Studies of the Antenna Effect in Polymer Molecules. 26. Preparation, Photophysics, and Photochemical Studies of Poly[2-(6-sulfo-2-naphthoxy)ethyl methacrylate sodium salt-*co*-lauryl methacrylate]

D. M. Gravett and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1

Received March 25, 1994®

ABSTRACT: The radical copolymerization of 2-(6-sulfo-2-naphthoxy)ethyl methacrylate sodium salt and lauryl methacrylate led to a water-soluble polymer that contained both hydrophobic and hydrophilic components. Studies showed that naphthalene excimer formation was dependent on both solvent and ionic strength, indicating that excimer formation occurred predominantly from across chain contacts. The hydrophilic–hydrophobic nature of the polymer gives it the ability to solubilize hydrophobic molecules such as perylene. Steady-state fluorescence depolarization and emission studies demonstrated that energy migration among the naphthalene sulfonate groups occurs as well as energy transfer from the naphthalene sulfonate groups to the solubilized perylene. Photochemical studies showed that the polymer sensitizes the photooxidation of perylene using both monochromatic and solar-simulated light.

Introduction

Numerous amphiphilic polyelectrolytes containing hydrophobic and hydrophilic components have been synthesized and their photophysical properties studied.[1] The presence of both hydrophobic and hydrophilic components results in a balancing of the attractive "hydrophobic bonding" interactions between the hydrophobic groups and of the electrostatic repulsive forces between the ionic hydrophilic groups. This may result in the polymer adopting a pseudomicellular conformation in which the hydrophobic groups form domains which are surrounded by the ionic hydrophilic groups. Such a conformation gives the polymer the ability to solubilize various organic molecules in these hydrophobic domains.

Careful selection of the polymer constituents results in polymers which can exhibit the phenomenon of energy migration as well as the ability to transfer energy to suitably solubilized probes. These types of polymers, called "antenna" or "photon-harvesting" polymers, have been reviewed by Guillet[2] and by Webber.[3] Because of the unique properties of antenna polymers, they are capable of sensitizing certain chemical reactions such as the photooxidation of numerous polynuclear aromatics,[4–6] the Norrish II cleavage of ketones,[7] and the dechlorination of polychlorinated biphenyls (PCBs).[8,9]

In all of the previous antenna polymers, the hydrophobic components have been the light-absorbing units in the system and are thus in the hydrophobic domains. As such, they are in close contact with each other, which often results in extensive excimer formation. The excimers can then compete with the solubilized probes as energy traps. If, however, the chromophores were to be part of the hydrophilic components and another group was used as the hydrophobic component, the chromophores should be kept apart by electrostatic repulsive forces and thus the extent of excimer formation should be reduced. This would represent a novel approach to the synthesis of antenna polymers.

This paper reports the synthesis poly[2-(6-sulfo-2-naphthoxy)ethyl methacrylate sodium salt-*co*-lauryl methacrylate] (NS–LM) in which the donor naphthalene groups are associated with the hydrophilic monomer units. Some photophysical properties, solubilizing abilities, and photocatalytic properties of this polymer are also reported.

Experimental Section

Lauryl methacrylate (Aldrich) and 2-hydroxyethyl methacrylate (Aldrich) were purified by vacuum distillation. Perylene (Aldrich, 99.9%), *p*-toluenesulfonyl chloride (BDH), lithium bromide (Fisher), dimethyl sulfoxide (DMSO; Anachem), dimethylformamide (DMF; BDH), pyridine (BDH), methanol (spectrograde; Caledon), and acetonitrile (HPLC grade; Aldrich) were used without further purification. Solvents were dried by storing over molecular sieves (4A, 8–12 mesh; Aldrich). 6-Hydroxy-2-naphthalene sulfonate sodium salt was prepared according to the method given by Fierz–David and Blangey.[10] 2,2′-Azobis(isobutryonitrile) (AIBN; Kodak) was recrystallized from spectrograde methanol.

All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. The ionic strength and pH of the solutions were adjusted using stock solutions of NaCl, HCl, and NaCl.

2-Tosylethyl methacrylate. The tosylation of 2-hydroxyethyl methacrylate was based on the reaction of Dykstra and Smith.[11] *p*-Toluenesulfonyl chloride (32.28 g) was added to a solution of 20 g of 2-hydroxyethyl methacrylate in 52 mL of dry pyridine at 0 °C. The reaction mixture was stirred for 6 h while maintaining the temperature in the 0–7 °C range. The reaction mixture was neutralized (litmus) with 2.5 M HCl. The resultant oil layer was taken up in CCl_4. The CCl_4 layer was washed with H_2O, dried over $MgSO_4$, and filtered, and then the solvent was removed under vacuum. The product was used without further purification.

^{1}H-NMR ($CDCl_3$): δ 7.8 (d, 2H, ArH), 7.35 (d, 2H, ArH), 6.05 (s, 1H, CH_2=C–), 5.58 (s, 1H, CH_2=C–), 4.2–4.4 (m, 4H, $-OCH_2CH_2O-$), 2.45 (s, 3H, $ArCH_3$), 1.80 (s, 3H, C=CH_3).

2-Bromoethyl methacrylate. 2-Tosylethyl methacrylate (20 g) was added to 16.70 g of LiBr in 50 mL of acetone. (Hydroxymethyl)quinone (0.1 g) was added as an inhibitor. The reaction was kept at 60 °C for 24 h. The white crystalline precipitate that formed was removed by filtration, after which the actone was removed under vacuum. The resultant solution was extracted with CH_2Cl_2/H_2O. The CH_2Cl_2 portion was dried over $MgSO_4$ and filtered, and then the solvent was removed under vacuum. The resultant product was used without further purification.

® Abstract published in *Advance ACS Abstracts,* November 15, 1994.

^{1}H-NMR (CDCl$_3$): δ 6.17 (s, 1H, CH$_2$=C–), 5.63 (m, 1H, CH$_2$=C–), 4.46 (t, 2H, –OCH$_2$C–), 3.57 (t, 2H, –CH$_2$Br), 1.96 (s, 3H, C=CCH$_3$).

2-(6-Sulfo-2-naphthoxy)ethyl Methacrylate Sodium Salt. 6-Hydroxy-2-naphthalenesulfonic acid (disodium salt) was prepared by dissolving sodium 6-hydroxy-2-naphthalenesulfonate in the minimum volume of water and then adjusting the solution pH 14 using a concentrated NaOH solution. The water was removed under vacuum, and the resultant solid was washed with absolute ethanol and dried under vacuum. 6-Hydroxy-2-naphthalenesulfonic acid (disodium salt) (5.5 g) and 12.2 g of 2-bromoethyl methacrylate were dissolved in 50 mL of dry DMSO. The resultant solution was kept at 50 °C for 16 h. At the end of the heating period, the solution which was initially dark brown had changed to a clear orange/brown color. The solution was then added dropwise to 500 mL of acetone, upon which a fluffy white precipitate formed. The precipitate was filtered, washed with acetone, and then dried under vacuum. The resultant product was recrystallized from cold water.

^{1}H-NMR (DMSO-d_6): δ 8.07 (s, 1H, ARH), 7.88 (d, 1H, ArH), 7.75 (d, 1H, ArH), 7.36 (s, 1H, ArH), 7.19 (d, 1H, ArH), 6.04 (s, 1H, CH$_2$=C–), 5.69 (s, 1H, CH$_2$=C–), 4.48 (d, 2H, –OCH$_2$–), 4.38 (d, 2H, OCH$_2$–), 1.87 (s, 3H, C=CCH$_3$). ^{13}C-NMR (DMSO-d_6): δ 166.9, 157.0, 143.8, 135.9, 134.3, 130.3, 127.7, 126.4, 124.7, 124.2, 119.1, 107.1, 65.9, 63.1, 17.9. Anal. Calcd for $C_{16}H_{15}NaO_6S$: C, 53.63; H, 4.22; O, 26.79; S, 8.95. Found: C, 53.47; H, 4.20; O, 26.92; S, 8.90.

Polymer Synthesis. 2-(6-Sulfo-2-naphthoxy)ethyl methacrylate sodium salt (NS; 1.00 g, 69.6 mol %), 0.305 g (30.1 mol %) of lauryl methacrylate (LM), and 1 mL (0.24 mol %) of a stock solution of 0.016 g of AIBN in 10 mL of DMSO dissolved in a solvent mixture of 7 mL of DMF and 5 mL of DMSO. The solution was transferred into a glass polymerization ampule, after which it was degassed by three freeze–pump–thaw cycles. The ampule was sealed and placed in a water bath at 60 °C for 24 h. The resultant viscous solution was added dropwise to 350 mL of acetone. The fluffy white precipitate was filtered and washed with acetone and with ether. The polymer was then dissolved in the minimum volume of water, exhaustively dialyzed (Fisher; cellulose tubing, cutoff 12000–14000) against deionized water, and then freeze dried.

A second polymer was made in a similar manner but using 1.00 g (79.3 mol %) of NS, 0.18 g (20.4 mol %) of LM, and 1 mL (0.24 mol %) of a stock solution of 0.014 g of AIBN in 10 mL of DMSO as the starting composition. In the remainder of this paper the polymer which had the starting composition of ≈70% NS and ≈30% LM will be referred to as 70/30 NS–LM. Similarly, the polymer with the starting composition of ≈80% NS and ≈20% LM will be referred to as 80/20 NS–LM. Elemental analysis (Galbraith Laboratories) showed that the final compositions (mol %) of the 70/30 NS–LM and 80/20 NS–LM polymers were 60.95:39.05 NS–LM and 69.45:30.55 NS–LM, respectively. All studies were performed on both polymer compositions with similar results, but only the data for 80/20 NS–LM will be displayed unless otherwise stated.

NMR Spectra. ^{1}H and ^{13}C NMR spectra were measured using a Varian Gemini 200-MHz spectrometer.

Ultraviolet Spectra. The ultraviolet (UV) absorption spectra of the samples were measured using a Hewlett-Packard 8451A diode array spectrophotometer.

Steady-State Fluorescence Spectra. Steady-state emission and excitation spectra were recorded at room temperature using a SLM 4800S fluorescence spectrophotometer. All fluorescence spectra are uncorrected. Fluorescence depolarization studies were measured using a SLM 4800s fluorescence spectrophotometer with 10-mm Glan–Thompson calcite prism polarizers.

Irradiation of Samples. Irradiations were carried out using a Bausch and Lomb irradiation setup equipped with a 200-W high-pressure mercury lamp. The 280-nm monochromatic light was obtained using a high-intensity monochromator. The light intensities were determined using an azobenzene actinometer.[12–14] Solar-simulated irradiations were performed using a solar simulator built by Sciencetech (London, Ontario) equipped with AM1.5 filters. All samples were irradiated in quartz cells.

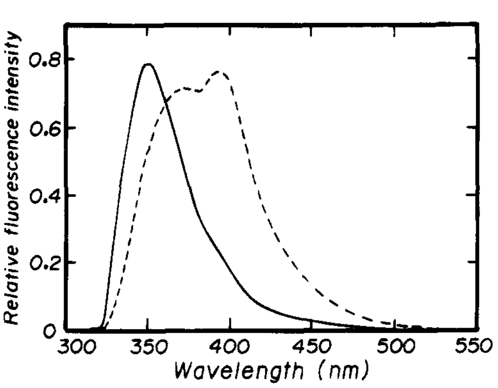

Figure 1. Steady-state fluorescence emission spectra of (—) NS (5.0 × 10^{-5} M) and (- - -) NS–LM (0.01 g dm^{-1}) in aqueous solution (λ_{ex} = 280 nm).

Solubilization of Perylene. Perylene was solubilized in the aqueous polymer solutions by slowly injecting microliter quantities of perylene dissolved in acetonitrile into milliliter quantities of the aqueous polymer solution. The samples were then shaken vigorously for 5 min, after which they were allowed to equilibrate in the dark for 3–12 h prior to any measurements.

Results and Discussion

Photophysics. Since the polymer synthesized in this work contains the chromophore as the hydrophilic unit, which contrasts to previous work in our group[15–18] and also to many other polyelectrolyte polymers,[19–22] the first stage of the study deals with the photophysical properties of the polymer. The steady-state fluorescence spectrum of an aqueous polymer sample (Figure 1) shows two peaks. By comparison with the spectrum of the naphthalenesulfonate monomer, the shorter wavelength peak (λ = 373 nm) was assigned to emission from an individual naphthalenesulfonate group, while the longer wavelength peak (λ = 395 nm) was assigned to excimer emission. The fluorescence excitation spectrum of NS–LM was virtually identical to that of its absorption spectrum, thereby indicating that no ground-state dimers are formed.

Excimer emission was unexpected since it was thought that the presence of sulfonate groups would result in sufficient electrostatic repulsion to prevent the close approach required for excimer formation. It is known[2] that excimer formation in polymers does not always follow Hirayama's *n = 3* rule, and chromophores separated by more than three atoms are capable of excimer formation. However, as the number of atoms separating adjacent chromophores increases, the number of available conformations also increases, leading to a lower probability of excimer formation (e.g., see Nakahira *et al.*[23]). Adjacent naphthalenesulfonate groups in the NS–LM polymer are separated by 11 atoms, and thus excimer formation between adjacent naphthalenesulfonate groups is expected to be minimal.

Because of the unexpected occurrence of excimer emission, it was further investigated to determine whether excimer formation was inter- or intramolecular. This was determined by observing the change in the ratio of the excimer fluorescence intensity (I_{Ex} = 395 nm) to the monomer fluorescence intensity (I_M = 373 nm) as a function of polymer concentration (Figure 2). As was expected, the fluorescence intensities of both the monomer and the excimer increased as the polymer concentration was increased, while the excimer–mono-

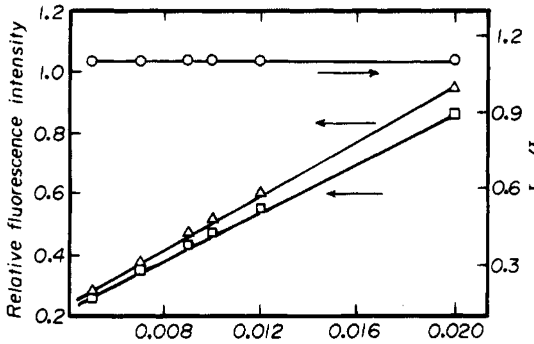

Figure 2. Dependence of the monomer (□, I_M) and excimer (△, I_{Ex}) intensities and the ratio of the excimer-to-monomer emission (○, I_{Ex}/I_M) on polymer concentration in an aqueous solution.

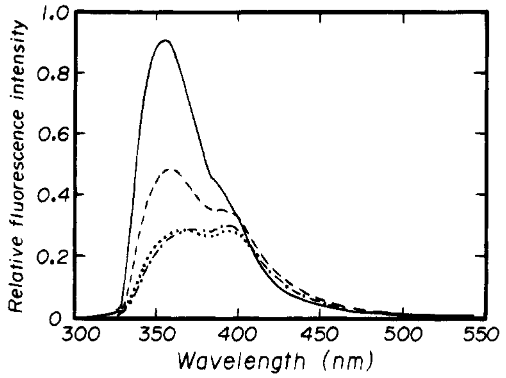

Figure 3. Steady-state fluorescence spectra of 0.01 g dm^{-3} NS–LM in (– • –) an aqueous soution, (• • •) 80:20 H_2O/DMSO, (- - -) 50:50 H_2O/DMSO, and (—) 10:90 H_2O/DMSO.

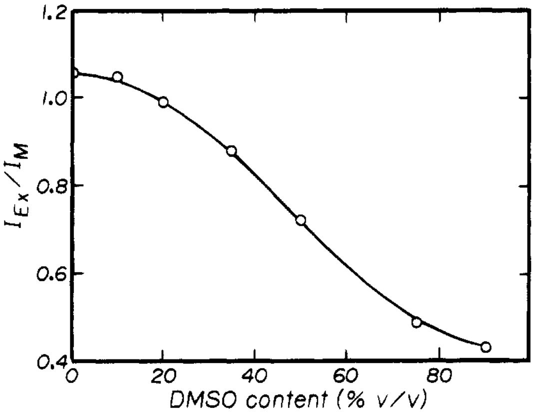

Figure 4. Dependence of the ratio of the excimer-to-monomer (I_{Ex}/I_M) of NS–LM (0.01 g dm^{-3}) on the DMSO content (v/v %) of the aqueous solution.

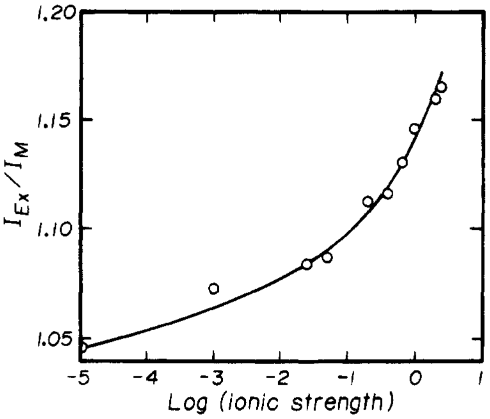

Figure 5. Dependence of the ratio of the excimer-to-monomer (I_{Ex}/I_M) of NS–LM (0.01 g dm^{-3}) on the ionic strength of the aqueous solution.

mer ratio remained constant within experimental error. This indicates that the excimer formation is strictly intramolecular, since if excimer formation were intermolecular, the intensity ratio would be dependent on the polymer concentration.

It was found that the intensity of the excimer emission in NS–LM depends on the solvent composition (Figure 3). In water there is significant excimer formation, but at 90% (v/v) DMSO/H_2O there is minimal excimer. Figure 4 shows the dependence of the ratio of I_{Ex}/I_M as a function of the DMSO content of the solvent. It can be seen that I_{Ex}/I_M decreased continuously as the DMSO content of the solution was increased. This shows that excimer emission decreases with increasing DMSO content. A similar solvent dependence was observed for methanol. It is known that excimer emission is not dependent exclusively on the polarity of the solvent but more on whether the solvent is "good" (chain expanding) or "poor" (chain contracting). NS–LM consists of hydrophilic naphthalenesulfonate groups and hydrophobic lauryl methacrylate groups. The hydrophobic lauryl methacrylate groups would be expected to cluster in such a way as to cause the polymer to adopt a more compact conformation. Since both the naphthalenesulfonate and lauryl methacrylate groups are soluble in DMSO, the aggregation of the lauryl methacrylate groups is not expected to occur to the same extent as in an aqueous solution and so the polymer would adopt a more expanded conformation, thereby decreasing the probability of close contact of the chromophores. This would explain the decrease in I_{Ex}/I_m as the DMSO content is increased. It has been shown previously[24,25] that such solvent effects are due to excimer formation occurring primarily across loops in the polymer chain rather than between nearest-neighbor monomer units. Thus the solvent dependence of the amount of excimer emission would indicate that excimers are formed predominantly from across loop contacts in the polymer chain.

It is also well-known that changes in the ionic strength of polyelectrolyte solutions can alter the dimensions of the polymer coil. The I_{Ex}/I_M ratio (Figure 5) increased gradually in the ionic strength range 1×10^{-5}–2×10^{-1} but then increases rapidly as the ionic strength is further increased. The increased ionic strength results in an increased screening effect on the sulfonate groups, thereby reducing the electrostatic repulsion between them. This allows closer approach of the naphthalenesulfonate groups and a decrease in the coil size. This would increase the probability of across-chain contacts, thereby increasing the probability of excimer formation.

It is also necessary to consider the importance of intramolecular energy migration in the excimer formation process. Potential excimer sites can act as energy traps for migrating energy, and thus, in the presence of energy migration, even a few potential excimer sites will be excited efficiently. Energy migration is more efficient in a compact coil than in an expanded coil,[2] and so if energy migration is responsible for excitation of preformed excimer sites, the compactness of the polymer coil is also important. The above results can also be explained in terms of changes in the efficiency of energy migration since as the DMSO content in H_2O/DMSO mixtures decreases, or as the ionic strength increases,

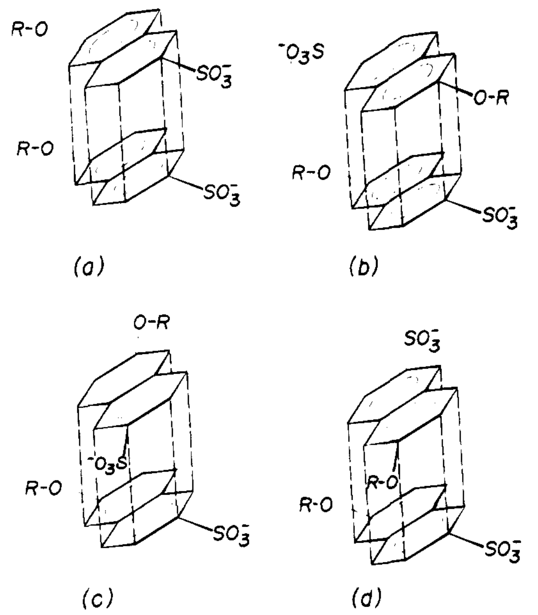

Figure 6. Possible conformations of naphthalenesulfonate groups that could lead to excimer formation.

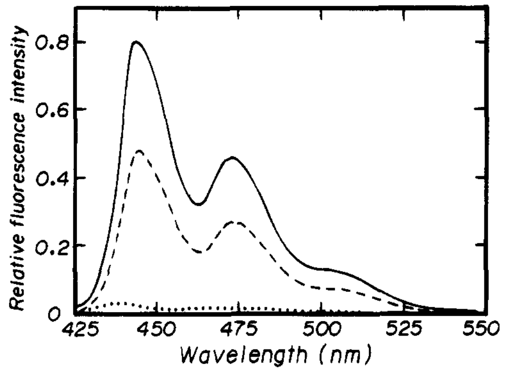

Figure 7. Steady-state fluorescence emission of perylene in (···) water, (- - -) 0.01 g dm^{-3} NS−LM (80/20), and (—) 0.01 g dm^{-3} NS−LM (70/30) (λ_{ex} = 415 nm).

the polymer coil becomes more compact, thereby increasing the efficiency of energy migration and thus the probability of excimer formation.

Therefore, the intensity of excimer emission seems to depend on a combination of two effects: (1) the probability of formation of excimer sites across loops in the chain and (2) the efficiency of intramolecular energy migration along and across the chain until a preformed excimer site is excited. The formation of an excimer requires close parallel approach of the naphthalene groups. In order for this requirement to be satisfied, there would seem to be four possible arrangements of the naphthalenesulfonate groups (Figure 6). Configurations a and c would result in substantial electrostatic repulsion between the sulfonate groups which would prevent the close approach required for excimer formation. Both conformations b and d would allow the close planar arrangement, and thus these two conformations would likely satisfy the steric requirements for potential excimer formation sites, with d being the most probable since it would experience the least electrostatic and steric effects of the four possible conformations.

Solubilization of a Hydrophobic Compound. The solubilizing ability of NS−LM was tested using perylene as a probe. Perylene is a useful probe since it has a very low solubility[26] as well as a low fluorescence emission in water.[27] Figure 7 shows the effect of adding NS−LM to an aqueous solution of perylene. It can be seen that the presence of the NS−LM polymer drastically enhances the fluorescence emission of the perylene. This enhanced fluorescence is due to an increased concentration of perylene in solution brought about by the transfer of perylene to the more hydrophobic environment of the NS−LM polymer.

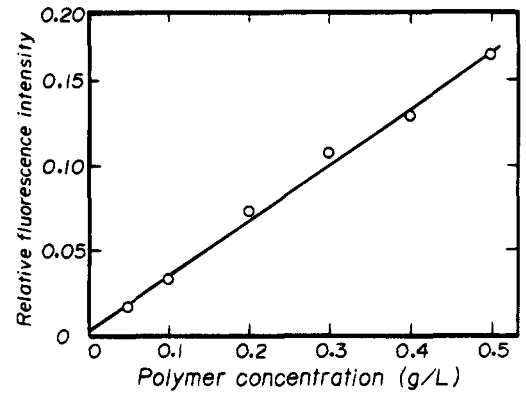

Figure 8. Dependence of the concentration of perylene solubilized as a function of NS−LM polymer concentration (λ_{ex} = 415 nm; λ_{em} = 446 nm).

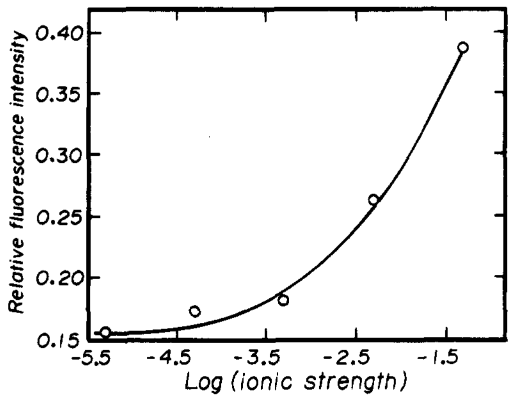

Figure 9. Dependence of the concentration of perylene solubilized as a function of the ionic strength of the NS−LM solution (0.4 g dm^{-3}) (λ_{ex} = 415 nm; λ_{em} = 446 nm).

The amount of perylene solubilized depends linearly on the polymer concentration (Figure 8). By assuming that an aqueous NS−LM polymer solution can be treated as consisting of two phases[28] (an aqueous phase and a polymer core pseudophase), the solubilizing ability of the NS−LM polymer can be characterized quantitatively by determining the distribution coefficient defined by

$$K = x_c/x_{aq} \qquad (1)$$

where x_c and x_{aq} represent the weight fraction of perylene solubilized in the polymer pseudophase and the water phase, respectively. Using eq 1, values for K of 6.0×10^6 and 2.6×10^6 were obtained for the 70/30 and 80/20 compositions, respectively. Thus, it can be seen that, by increasing the lauryl methacrylate content of the polymer, the solubilizing ability is increased. This confirms that it is the hydrophobic lauryl methacrylate groups which are responsible for the solubilization of the perylene.

Figure 9 shows the effect of ionic strength on the solubilizing ability of the polymer. It can be seen that as the ionic strength is increased from 5×10^{-6} to 5×10^{-4} there is little change in the amount of perylene solubilized, but further increases in the ionic strength

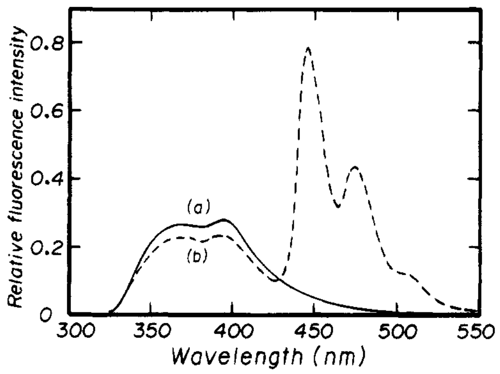

Figure 10. Steady-state fluorescence spectra of (a) NS–LM (0.01 g dm^{-3}) in an aqueous solution and (b) NS–LM (0.01 g dm^{-3}) containing solubilized perylene (7.6 × 10^{-7} M) (λ_{ex} = 280 nm).

results in a significant increase in the amount of perylene solubilized. This can be explained on the basis that the increased ionic strength reduces the mutual repulsion of the charged species to produce a more compact coil, having greater hydrophobicity and hence great solubilizing ability for hydrophobic probes.

Energy Transfer and Energy Migration. The foregoing discussion shows that perylene is solubilized by NS–LM. Thus, the next question was whether energy transfer from the naphthalenesulfonate groups to the solubilized perylene is possible. Energy transfer was expected to occur by the long-range Förster mechanism, and thus the radius of interaction (R_0) between the naphthalenesulfonate and the perylene was calculated[2] using

$$R_0^{\,6} = \frac{8.8 \times 10^{-25}\kappa^2\phi_D}{n^4}\int_0^\infty F_D(\bar\nu)\,\epsilon_A(\bar\nu)\,d\bar\nu/\bar\nu^4 \qquad (2)$$

where ϵ_A is the extinction coefficient of the acceptor, F_D is the relative fluorescence intensity of the donor at $\bar\nu$ satisfying $\int_0^\infty F_D(\bar\nu)\,d\bar\nu = 1$, $\int_0^\infty F_D(\bar\nu)\,\epsilon_A(\bar\nu)\,d\bar\nu$ is the overlap integral between the emission profile of the donor and the absorption spectrum of the acceptor, ϕ_D is the fluorescence quantum yield of the donor in the absence of the acceptor, n is the refractive index of the solvent, and κ^2 is the molecular orientation factor. If the molecular transition dipole moments are averaged over a random distribution of orientations, κ^2 takes a value of two-thirds. A value of 1.33 was used for the refractive index, while $\phi_f = 0.20$ for the model compound sodium 6-methoxy-2-naphthalenesulfonate[29] was used for ϕ_D. A value for R_0 of 27.4 Å was obtained, thus showing that energy transfer by the Förster mechanism from the naphthalenesulfonate moieties to solubilized perylene is possible.

Figure 10 shows the steady-state fluorescence spectrum of NS–LM in an aqueous solution (curve a) and of a NS–LM solution containing perylene (curve b). Under the experimental conditions used, virtually all of the incident light was absorbed by the polymer with no direct excitation of the perylene. Comparison of the spectra shows that the presence of perylene results in a decreased fluorescence emission from the polymer as well as the appearance of peaks in the 430–530-nm region which are characteristic of perylene. The decreased polymer fluorescence emission shows that the emission is being quenched by the presence of the perylene, while the appearance of the characteristic perylene emission peaks shows that the perylene is being indirectly excited. These observations are consistent with the occurrence of energy transfer from the naphthalenesulfonate groups to the solubilized perylene.

Table 1. Fluorescence Depolarization Measurements for Perylene via Direct and Indirect Excitation (λ_{em} = 446 nm)

excitation wavelength (nm)	degree of depolarization (P)
313[a]	0.0186 ± 0.0015
415[b]	0.3235 ± 0.0014

[a] Excitation of polymer. [b] Direct excitation of perylene.

In order to determine whether energy migration plays an important role in the energy transfer process, steady-state fluorescence depolarization studies were performed. Fluorescence depolarization has been shown to be a useful method to study energy migration.[2,30–33] The degree of polarization, P, is defined[34] as

$$P = (I_\parallel - GI_\perp)/(I_\parallel + GI_\perp) \qquad (3)$$

where $I_\parallel$ and $I_\perp$ are the fluorescence intensities observed through a polarizer oriented parallel and perpendicular to the plane of polarization of the excitation beam, and G is an instrumental correction factor.

The depolarization of the perylene was determined by direct and by indirect excitation via energy transfer.[35] If the energy transfer is a single step which is not preceded by energy migration, then the depolarization values of perylene for direct and indirect excitation should be comparable since the emission and adsorption dipoles must have similar orientation for energy transfer. If, however, energy migration precedes the energy transfer step, the group absorbing the excitation light will be different from the group transferring the excitation energy to the perylene and thus the perylene emission should be significantly depolarized. Results of the depolarization study are give in Table 1.

The results show that, for the perylene excited via the antenna, there is almost complete depolarization of the incident light, whereas substantial retention of polarization occurs on direct excitation of perylene. Excimer formation and dissociation can result in some depolarization, but since the amount of excimer formation in this system is small, depolarization due to this phenomenon is expected to be minimal.

It is also interesting that the relatively large value for P for the direct excitation of perylene shows that it does not undergo significant rotational motion during its fluorescence lifetime. This would suggest that the solubilized perylene is held rather tightly by the hydrophobic portion of the polymer and that the polymer coil itself is not undergoing significant rotational motion during the perylene fluorescence lifetime. This confirms that depolarization due to polymer motion is not the main reason for the observed depolarization. We conclude that the observed fluorescence depolarization is due to energy migration among the naphthalenesulfonate groups prior to the final energy transfer step to the solubilized perylene. The occurrence of energy migration shows that the polymer has the ability to act as an antenna-type polymer.

Photochemical Reaction. The photosensitized oxidation of perylene has been used to study the photoactivity of various polymer systems.[5,6,8,17] Previous studies of the photosensitized oxidation of perylene in aqueous solutions of poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS–VN)[5] have shown that the reaction leads to the formation of nonfluorescent perylenequi-

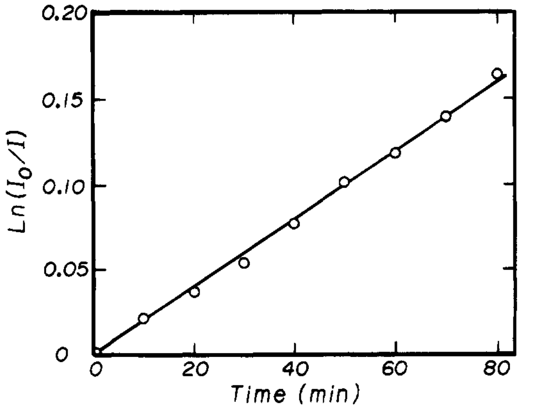

Figure 11. Dependence of ln (I_0/I) on irradiation time for the photooxidation of perylene (2.28×10^{-6} M) solubilized in NS–LM (0.4 g dm^{-3}) using 280-nm light.

Table 2. Comparison of Quantum Efficiencies of Photooxidation (γ_P) of Perylene for Various Antenna Polymers

polymer	$\gamma_P \times 10^4$
PSSS–VN	2.5
methacrylic acid-*co*-(9-vinylphenanthrene) (random)	0.76–2.0
methacrylic acid-*co*-(9-vinylphenanthrene) (block)	2.9
NS–LM (70/30)	1.6
NS–LM (80/20)	0.67

nones. Irradiation of an oxygen-saturated aqueous NS–LM solution containing solubilized perylene with monochromatic light at 280 nm results in a decrease in perylene concentration, as observed by a decrease in the perylene fluorescence intensity. The reaction can be described as a pseudo-first-order reaction (Figure 11). The overall quantum efficiencies of the photooxidation of perylene in an aqueous NS–LM solution were 1.6×10^{-4} and 6.7×10^{-5} for 70/30 NS–LM and 80/20 NS–LM, respectively. This compared favorably with the values of the overall quantum efficiencies of the photooxidation of perylene in other antenna polymers (Table 2).

In order to see whether NS–LM could be used as a photocatalyst in a practical sense, the photooxidation of perylene solubilized by NS–LM was studied under simulated solar conditions. Figure 12 illustrates how perylene photooxidation under these different conditions can be described by pseudo-first-order kinetics. Figure 12 also shows that the photooxidation of perylene solubilized in NS–LM decomposes 1.4 times faster than that the self-sensitized photooxidation of similar concentrations of perylene in methanol. As discussed previously, an increase in the ionic strength of the polymer solution should result in a more compact coil with an increase in the efficiency of energy migration. Figure 12 also shows that increasing the ionic strength of the polymer solution had minimal effect on the rate constant for the photooxidation of perylene under solar-simulated conditions (Table 3).

Conclusion

From the above results, it can be seen that NS–LM, which represents a new type of antenna polymer, can act as a photoenzyme. In spite of the presence of charged ionic groups on the chromophore, the polymer does exhibit intramolecular excimer formation. The degree of excimer formation was found to be dependent on both the solvent composition and the ionic strength of the solution. The hydrophobic lauryl methacrylate groups give the polymer the ability to solubilize a hydrophobic probe molecule to a degree depending on the lauryl methacrylate content of the polymer. Steady-state fluorescence emission and depolarization studies showed energy migration among the naphthalene sulfonate groups, as well as energy transfer via the Förster mechanism from the naphthalenesulfonate groups to a solubilized perylene probe molecule.

Photooxidation studies of perylene with both monochromatic (280 nm) and solar-simulated incident light showed that the rate of reaction was enhanced by the presence of NS–LM.

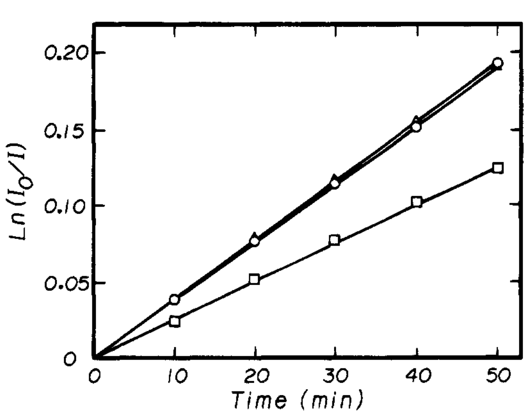

Figure 12. Dependence of ln (I_0/I) on irradiation time for the photooxidation of perylene (1.14×10^{-6} M) (□) in methanol, (○) solubilized in NS–LM (0.4 g dm^{-3}), and (△) solubilized in a NaCl (ionic strength = 0.05) containing NS–LM (0.4 g dm^{-3}) solution using solar-simulated light.

Table 3. First-Order Rate Constants and Relative Rate Constants for the Photooxidation of Perylene[a] under Solar-Simulated Conditions

solution	$k \times 10^5$ (s^{-1})	k_{rel}
methanol	4.2	1.00
NS–LM (80/20)[b]	6.3	1.50
NS–LM (80/20)[b] (log $I = -1.3$)	6.4	1.52

[a] [Perylene] = 1.14×10^{-6} M. [b] [NS–LM] = 0.4 g/L.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the Ontario Center for Materials Research for financial support of this work. D.M.G. thanks the University of Toronto for Fellowship support from the Connaught Fund and for a University of Toronto Open Fellowship.

References and Notes

(1) Morishima, Y. *Prog. Polym. Sci.* **1990**, *15*, 949.
(2) Guillet, J. E. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, U.K., 1985.
(3) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469.
(4) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1989**, *22*, 2317.
(5) White, B.; Nowakowska, M.; Guillet, J. E. *J. Photochem. Photobiol. A: Chem.* **1989**, *50*, 147.
(6) Nowakowska, M.; Bakhtiyari, H.; Osselton, E.; Steele, M. R.; Guillet, J. E. *J. Photochem. Photobiol. A: Chem.* **1992**, *64*, 329.
(7) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1988**, *21*, 3430.
(8) Nowakowska, M.; Sustar, E.; Guillet, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 253.
(9) Sustar, E.; Nowakowska, M.; Guillet, J. E. *J. Photochem. Photobiol. A: Chem.* **1992**, *63*, 357.
(10) Fierz-David, H. E.; Blangey, L. *Fundamental Processes of Dye Chemistry*; Interstate Publishers, Inc.: New York, 1949.

(11) Dykstra, T. H.; Smith, D. A. U.S. Patent 3 306 884, 1967; *Chem. Abstr.* **1967**, *66*, 116153u.
(12) Gauglitz, G. *J. Photochem.* **1976**, *5*, 41.
(13) Gauglitz, G.; Hubig, S. *J. Photochem.* **1981**, *15*, 255.
(14) Gauglitz, G.; Hubig, S. *J. Photochem.* **1985**, *30*, 121.
(15) Guillet, J. E.; Rendall, W. A. *Macromolecules* **1986**, *19*, 224.
(16) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1988**, *21*, 3430.
(17) Nowakowska, M.; White, B.; Vogt, S.; Guillet, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 271.
(18) Sustar, E.; Nowakowska, M.; Guillet, J. E. *J. Photochem. Photobiol.* **1990**, *53*, 223.
(19) Morishima, Y.; Itoh, Y.; Nozakura, S. *Macromol. Chem.* **1981**, *182*, 3135.
(20) Morishima, Y.; Itoh, Y.; Hashimoto, T.; Nozakura, S. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2007.
(21) Kamioka, K.; Webber, S.; Morishima, Y. *Macromolecules* **1988**, *21*, 972.
(22) Morishima, Y.; Tsuji, M.; Kamachi, M.; Hatada, K. *Macromolecules* **1992**, *25*, 4406.
(23) Nakahira, T.; Maruyama, I.; Iwabuchi, S.; Kojima, K. *Makromol. Chem.* **1979**, *180*, 1853.
(24) Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 218.
(25) Aspler, J. S.; Guillet, J. E. *Macromolecules* **1979**, *12*, 1082.
(26) Pearlman, R. S.; Yalkowsky, S. H.; Banerjee, S. *J. Phys. Chem. Ref. Data* **1984**, *13*, 555.
(27) Patterson, L. K.; Vieil, E. *J. Phys. Chem.* **1973**, *77*, 1191.
(28) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1990**, *23*, 3375.
(29) Gravett, D. M.; Guillet, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 5970.
(30) MacCallum, J. R. In *Photophysics of Synthetic Polymers*; Phillips, D., Roberts, A. J., Eds.; Science Reviews, Ltd.: Northwood, Middlesex, U.K., 1982.
(31) Phillips, D.; Rumbles, G. *Polym. Photochem.* **1984**, *5*, 155.
(32) Anderson, R. A.; Reid, R. F.; Soutar, I. *Eur. Polym. J.* **1980**, *16*, 945.
(33) McInally, I.; Reid. R. F.; Rutherford, H.; Soutar, I. *Eur. Polym. J.* **1979**, *15*, 723.
(34) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum: New York, 1983.
(35) Soutar, I.; Phillips, D. In *Photophysical and Photochemical Tools in Polymer Science*; Winnik, M., Ed.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1986.

MA9409705