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Studies of the Antenna Effect in Polymer Molecules. 8. Photophysics of Water-Soluble Copolymers of 1-Naphthylmethyl Methacrylate and Acrylic Acid

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ABSTRACT: Intramolecular singlet electronic energy transfer from naphthalene to anthracene end groups in copolymers of acrylic acid with 1-naphthylmethyl methacrylate has been studied. This work represents the first investigation of efficient singlet electronic energy transfer in such polymeric systems in the aqueous phase. Results in the aqueous phase are compared with those for the same polymers in dioxane. The efficiency of the energy-transfer process was greatly enhanced in aqueous media. In dioxane the energy-transfer efficiency was roughly 15%, while the same copolymers in the aqueous phase exhibited energy-transfer efficiencies up to 70%. Fluorescence decay measurements and time-resolved emission spectroscopy provide further details about the time scale of the energy-transfer process. In the aqueous phase the average energy-transfer time was substantially shorter than in dioxane. In addition, energy transfer to anthracene was observed to occur over a period of several tens of nanoseconds following excitation of the naphthalene chromophores.

Introduction

The existence of electronic energy transfer between chromophores attached to a polymer chain has been widely employed in accounting for certain aspects of polymer photophysics. For example, in the study of vinylaromatic polymers, Reid and Soutar[1,2] and Anderson et al.[3] have invoked singlet energy migration as an essential part of a model to describe excimer formation in terms of nearest-neighbor interactions in these systems. Other studies of excimer formation have also discussed the role of electronic energy transfer.[4-8]

The possibility of using polymer molecules bearing suitable donor and acceptor chromophores to produce synthetic antennae capable of efficiently modeling the light-harvesting function of the photosynthetic process has generated considerable interest in the study of energy migration and energy-transfer phenomena in polymer systems. Energy transfer to chemically bound traps in polymers was first described by Fox and Cozzens.[9] More recently Guillet and co-workers have shown that these processes can occur within a single polymer chain.[10-12]

Initially, intramolecular energy transfer was studied in poly(1-naphthyl methacrylate) (PNMA) polymers possessing terminal 9-vinylanthracene traps.[10,12] This work

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Table I
Properties of Acrylic Acid Copolymers with 2-Naphthylmethyl Methacrylate

	polymer composition, mol %				
polymer sample	acrylic acid	1-NMMA	anthracene	M_n ($\times 10^{-3}$)	anthracene units per chain
1	84	16[a]	0	260[b]	0
2	93	6.9	0.20	41[b]	0.98
3	77.5	22[a]	0.54	18[c]	0.90
4	92	7.6	0.25	31[c]	0.91

[a] Copolymer insoluble in aqueous alkali. [b] By membrane osmometry. [c] By vapor pressure osmometry.

was extended by Holden and Guillet[13] to show the efficiency of singlet electronic energy transfer from poly(1-naphthylmethyl methacrylate) (PNMMA) and poly(2-(1-naphthyl)ethyl methacrylate) (PNEMA) to anthracene end groups or copolymerized 9-anthrylmethyl methacrylate (AMMA). Singlet energy transfer efficiencies as high as 30% were measured in fluid solution, while in a rigid matrix of poly(methyl methacrylate), efficiencies up to 43% were obtained, even though anthracene constituted only 0.5 mol % of the polymer.

The present studies on water-soluble copolymers of acrylic acid and NMMA were undertaken because of the general lack of knowledge concerning the photophysical behavior of such systems in aqueous media. The possible practical advantages to be gained by a man-made light-harvesting process employing water-soluble polymeric antennae provided further motivation.

Experimental Section

The preparations of the 1-naphthylmethyl methacrylate (NMMA) monomer and 9-bromomethylanthracene, used as a chain transfer agent, have been described previously.[13,14]

Commercial acrylic acid (BDH, stabilized with 0.5% *p*-methoxyphenol) was distilled in the dark at reduced pressure (bp 40 °C, 2.0 kPa) from a small amount of a suitable copper salt such as $CuCl_2$. This distillation was performed immediately prior to polymerization.[15]

Polymers were prepared by free-radical polymerization in purified, degassed dioxane at 70 °C using decanoyl peroxide as the initiator species. Labeling of the polymer chains with anthracene was accomplished by using 9-bromomethylanthracene as a chain transfer agent. The mechanism for this process has already been described.[13] The polymers were purified by multiple precipitation from dioxane into hexane and dried in vacuo over P_2O_5 for 24 h.

The composition of the copolymers was determined by UV spectroscopy (Cary 14 UV-visible spectrophotometer) by using extinction coefficients determined for the PNMMA homopolymer and 9-methylanthracene for analysis of naphthalene and anthracene content, respectively. The details of the copolymers prepared are summarized in Table I.

For fluorescence measurements dioxane was purified in a series of stages. Dioxane (Caledon Laboratories, ACS reagent grade) was initially refluxed under nitrogen for 12 h in the presence of 10% v/v of a 1 N HCl solution. The dioxane was then treated with KOH, dried for 12 h over Na, and finally distilled under nitrogen. All solvents used for fluorescence studies were free from absorbing or emitting impurities.

Steady-state fluorescence spectra of polymer solutions were recorded on a Hitachi-Perkin-Elmer MPF-2A spectrofluorimeter. The reported spectra have been corrected for the wavelength dependence of the detector response by comparison of spectra for quinine sulfate in ethanol and 1 M H_2SO_4 with corrected literature spectra.[16] The method of evaluating the efficiency of electronic energy transfer from naphthalene to anthracene was described by Holden and Guillet.[13] For the present study the unlabeled acrylic acid–NMMA copolymer served as a model for the naphthalene emission.

Transient fluorescence results were obtained by single photon counting, as previously described.[10,11,17]

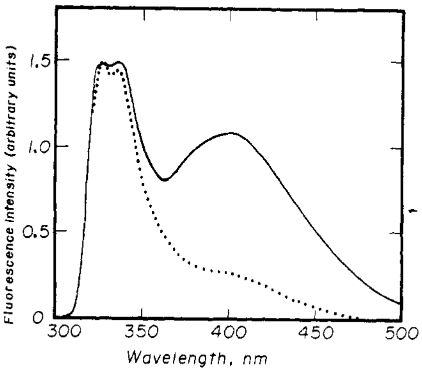


Figure 1. Steady-state fluorescence emission from (···) copolymer 1 (84% AA, 16% NMMA) and (—) PNMMA in dioxane; λ_{ex} = 280 nm.

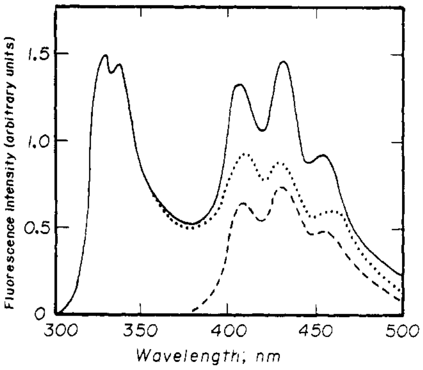


Figure 2. Steady-state fluorescence emission from (—) copolymer 3 (78% AA, 22% NMMA) and (···) copolymer 4 (92% AA, 8% NMMA) in dioxane at 25 °C: (···) copolymer 4, λ_{ex} = 280 nm; (- - -) copolymer 4, λ_{ex} = 365 nm.

Results and Discussion

The dramatic reduction in molecular weight of the labeled copolymers prepared by chain transfer to bromomethylanthracene is evident from a comparison of the molecular weight of the unterminated copolymer 1 with those measured for the anthracene-terminated copolymers (Table I). The number average of anthracene units per copolymer chain was approximately 1 in all cases. In the absence of chain branching, which would result in more than two anthracene units per polymer chain, the mechanism of incorporation of anthracene traps[13] theoretically permits the inclusion of 0, 1, or 2 anthracene units per polymer chain. Possibly a small fraction of unlabeled polymer chains was present in the acrylic acid–NMMA copolymers studied. Assuming that the rest of the polymer chains were monolabeled allowed an upper limit of ~90% to be predicted for the maximum efficiency attainable by an exclusively intramolecular singlet energy transfer process in these polymers.

Steady-State Fluorescence Results. The steady-state fluorescence spectra of the NMMA homopolymer and copolymer 1 in dioxane are shown in Figure 1. Dilution of the NMMA units with acrylic acid comonomer substantially reduced the extent of excimer emission at 400 nm as compared with that for pure PNMMA. The emission spectrum of copolymer 1 was a valuable model for the naphthalene emission from the anthracene-terminated copolymers. This model was necessary for evaluating the efficiency of singlet energy transfer in these systems. Since the anthracene emission was negligible from 350 to 370 nm (see Figure 2), all copolymer emission in this region was assigned to naphthalene monomer and excimer species. This principle was used to reconstruct

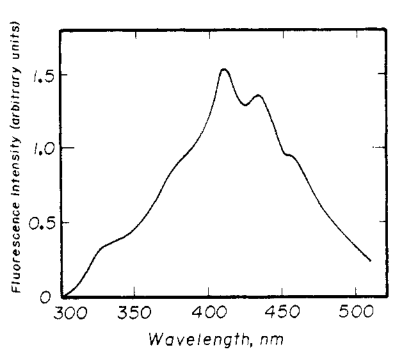


Figure 3. Steady-state fluorescence emission from copolymer 2 (93% AA, 7% NMMA) in dilute NaOH (pH 12).

the symmetrical excimer band that lies beneath the anthracene emission.

Several studies have demonstrated an increase in the relative extent of excimer fluorescence I_D/I_M with increasing molecular weight.[19-21] Since the anthracene-terminated copolymers had much lower molecular weights than the unterminated copolymer, they would tend to have a smaller relative amount of excimer fluorescence in the absence of the anthracene traps. In addition, copolymers 2 and 4 also had substantially lower NMMA content than the unterminated copolymer used as a model for the naphthalene emission. Therefore, the procedure used to approximate the naphthalene excimer emission probably tended to underestimate the efficiency of energy transfer to anthracene.

Figure 2 shows the fluorescence spectra of the anthracene-capped copolymers 3 and 4 in dioxane on excitation of the naphthalene chromophores at 280 nm. On the basis of the naphthalene and anthracene content in these copolymers and the appropriate extinction coefficients, it was determined that less than 0.12% of the incident radiation at 280 nm was directly absorbed by anthracene chromophores located at chain ends. Essentially all of the light was absorbed by naphthalene units. The observed emission spectra, however, show substantial anthracene fluorescence in the 380–480-nm region, indicating that naphthalene to anthracene transfer has occurred. This copolymer emission has been compared with the anthracene fluorescence observed on direct excitation of the terminal anthracene units at 365 nm, as also shown in Figure 2.

Slight differences in the positions and relative intensities of the vibrational maxima for anthracene emission from the copolymers are attributed to the minor amount of naphthalene excimer emission hidden under the anthracene fluorescence on excitation at 280 nm. For instance, in the steady-state spectrum of copolymer 4 the (0,0) vibrational band of anthracene actually appears to be more intense than the (0,1) band.

It is evident in Figure 2 that the increased density of naphthalene donor chromophores in copolymer 3 enhanced the energy-transfer efficiency in dioxane, resulting in a greater relative fluorescence yield from the anthracene traps. The emission spectrum of copolymer 2 in dioxane was very similar to that of copolymer 4, with comparable relative intensities of naphthalene and anthracene fluorescence.

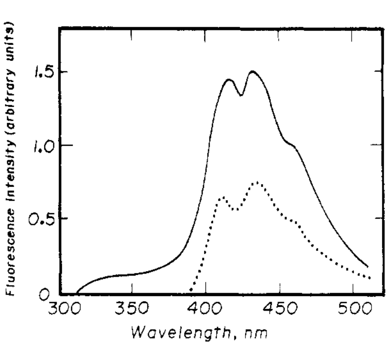


Figure 4. Steady-state fluorescence emission from copolymer 4 in dilute NaOH solution (pH 12): (—) λ_{ex} = 280 nm; (···) λ_{ex} = 365 nm.

Table II
Quantum Efficiencies χ of Energy Transfer to Anthracene in Anthracene-Terminated Copolymers of Acrylic Acid with 1-Naphthylmethyl Methacrylate

polymer sample	% anthracene	solvent	ϕ_N	ϕ_A	χ, %
2	0.2	dioxane	0.11	0.88	13.6
2	0.2	aq NaOH (pH 12.0)	0.073	0.70	43.5
3	0.54	dioxane	0.11	0.88	17.4
4	0.25	dioxane	0.11	0.88	12.1
4	0.25	aq NaOH (pH 12.0)	0.073	0.70	69.7

A substantial increase in the efficiency of energy transfer from naphthalene to anthracene was observed when solutions of copolymers 2 and 4 were prepared in aqueous NaOH. The steady-state emission spectra of these solutions are illustrated in Figures 3 and 4, respectively. The important feature of these spectra was the predominance of the anthracene fluorescence. In each spectrum, small amounts of naphthalene monomer and excimer emission were observed, but the major contribution to the overall fluorescence was from anthracene. This is particularly evident in Figure 4, which shows the emission from copolymer 4 on excitation of naphthalene as well as direct excitation of the anthracene. The appearance of each spectrum is very similar. A substantial loss of resolution of the anthracene vibrational structure occurred in the aqueous phase, as compared with dioxane solutions.

The energy-transfer efficiency χ is given by the relation

$$\chi/(1-\chi) = \phi_N I_A/\phi_A I_N \qquad (1)$$

where ϕ_A and ϕ_N are the fluorescence quantum yields of chemically bound anthracene on direct excitation and of naphthalene evaluated from the copolymer without terminal anthracene units. I_A and I_N are the relative integrated emission intensities of the same groups estimated from analysis of curves such as those shown in Figures 2–4. χ in this case represents the efficiency with which photon energy absorbed by naphthalene is transferred to anthracene, and its values are summarized for the polymers studied here in Table II. In dioxane solution, the three anthracene-terminated copolymers show similar, relatively low efficiencies ranging from 12 to 17%, consistent with their low concentrations of naphthalene-containing comonomer (7–22%).

However, the most important observation is the 3- to 6-fold increase in χ when these polymers were dissolved in dilute (0.02 M) aqueous NaOH. In sample 4 the efficiency approached 70%, even though the copolymer contained only 7.6% of copolymerized naphthalene units and 0.25% AMMA. These measurements were made at pH 12.0. Increasing the pH of these polyelectrolyte systems had no effect on either the qualitative appearance of the emission spectrum or the efficiency of naphthalene to anthracene energy transfer. As the pH was decreased, the copolymers precipitated from solution, and it was not possible to study energy-transfer efficiency in acidic solutions. Dilution of the aqueous alkaline solutions of copolymers 2 and 4 to naphthalene chromophore concentrations of less than 10^{-6} M produced no detectable changes in either the observed emission spectra or the singlet en-

Table III
Decay Parameters of PNMMA[a] Monomer and Excimer[b]

species	emission, nm	solvent	τ_1, ns	τ_2, ns
fitting function:	$I(t) = A_1 \exp(-t/\tau_2) + A_2 \exp(-t/\tau_2)$			
monomer[c]	345	toluene	7.0	40
monomer	345	dioxane	7.5	47
excimer[c]	440	toluene	3.0	63
excimer	440	dioxane	5.0	64

[a] Homopolymer $M_n \cong 225\,000$. [b] Emission, $\lambda_{ex} = 280$ nm at 25.0 °C. [c] Results from ref 12.

ergy transfer efficiencies. This was taken as evidence that the energy-transfer process is substantially intramolecular.

Thus the aqueous emission spectra, as compared with those of the copolymers in dioxane, are characterized by broadening of the anthracene emission lines, an increase in the excimer emission of naphthalene relative to its monomer emission, and a dramatic increase in the efficiency of energy transfer to anthracene.

Transient Fluorescence Results. Single photon counting was used to further probe the singlet energy transfer process observed in the steady-state measurements by fluorescence decay measurements. Decay times measured for PNMMA in dioxane are given in Table III along with comparable values reported for PNMMA in toluene by Holden and Guillet.[13] Holden et al.[18] have suggested that the long-lived component (τ_2) of the monomer emission in PNMMA should be attributed to excited singlet naphthalene units unable to form excimer during their excited-state lifetime.

Fluorescence decay parameters determined for the acrylic acid–NMMA copolymers are summarized in Table IV. The excimer decay times determined in dioxane were similar in each copolymer and in good agreement with the PNMMA data reported in Table III. On the basis of the fluorescence decay measurements obtained for PNMMA and copolymer 1, a triexponential decay was expected to provide the simplest physical representation of the emission from the anthracene-terminated copolymers at 440 nm. Because the anthracene fluorescence overlaps the naphthalene excimer emission, a difference of exponentials was required to account for the excimer species as well as an additional intermediate component corresponding to the fluorescence decay time of the anthracene units.

The anthracene decay time was much shorter in aqueous NaOH than in dioxane. The reduced excimer decay time observed in the aqueous phase is a real effect, which is also observed in studies of PNMMA in mixed-solvent systems.[13]

An estimate of the average energy-transfer time was made from the difference $\Delta\tau$ between the average decay time of anthracene traps excited by energy transfer from naphthalene donors and that of anthracene units on direct excitation. The values of $\Delta\tau$ obtained for the acrylic acid–NMMA copolymers in dioxane and aqueous NaOH are given in Table V. The decay times measured on direct excitation of chemically bound anthracene trap (10–11 ns) were very similar to corresponding values for 9-methylanthracene in solution. The average energy-transfer time for copolymer 4 in dioxane was 11.3 ns, while for the same polymer in aqueous NaOH (pH 12.0) this value was reduced to 6.4 ns. Apparently, a more rapid average energy-transfer process occurs in aqueous solution.

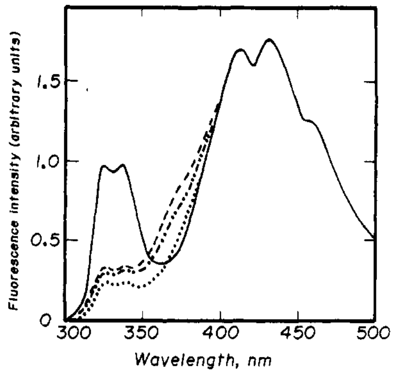


Figure 5. Time-resolved fluorescence emission for copolymer 4 in dilute NaOH solution (pH 12); $\lambda_{ex} \sim 280$ nm. Lower and upper time limits from maximum of exciting pulse are (—) 0–2.5 ns; (···) 26.6–32.6 ns; (- - -) 101–106 ns; (-··-) 260–269 ns. Spectra are normalized to peak of anthracene emission.

Time-Resolved Emission Spectra. A series of time-resolved emission spectra for copolymer 4 in aqueous NaOH solution is shown in Figure 5. Several spectra were recorded over a range of more than 250 ns following the excitation pulse. These spectra revealed that substantial anthracene emission was present even at very short time intervals following excitation of the naphthalene chromophores. Immediately following excitation, strong naphthalene monomer fluorescence was present in the time-resolved spectrum, but as the time interval was increased, the observed emission contained much larger relative contributions from anthracene fluorescence. Approximately 30 ns after the excitation pulse, anthracene emission predominated, with naphthalene monomer and excimer species providing small contributions to the total fluorescence spectrum. The ratio of anthracene to naphthalene emission was at a maximum from about 20 to 70 ns following naphthalene excitation. Time-resolved emission spectra recorded at much longer time intervals revealed that the predominance of anthracene fluorescence continued for several tens of nanoseconds. Even in spectra recorded at 205 and 265 ns following naphthalene excitation, anthracene fluorescence dominated the emission, although at these longer time intervals the ratio of fluorescence intensities of anthracene to both naphthalene "monomer" and excimer was observed to decrease gradually with time. This interesting observation suggests that

Table IV
Decay Parameters of Acrylic Acid–NMMA Copolymers[a,b]

polymer sample	% naphthalene	% anthracene	species	λ_{em}, nm	χ	solvent	τ_1, ns	τ_2, ns	τ_3, ns	χ_R^2
1	16	0	monomer	345	0	dioxane	9.0	42.2		1.2
			excimer	440	0	dioxane	9.2	60.2		1.7
3	22	0.54	monomer	345	17.4	dioxane	9.8	41.2		1.1
			excimer + anthracene	440	17.4	dioxane	1.6	21.0	62.1	1.0
4	7.6	0.25	monomer	345	12.1	dioxane	11.1	35.8		1.5
			excimer + anthracene	440	12.1	dioxane	2.3	21.1	62.7	2.4
			monomer	345	69.7	aq NaOH	4.4	23.2		3.6
			excimer + anthracene	440	69.7	aq NaOH	0.66	14.6	41.5	1.0

[a] $\lambda_{ex} = 280$ nm at 25.0 °C. [b] Fitting function: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ (monomer); $I(t) = -A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$ (excimer + anthracene).

Table V
Variation of Anthracene Fluorescence Decay Time on Direct Excitation at 366 nm and on Excitation of the Naphthalene Chromophore at 280 nm[a]

polymer sample	solvent	τ_{anth}, ns[b] $\lambda_{\text{ex}} = 366$ nm	$\lambda_{\text{ex}} = 280$ nm	$\Delta\tau$, ns
3	dioxane	11.4	21.0	9.6
4	dioxane	9.8	21.1	11.3
4	aq NaOH (pH 12.0)	8.2	14.6	6.4

[a] $\lambda_{\text{em}} = 440$ nm at 25.0 °C. [b] Anthracene decay times evaluated with triexponential fitting function (see Table IV).

some of the long-lived naphthalene monomer emission observed at these long times after the initiating pulse results from the dissociation of excimer traps located sufficiently far away from the anthracene trap so that the excitation is not immediately quenched.

The high efficiency of energy transfer of these acrylic acid copolymers in dilute aqueous solution is quite surprising. Single-step energy transfer from naphthalene to anthracene has been shown to occur by dipole–dipole interactions and obeys the theory developed by Förster.[23] The rate constant $k_{\text{D}^* \to \text{A}}$ for resonance energy transfer between isolated donor and acceptor pairs is given by

$$k_{\text{D}^* \to \text{A}} = \frac{8.8 \times 10^{-25} \kappa^2 \phi_{\text{D}}}{n^4 \tau_{\text{D}} R^6} \int_0^\infty F_{\text{D}}(\nu) \epsilon_{\text{A}}(\nu) \frac{\mathrm{d}\nu}{\nu^4} \tag{2}$$

where $k_{\text{D}^* \to \text{A}}$ is the rate constant for energy transfer, R is the donor–acceptor separation, κ^2 is an orientation factor, usually assumed to be $^2/_3$ for a random distribution of D and A, ϕ_{D} is the quantum yield for emission from the donor, n is the refractive index of the solvent, τ_{D} is the mean lifetime of the donor excited state, $F_{\text{D}}(\nu)$ is the normalized spectral distribution of donor emission, and $\epsilon_{\text{A}}(\nu)$ is the molar extinction coefficient of the acceptor as a function of ν. If one defines a critical distance R_0 as that distance between the donor and the acceptor at which energy transfer occurs with 50% probability, it follows that

$$R_0^6 = \frac{8.8 \times 10^{-25} \kappa^2 \phi_{\text{D}}}{n^4} \int_0^\infty F_{\text{D}}(\nu) \epsilon_{\text{A}}(\nu) \frac{\mathrm{d}\nu}{\nu^4} \tag{3}$$

For fully allowed transitions, that is, with $\epsilon_{\max}$ of the order of 10^4 in the acceptor and with significant spectral overlap and donor emission quantum yields of 0.1–1, R_0 values of 5–10 nm are predicted and were experimentally confirmed by Bowen and Livingston.[24] Efficient transfer only occurs when there is significant overlap between donor emission and acceptor absorption spectra, the same requirement as for trivial transfer, i.e., donor emission followed by acceptor absorption.

The probability of energy transfer derived from this relation is shown as a function of interchromophore distance in Figure 6. It is clear from this that in order to achieve efficiencies of the order of 70% most of the donor chromophores must lie within a distance less than R_0 of the trap, estimated to be about 24 Å for naphthalene and anthracene. In a copolymer containing only 7% NMMA groups, energy migration is unlikely to occur along the chain, so the only reasonable explanation for the high efficiencies observed must be that the hydrophobic naphthalene and anthracene groups are clustered in such a way as to bring the majority of them within a spherical region of approximately 24-Å radius.

Poly(acrylic acid), when dissolved in water at high pH, usually assumes an extended (rod-like) conformation due to the mutual repulsion of the negatively charged carboxyl ions. However, such an extended structure can hardly explain the clustering of the aromatic groups in the acrylic acid–NMMA copolymer. It is therefore proposed that these copolymers in dilute alkaline solution adopt a "hypercoiled" structure, somewhat as shown in Figure 7, in which the hydrophobic aromatic groups form the interior of the coil and the carboxyl groups, with their counterions nearby, form an outer "shell".

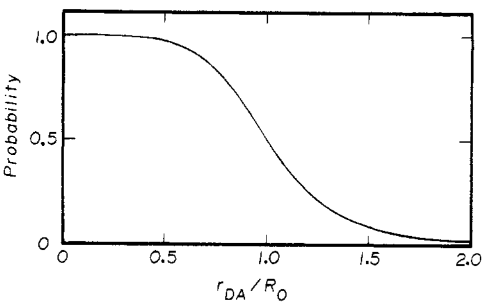


Figure 6. Probability of single-step Förster energy transfer as a function of interchromophore distance γ_{DA}.

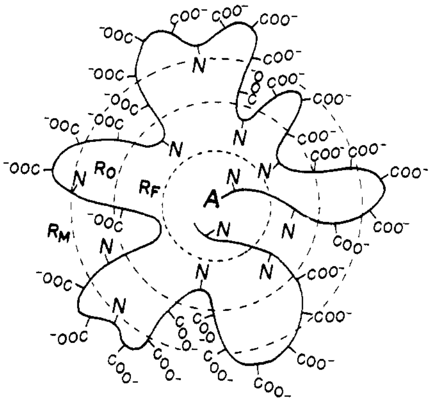
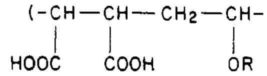


Figure 7. Proposed hypercoiled structure of anthracene end-trapped copolymers of acrylic acid and NMMA in dilute alkaline solution showing Förster radii for various energy-transfer processes.

Hypercoiling has been observed in other polymers containing large hydrophobic groups and carboxyl groups. For example, Dubin and Strauss[25-27] studied aqueous solutions of polyacids containing hydrophobic aliphatic side chains of various lengths and then used the term hypercoiled to describe the phenomena observed in these systems. A series of alternating copolymers of maleic anhydride with alkyl vinyl ethers was prepared and hydrolyzed to the diacid. These polyelectrolytes did indeed assume coil



$$\left(-\underset{\text{HOOC}}{\text{CH}}-\underset{\text{COOH}}{\text{CH}}-\text{CH}_2-\underset{\text{OR}}{\text{CH}}-\right)_n$$

$\text{R} = \text{C}_n\text{H}_{2n+1}$

$n = 1, 2, 4, 6, 8,$ and 10

dimensions that reflected a balance between cohesive hydrophobic interactions of apolar side chains and electrostatic repulsive forces of charged carboxyl groups. At low degrees of dissociation of the acid units the copolymers with alkyl side chains containing four or more methylene groups exhibited dimensions in the aqueous system lower than the values measured under θ conditions. The octyl and decyl copolymers remained hypercoiled, even at very high charge density, their conformation being essentially insensitive to changes in pH of the solution. Similar effects have been observed in polypeptides and ascribed to the occurrence of hydrophobic bonding.

This model explains the photophysical evidence quite well. From the time-resolved emission spectra in Figure

5 it was evident that considerable energy transfer occurred from excited naphthalene chromophores to the anthracene acceptor species within a time period of less than 2 ns. This energy transfer probably originates from excited naphthalene chromophores close enough (i.e., $<R_0$) to an anthracene acceptor to be rapidly quenched by a single-step Förster-transfer process. The persistence of anthracene emission at times much longer than the normal anthracene lifetime was attributed to anthracene traps excited either by direct single-step transfer from naphthalenes outside R_0 or by a migration process between naphthalenes clustered around the anthracene trap, a mechanism similar to that proposed by Guillet[29] to explain energy migration in antenna polymers with regularly repeating donor groups.

A theory may be derived from the assumption that on the short time scale available during the lifetime of the singlet state in typical aromatic chromophores, i.e., $\tau < 100$ ns, collisional energy transfer is a relatively minor factor. Energy migration and transfer in such systems are therefore assumed to be primarily due to long-range Förster transfer by the dipole–dipole mechanism outlined previously. Combining eq 2 with eq 3, one obtains for the rate of exchange between donor and acceptor in the chain

$$k_{\mathrm{DA}} = (1/\tau_{\mathrm{D}})(R_0/R)^6 \tag{4}$$

where R is now the distance between the donor and acceptor chromophores in the polymer. If we visualize the migration process as occurring between donor units on the chain but not necessarily adjacent units, the rate constant k_{DD} for the migration step is

$$k_{\mathrm{DD}} = (1/\tau_{\mathrm{D}})(R_0'/R_{\mathrm{D}})^6 \tag{5}$$

where R_0' is the Förster radius for transfer between identical donor chromophores and R_{D} is the distance between them. The number of hops n is given by

$$n = k_{\mathrm{DD}}\tau_{\mathrm{D}} = (R_0'/R_{\mathrm{D}})^6 \tag{6}$$

where R_{D} is now the average distance between donor chromophores. In the absence of any trap in the polymer, this hopping will follow a random walk among donor chromophores until the energy is deactivated by other processes. A similar process has been described for energy migration in solid solutions of donor and acceptor chromophores in a polystyrene matrix.[28] The average displacement of the excitation in this one-dimensional random-hopping mechanism will be given by

$$l = n^{1/2}R_{\mathrm{D}} \tag{7}$$

However, in the presence of a singlet energy trap, the lifetime of the excitation will be reduced and the number of hops as well as the distance diffused by energy migration will be reduced. The probability of an energy hop from donor to donor vs. one directly to the acceptor trap is given by the ratio of the two rate constants:

$$k_{\mathrm{DD}}/k_{\mathrm{DA}} = (R_0'/R_{\mathrm{D}})^6/(R_0/R)^6 \tag{8}$$

Since R_0 and R_0' can be calculated from spectroscopic data, if R_{D} could be estimated, this equation would permit an evaluation of the relative sphere of influence of the two types of energy transfer.

The anthracene trap, as shown in Figure 7, can be considered to be surrounded by three spherical regions of space defined by radii R_{F}, R_{M}, and R_0. Excited naphthalene chromophores lying in the internal region defined by R_{F} will be quenched by single-step Förster transfer to the trap. Those lying between R_{F} and R_{M} will undergo at least one migration step before being quenched, while those outside R_{M} will be too far removed for trapping, even though they may undergo a considerable number of migration steps. The region between R_0 and R_{M} represents the extra space contributed for the trapping process by the energy-migration mechanism.

The relative values of these radii could be assessed if one knew the average distance of separation of the donor chromophores R_{D} in the core of the proposed "macromolecular micelle".

The photophysical evidence of a significant increase in excimer fluorescence from all of these polymers in dilute aqueous solution suggests that at least some of the naphthalene groups in the core are within 3 Å of each other. This is the distance required to form the parallel plane geometry now recognized as an essential feature of the excimer configuration. The best estimates for R_0 and R_0' are about 24 and 7 Å for the Förster radii for naphthalene–anthracene and naphthalene–naphthalene transfer, respectively.[16] If the naphthalene groups in the core were as close as 4 Å apart on average (i.e., $R_{\mathrm{D}} = 4$ Å), then the value of R_{F} can be calculated from eq 8 to be about 14 Å.

From Figure 7 it can be seen that although a substantial number of naphthalene to naphthalene transfers may occur at distances well within the Förster radius, they will not be expected to contribute to efficiency of energy collection, since the energy would be transferred to anthracene in any case, as long as the radius was less than the Förster radius. The only increase in efficiency of energy collection due to the energy-migration process will occur for naphthalene chromophores outside the Förster radius R_0, where migration will occur at a rate corresponding to that in the absence of the anthracene trap. The number of migration steps can be calculated from (6). Substituting the value of the natural lifetime of the naphthalene chromophores would give an average number of hops of 29 and a migration distance l of 21 Å.

The contribution of this energy migration in increasing the efficiency of photon energy collection in these polymers is difficult to assess without more detailed knowledge of the actual distribution of donor chromophores in the hydrophobic core. For a homogeneous distribution of chromophores in the spherical region surrounding the trap one can calculate that for the particular example given above the additional contribution to the radius of trapping would be about 9 Å outside the Förster radius R_0. Although this represents a substantial increase in the total volume of the sphere of action, it is not known how many additional donor chromophores might be located in this region.

Conclusions

In this paper the synthesis and photophysics of some unusual water-soluble polymers containing hydrophobic naphthalene and anthracene groups have been described. While energy trapping and migration appear to be of minor importance for these compositions in solution in organic solvents, a dramatic increase is observed when the polymers are dissolved in a dilute aqueous base. It is proposed that under these conditions the polymers hypercoil to form an interior region containing relatively high concentrations of the hydrophobic aromatic groups surrounded by an outer region of negatively charged carboxyl groups, forming essentially a macromolecular micelle. The increased trapping efficiency has been attributed to the greater proximity between donors and the trap site in the core of the proposed structure, promoting trapping by both single-step Förster transfer from donor to acceptor and migration among donor chromophores. Although the relative contributions of these two mechanisms cannot be quantified on the basis of the present experiments, the synthesis and use of an antenna polymer system in an aqueous solution have been demonstrated. Since water is a likely component in terrestrial solar devices designed to produce storable fuels, these results have considerable importance in the development of practical solar photochemical processes.

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Registry No. PNMMA (homopolymer), 29320-20-5; 9-(bromomethyl)anthracene, 2417-77-8; (NMMA)·(acrylic acid) (copolymer), 98821-46-6.

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Activation Parameters and Color Effects in the Thermal Dehydrochlorination of Chemically Pretreated Poly(vinyl chloride)

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ABSTRACT: The thermal dehydrochlorination rate of poly(vinyl chloride), measured under nitrogen at temperatures ranging from 170 to 200 °C, has been reduced significantly by chemical pretreatment of the polymer with a mixture of 1-dodecanethiol, di-*n*-butyltin bis(*n*-dodecyl mercaptide), and di-*n*-butyltin dichloride in *o*-dichlorobenzene at 180 °C. Arrhenius plots for the dehydrochlorination, derived from the rates at 0.10% conversion, reveal that the rate reductions caused by pretreatment are associated with decreases of the preexponential factor, *A*, rather than with increases in the energy of activation. The reductions in *A* can be related to decreases in the number of thermally labile starting sites for the polyene growth reaction, owing to the deactivation of these structures during the pretreatment process. Activation energies (*E*'s) for pretreated specimens are in the range 21-24 kcal/mol, as compared to a value of 30 kcal/mol for the virgin polymer. These data are shown to be inconsistent with a chain reaction mechanism for which the experimental value of *E* is equivalent to the energy of activation for the polyene growth reaction (i.e., for chain propagation). However, the *E* diminutions caused by pretreatment can be related to increased fractional contributions by allylic chlorides to the rate-determining process. At a given extent of dehydrochlorination, reached at a given temperature, the chemically modified polymers are more lightly colored than those that have not been pretreated. This result is ascribed to a decreasing (polyene growth):(polyene shortening) rate ratio with decreasing HCl concentration, and some specific reactions are suggested in order to account for this effect.

In a previous study of the thermal dehydrochlorination of poly(vinyl chloride) (PVC),[1] the reaction was examined in the presence of substances possessing weak carbon-hydrogen bonds, which make highly effective free-radical scavengers. The process carried out in the presence of excess triphenylmethane, found to be the most effective scavenger, was reduced to a constant rate, about 30% of the uninhibited rate at 194 °C. It was argued that determination of the Arrhenius parameters of the so-called maximally inhibited reaction, proposed to be a molecular elimination, would allow the identification of the rate-determining step. Consequently, the latter was identified as the formation of isolated carbon-carbon double bonds along the backbone with the concomitant evolution of

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