

STUDIES OF THE ANTENNA EFFECT IN POLYMER MOLECULES ENERGY MIGRATION AND TRAPPING IN NAPHTHALENE-CONTAINING POLYELECTROLYTES*

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Abstract Polymers of 1- and 2-vinylnaphthalene containing more than about 50 mol% sulfonic acid groups dissolve in water to form "hypercoiled" conformations which have many of the properties of micelles. Hydrophobic molecules such as anthracene and perylene are selectively absorbed in these pseudo micellar structures, and their fluorescence emission is sensitized by energy transfer from the surrounding naphthalene chromophores. When irradiated with UV light in the presence of oxygen, the emission of perylene rapidly decreases. It is proposed that this is due to reaction of singlet oxygen with the perylene trapped in the hypercoiled polymer.

Keywords Sulfonated vinyl naphthalene polymers; Transport of excitation energy; Anthracene; Perylene; Trapping

INTRODUCTION

In the previous papers of this series^[1~3] it has been shown that copolymers containing hydrophobic and ionogenic groups, when dissolved in water, undergo hypercoiling to form conformations which may resemble micellar structures. In particular, these polymers have the ability to solubilize large hydrophobic aromatic compounds in water, and are also able to transport singlet excitation to these molecules in a manner similar to that observed when the trap is chemically attached to the antenna polymer chain. It was also shown that partially sulfonated poly(2-vinylnaphthalene) (SP2VN) was able to solubilize perylene in water solution, and to transport excitation energy absorbed by the naphthalene groups to the perylene molecules^[3].

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EXPERIMENTAL

Materials

Commercial 1-vinylnaphthalene (Aldrich) was purified by adsorption chromatography on alumina using cyclohexane as eluent, then sublimed under vacuum.

Polymers of 1- and 2-vinylnaphthalene were prepared by heating the respective monomers at 60°C in benzene solution using 2, 2'-azobisisobutyronitrile (AIBN) catalyst and purified as described previously^[3].

Sulfonation of the polymers was carried out in solution with chlorosulfonic acid as the sulfonating agent. Its degree of sulfonation depended on the conditions used. These are summarized in Table 1. After sulfonation, the samples were precipitated with diethyl ether and washed several times with ether before drying in an air oven at 40°C. The degree of sulfonation was determined by titration of the aqueous sulfonated PVN (SPVN) solution with 0.01 N NaOH using phenolphthalein as indicator.

Table 1 Preparation of Sulfonated Poly(vinylnaphthalene)

Polymer	Wt (g)	Solvent	W_t (g) ClSO ₃ H	Addition	Reaction	SO ₃ (%)
A	P1VN	20 mL CCl ₄ +C ₂ H ₄ Cl ₂ (1:4)	0.12	10 min/23°C	50 min/23°C	50
B	P2VN	80 mL CHCl ₃	0.21	20 min/0°C	10 min/25°C 30 min/40°C	88
C	P2VN	40 mL CCl ₄ +C ₂ H ₄ Cl ₂ (1:1)	0.18	35 min/0°C	35 min/25°C	77
D	P2VN	35 mL CHCl ₃	0.13	10 min/23°C	50 min/45°C	95

Solution preparation

Aqueous SPVN solution (10 mL) of the required concentration was allowed to contact with 1 mL of the probe molecule (e.g., anthracene) in ether ($C \doteq 10^{-4}$ M) in a glass-stoppered test tube. After tumbling at room temperature for two to five days, the ether layer was decanted. The water layer was washed twice with ether to remove any occluded anthracene and then the ether was removed by evacuation with a water pump. The aqueous solution was centrifuged and decanted to remove any precipitated material and was then studied spectroscopically.

Fluorescence measurements

Steady-state fluorescence measurements were made using a Hitachi-Perkin Elmer MPF-2A fluorescence spectrometer and are uncorrected for detector response. UV-visible absorption spectra were determined using a Hewlett Packard SP1800A UV spectrometer.

RESULTS AND DISCUSSION

As reported previously^[3], the steady-state fluorescence emission from SPVNS in aqueous solution is dominated by excimer emission. It is concluded that the hypercoiled conformation provides both a higher concentration of excimer sites, and a more rapid migration of singlet excitons to populate these sites. Transient measurements of fluorescence decay on similar polymers support this hypothesis. When an aqueous SPVN is shaken with an ether solution of anthracene, some of the anthracene is transferred to the aqueous solution, resulting in a reduction of fluorescence intensity from the excimer and there is evidence for emission from the anthracene at 392 and 406 nm.

An excitation spectrum for emission at 450 nm (Fig. 1, curve a) shows several peaks at 330, 362, 383 and 400 nm which are red-shifted from the normal emission of anthracene in hydrocarbon solvents by about 5 nm, presumably due to the greater polarity of the aqueous medium. It is not possible to extend the excitation spectrum to wavelengths of less than 325 nm, because the strong absorbance of the naphthalene groups prevents transmission of shorter wavelength light to the centre of the cell. However, because of the reversal of the normal intensity of the anthracene bands it

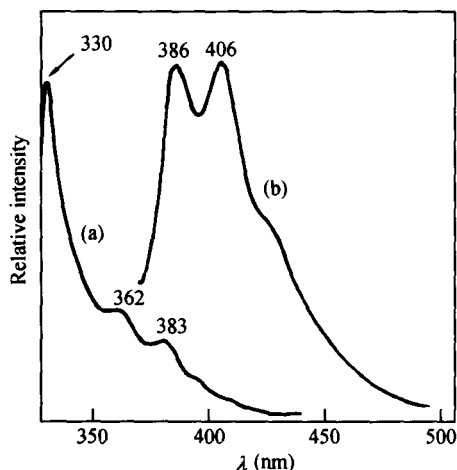


Fig. 1 Fluorescence emission spectrum of polymer B: $\lambda_{\text{ex}} = 360 \text{ nm}$, $C = 2.5 \times 10^{-3} \text{ base mol L}^{-1}$ pH=6.8

(a) No anthracene; (b) $1 \times 10^{-6} \text{ mol L}^{-1}$ anthracene

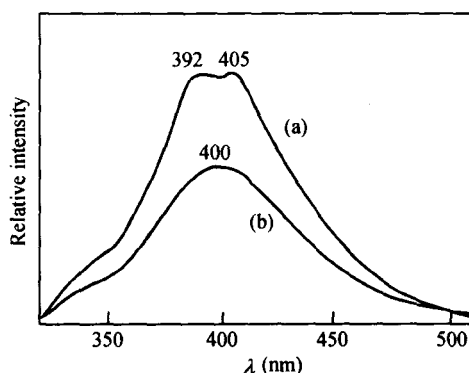


Fig. 2 Fluorescence emission spectrum of polymer B: $\lambda_{\text{ex}} = 280 \text{ nm}$, $C = 5 \times 10^{-4} \text{ mol L}^{-1}$, pH=6.8

(a) $2 \times 10^{-7} \text{ mol L}^{-1}$ anthracene; (b) no anthracene

is clear that a large part of the emission at 450 nm results from original absorption on the naphthalene moiety in the polymer. When the excitation wavelength is 360 nm (Fig. 1, curve b), the fluorescence emission is primarily from direct excitation of the anthracene trapped in the polymer solution, and the characteristic

anthracene emission peaks are readily observed at 386, 406 and 430 nm. There still, however, appears to be some naphthalene excimer underlying this emission, since the anthracene peaks at 386 and 406 nm are of approximately equal intensity.

At a lower concentration ($5 \times 10^{-4} \text{M}$), the results are less ambiguous. Fig. 2 shows the emission spectra of SP2VN with and without anthracene traps on excitation at 280 nm. At this wavelength and lower concentration, direct absorption by the anthracene is much reduced and 99.9% of the light is absorbed by the naphthalene moiety. As a result of energy transfer, however, a significant fraction of anthracene is excited and the fluorescence emission intensity actually increases, with poorly

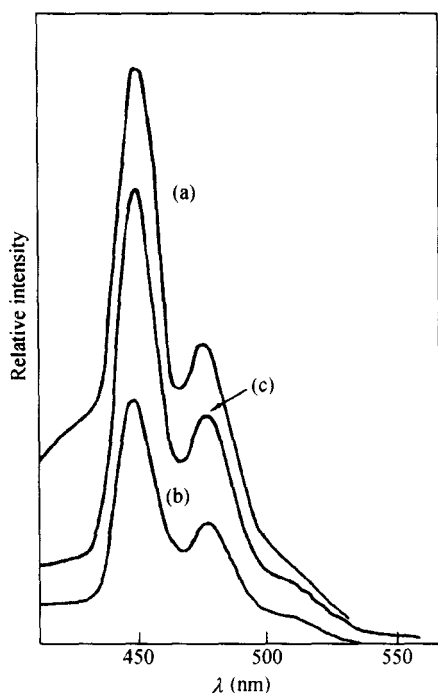


Fig. 3 Fluorescence emission spectrum of polymer A: $\lambda_{\text{ex}} = 330 \text{ nm}$, $C = 2.5 \times 10^{-3} \text{ mol L}^{-1}$, $\text{pH} = 6.8$, $3.8 \times 10^{-6} \text{ mol L}^{-1}$ anthracene

resolved peaks visible at 392 and 405 nm characteristic of anthracene emission (Fig. 2 curve a). Excitation spectra for the peak at 390 nm in both solutions confirm that the higher emission intensity is due to emission from anthracene and that a major part of the excitation at short wavelengths is due to absorption by naphthalene units. From this evidence it is not possible to confirm whether or not energy migration is involved in the population of the anthracene traps. However, the efficiency with which the very low concentration of anthracene ($2 \times 10^{-7} \text{M}$) is populated (the molar concentration of naphthalene is $5 \times 10^{-4} \text{M}$) lends some credence to this postulate. However, the apparent high concentration of excimer traps in SP2VN may reduce the effective range of the migrating exciton.

Experiments similar to those reported above were carried out with sulfonated poly(1-vinylnaphthalene) (SP1VN). In this case, sulfonation is expected to occur on the 4 position of the naphthalene ring. The degree of sulfonation was considerably lower (55%). It was observed that nearly four times as much anthracene was trapped under identical conditions, and as a result anthracene emission was readily detectable in the fluorescence spectrum (Fig. 3) for irradiation at 330 nm, where both naphthalene and anthracene absorb. The concentration of naphthalene was $2.5 \times 10^{-3} \text{M}$ and that of anthracene was $3.8 \times 10^{-6} \text{M}$. Based on the molar extinction

coefficients at 330 nm, one would expect only about 5% of the light would be directly absorbed by anthracene. In spite of this, the anthracene emission clearly dominates the spectrum, indicating the high efficiency of energy transfer occurring in these aqueous solutions.

Because of the strong overlap of its fluorescence emission with that of the naphthalene excimer, anthracene is not as useful a probe as certain other aromatic hydrocarbons. For example, perylene has emission bands at 443, 468, 501, and 540 nm, the latter two being well above the emission maxima for naphthalene excimer. Experiments with perylene were therefore carried out in a manner similar to those with anthracene.

Fig. 4 shows the emission spectra for an aqueous solution of SP2VN containing trapped perylene using (a) 300, (b) 330 and (c) 420 nm excitation. In this case the perylene emission is readily resolved from the underlying naphthalene excimer, both at 300 nm when substantially all of the light is being absorbed by naphthalene as well as at 420 nm where the perylene is excited directly. The ease with which perylene can be identified and detected by fluorescence, permits experiments to test the efficacy of the trapping process in various polymers at different pH. It was found that both a lower degree of sulfonation and a higher pH appear to assist the efficiency with which perylene is trapped by the polyampholyte.

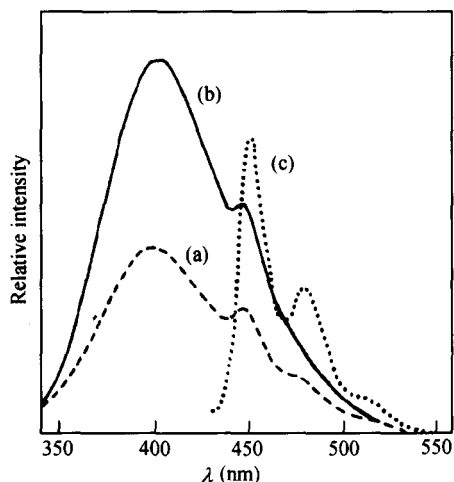


Fig. 4 Fluorescence emission spectrum of polymer A: $\lambda_{ex} = 300$ nm, $C = 2.5 \times 10^{-3} \text{ mol L}^{-1}$, pH=13.3, with perylene ($1.6 \times 10^{-7} \text{ mol L}^{-1}$) (a) $\lambda_{ex} = 300$ nm; (b) $\lambda_{ex} = 330$ nm; (c) $\lambda_{ex} = 420$ nm.

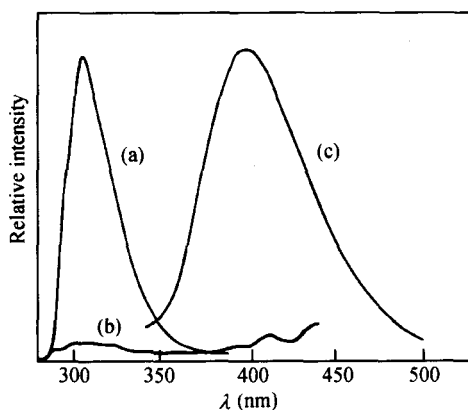


Fig. 5 Fluorescence emission from polystyrene sulfonate

(a) $\lambda_{ex} = 270$ nm, $C = 2.5 \times 10^{-3} \text{ mol L}^{-1}$, pH=7.0; (b) excitation spectrum of (a) in the presence of perylene, $\lambda_{em} = 450$ nm; (c) SP2VN, $\lambda_{ex} = 330$ nm, $C = 1.9 \times 10^{-3} \text{ mol L}^{-1}$, pH=6.8

It has been reported previously that many polyelectrolytes have the ability to trap large aromatic hydrocarbons in aqueous solution. Accordingly, experiments with perylene were carried out by identical procedures using a commercial sample of poly(styrene sulfonate). The emission and excitation spectra are shown in Fig. 5. Under comparable conditions, the emission (curve a) is also mostly derived from polystyrene excimer with $\lambda_{\max}$ at 323 nm and no observable peaks for perylene. The excitation spectrum for emission at 450 nm (curve b) shows that a small amount of perylene was trapped and could be detected by direct excitation. By comparison with the SP2VN polymers, the amount of perylene trapped is at least an order of magnitude smaller, and there is little evidence for energy transfer from the absorbing styryl groups to the small amount of perylene which is trapped.

In the course of these studies it was observed that the intensity of emission from perylene decreased with time when the sample was exposed to light in the presence

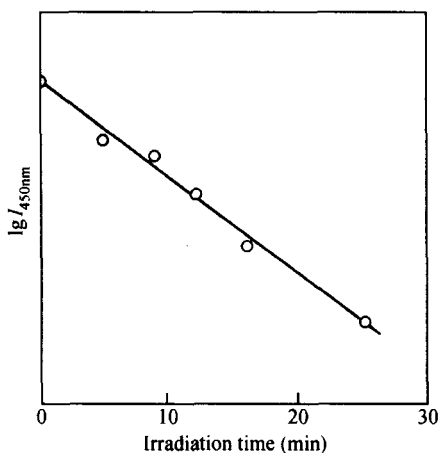
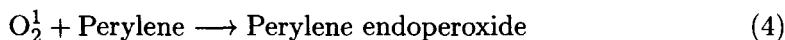


Fig. 6 First-order plot for perylene fluorescence decay

of air. A plot of the logarithm of the peak intensity at 450 nm as a function of irradiation time is linear (Fig. 6) over the entire range, indicating a first-order decay of the perylene concentration. Perylene is known to form a non-emitting endoperoxide in the presence of singlet oxygen. Since the rate of intersystem crossing from S^1 to T^1 in perylene is low, it is not a very efficient generator of singlet oxygen. Furthermore, nearly all of the light is absorbed by naphthyl groups. Accordingly, we propose that the loss of perylene is due

to the following sequence of reactions:



In this case the PS2VN acts both to solubilize the perylene in aqueous solution and also as a catalyst for the generation of singlet oxygen. The proximity of both naphthalene and perylene in the core of the hypercoiled PS2VN might be expected to increase the efficiency of singlet oxygen addition in this case.

Based on these experiments we conclude that polyelectrolytes containing naphthyl groups are able to trap large aromatic molecules such as anthracene and perylene in aqueous solution. Exciton migration among the proximate naphthyl groups in the centre of the hypercoiled conformation can lead to excitation of the aromatic trap, which in this case is not chemically attached to the polymer chain. That this process can lead to chemical reaction is demonstrated by the addition of singlet oxygen to perylene dissolved in an aqueous solution of SP2VN. This property does not seem to be a general characteristic of all aromatic polyelectrolytes, because aqueous solutions of poly(styrene sulfonate) do not trap significant amount of anthracene and perylene under the conditions of our experiments.

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