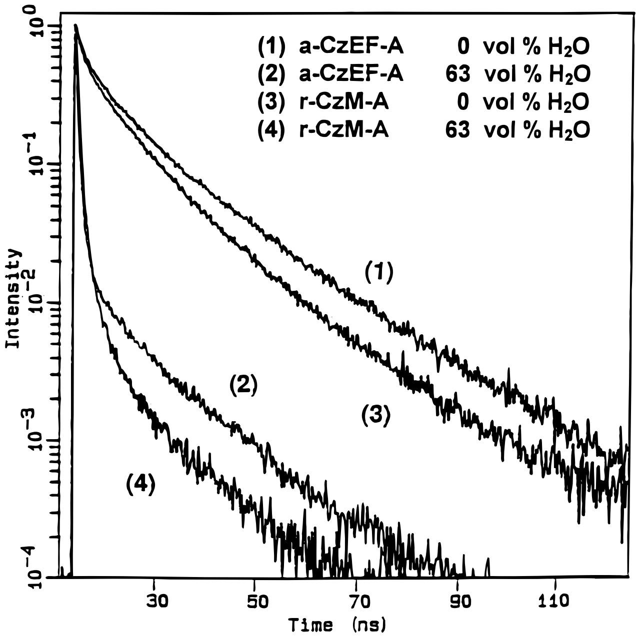

Figure 4. Fluorescence decays for a-CzEF-A(0.7) and r-CzM-(45)-A(0.7) for 0 and 63 vol % water; excitation, 293 nm; emission, 350 nm.

Table 3. Fluorescence Quantum Yields and Efficiency of Energy Transfer for Tagged Polymers as Functions of vol % H$_2$O

vol % H$_2$O	ϕ^{fl}	$\phi_D{}^{a,b}$	$\phi_{anth}{}^{b}$	$\chi_{SS}^{[T]\,c}$	$\chi_\tau^{[T]}$
	Alternating Sample, a-CzEF−A(0.7)				
0	0.43	0.29	0.13	0.53	0.42
13	0.41	0.26	0.13	0.53	0.48
31	0.32	0.082	0.22	0.74	
38					0.84
48	0.297	0.038	0.25	0.86	
58					0.90
63	0.270	0.027	0.23	0.89	
74					0.91
	Random Sample, r-CzM(45)−A(0.7)				
0	0.40	0.26	0.13	0.58	0.60
13	0.37	0.26	0.11	0.44	0.47
31	0.29	0.13	0.15	0.70	
38					0.82
48	0.30	0.050	0.23	0.79	
58					0.94
63	0.21	0.024	0.17	0.81	
74					0.96

[a] ϕ_D is the fluorescence quantum yield of the donor, carbazole. [b] 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. [c] 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 ϕ_D and $\phi_D{}^0$ are large rather than when they are small, since $\chi_{SS}^{[T]}$ is bounded by unity.

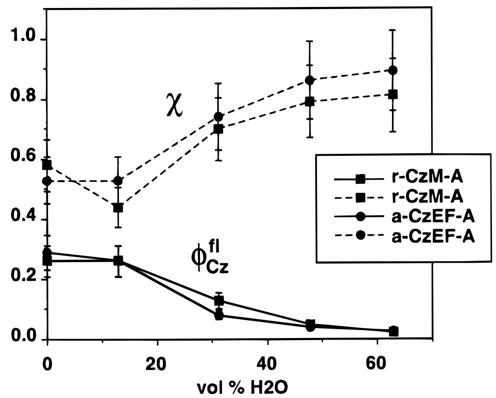

Figure 5. The efficiency of sensitization χ_{SS}, and the quantum yield of carbazole fluorescence, ϕ^{fl}_{Cz}, both as a function of vol % water for a-CzEF-A(0.7) and r-CzM(45)-A(0.7). The total error in the reported values for χ_{SS} and ϕ^{fl}_{Cz} is ±15%.

3, Figure 5) from the change in carbazole quantum yields for tagged and untagged polymers using eq 2. We choose to use this equation rather than eq 1 because the low OD in the anthracene absorption region at the concentrations we use makes determination of ϕ^{fl}_A difficult.[25] The anthracene-tagged random and alternating carbazole polymers behave very similarly if we compare the change in ϕ^{fl}_{Cz} and $\chi_{SS}^{[T]}$ values upon addition of water (Figure 5), and also when comparing the general appearance of the fluorescence decay curves (Figure 4). One difference is an initial decrease in $\chi_{SS}^{[T]}$ with the first addition of water for the random polymer, r-CzM(45)−A(0.7), that is not observed in the alternating polymer, a-CzEF−A(0.7). This is a result of a significant decrease in quantum yield for r-CzM(45) from 0.61 to 0.46 over the 0 to 13 vol % water range (Figure 2). Although the average values of $\chi_{SS}^{[T]}$ for the alternating and random polymers are different, when considering the error bars and the total error in determining $\chi_{SS}^{[T]}$ (see Table 3, footnote *c*), this difference may not be significant. In any case, the general trend of increasing $\chi_{SS}^{[T]}$ with polymer coil collapse is evident. The maximum value of $\chi_{SS}^{[T]}$ is slightly lower for r-CzM(45)−A(0.7) than for a-CzEF−A(0.7), which is consistent with the idea that self-quenching is more significant for a random polymer with the addition of a nonsolvent that collapses the coil.

While it is not possible to ascribe any physical significance to the lifetime components of the decay fits, the zeroth-moment lifetime defined by eq 4 can be used to estimate χ_τ (see eq 5 and data in Table 3). For the alternating polymer a-CzEF−A(0.7) at low water content, $\chi_\tau^{[T]} < \chi_{SS}^{[T]}$, which implies that a fraction of the sensitization of the trap is too fast to be observed in the donor fluorescence.[4] This is consistent with the fact that there is finite fluorescence intensity at 460 nm (anthracene only) that is present at time zero, as discussed above.

Conclusion

In this paper we have demonstrated that the efficiency of EET to a covalently bound trap (anthracene) increases as the polymer coil is collapsed. It is expected that this is a general effect. The efficiency of this process can be quite high, from ca. 50% for an expanded polymer in a good solvent to ca. 90% when the polymer coil is collapsed. However, this efficiency is the net result of a photophysically complex chain of events. In all cases investigated here, the coil collapse was accompanied by an overall decrease in quantum yield and fluorescence lifetime of the donor species for the untagged polymer. Thus in general, the increase of sensitized fluorescence with coil collapse is the net result of two competing effects: EET to the trap and an increase in chromophore−chromophore self-quenching interactions which decrease the excited state lifetime. If chromophores that did not exhibit self-quenching were attached to the polymer, we anticipate that χ would approach unity for a relatively small degree of chain collapse. It seems clear that the geometric requirements for excimer fluorescence are much more stringent than for self-quenching such that the absence of excimer fluorescence cannot be taken as "proof" that intrachromophore interactions are absent.

The fluorescence decay kinetics are very complex in general. Part of this complexity can be understood from the EET process itself, which leads to nonexponential decay of the donor state even for a simple one-dimensional lattice.[13] If one introduces cross-chain EET, the decay curves become even more complicated. Since chain collapse induces additional quenching, any mathematical modeling will have to include this effect,[5] even though the exact nature of the chromophore interaction that leads to self-quenching is not known. Site inhomogeneity can also lead to a distribution of intrinsic lifetimes.

The differences that arise from polymer sequence distributions (e.g. comparing alternating and random polymers) is less than anticipated, although this may be because of the very strong precipitating conditions studied. We are not aware of any polymer coil simulations that directly bear on this question, and we have not yet applied our methods to this problem. While it is clear that computer simulations can capture the qualitative features of EET kinetics in polymers, including self-quenching, it is not easy to see how photophysical data of the type presented herein can be uniquely interpreted in terms of a conformational model.[6]

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Supporting Information Available: Fluorescence decay fitting parameters (a_i, τ_i, see eq 4) for excitation at 293 nm and emission at 350 nm (carbazole) or 460 nm (anthracene) (3 pages). Ordering information is given on any current masthead page.

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