*Macromolecules* **1986**, *19*, 2793–2798

to the network. Their reactivities are thought to be different. They may form cross-linkages, exchange SiO bonds, or simply deactivate to be dangling ends, depending on the local constraints. A comprehensive understanding of all these reaction rates and routes is thus a prerequisite for further fine tuning of the simulation model.

It should be noted that the good agreement of our results with experiments and with Tonelli's calculations manifests the credibility of these simulations. The interpretation of network structures in randomly cross-linked systems should be aided by results reported here, and the presumed correlation between elastically ineffective material and $2C_2$ should be settled as a consequence of this work.

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# Studies of the Antenna Effect in Polymer Molecules. 10. Preparation and Luminescence Studies of Sulfonated Poly(2-vinylnaphthalene)

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ABSTRACT: Partial sulfonation of poly(2-vinylnaphthalene) (P2VN) yields water-soluble copolymers (SP2VN) that appear to exhibit hypercoiling in aqueous media. Luminescence emission studies show that excimer emission is much higher in aqueous solution than in conventional organic solvents, presumably because of closer packing of the naphthalene groups in the interior of the hydrophobic "core". Photon-counting measurements of fluorescence decay are consistent with very rapid migration and trapping of singlet energy in the hypercoiled conformation. Evidence is also presented for the preferential trapping of large aromatic groups such as perylene in the interior of the coil. Luminescence emission depends strongly on the pH and ionic strength of the medium. In frozen aqueous media at 77 K delayed emission is almost exclusively from the naphthalene excimer rather than from the "monomer" as in conventional solvents, thus confirming the ease of population of excimer sites in hypercoiled conformations.

In previous studies in this series it has been shown that polyelectrolytes containing large aromatic chromophores such as naphthalene behave as if they are "hypercoiled" in dilute aqueous solution, such that the hydrophobic aromatic groups are clustered near the center of the polymer coil, while the hydrophilic ionic groups are located on the exterior.[1,2] The first report of this work was given by Guillet and co-workers in 1981.[1] In these early studies, the polymers used were copolymers of acrylic acid containing minor quantities (8–22 mol %) of naphthylmethyl methacrylate (NMMA) which were end-trapped with anthracene to demonstrate the efficiency of energy transfer. The much higher efficiency of singlet energy migration and trapping that occurred when these polymers were dissolved in aqueous media (as compared to organic solvents) was explained as being the result of hypercoiling to form a pseudomicellar conformation in which the hydrophobic aromatic groups form the core, stabilized by hydrogen bonding, and the inorganic carboxyl groups are located on the exterior.

These conclusions have been confirmed by more recent work of Itoh et al.[3] and Morishima et al.,[4] who studied the quenching of fluorescence from amphiphilic copolymers of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) with vinyl aromatic monomers. On the basis of the increased emission of the amphiphilic probe 8-anilino-1-naphthalenesulfonate (ANS) and the higher quenching efficiency of the hydrophobic quencher bis(2-hydroxyethyl) terephthalate (BHET), it was concluded that the polymer

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solution did contain hydrophobic microdomains. However, these domains were not as effective at solubilizing hydrophobic probes as surfactant micelles such as those from cetyltrimethylammonium bromide. Morishima et al.[5] also demonstrated that block copolymers of vinylphenanthrene with methacrylic acid were more effective at forming hydrophobic microdomains in aqueous solution than were the corresponding random copolymers. The present report concerns studies of novel polymers in which the ionic groups that solubilize the polymer in water are introduced by sulfonation of poly(2-vinylnaphthalene) (P2VN). In this case all of the repeating groups in the polymer contain the naphthalene moiety and hence should contribute to the energy capture and transfer mechanism.

## Experimental Section

**Materials.** Commercial 2-vinylnaphthalene (2VN, Aldrich) was purified by adsorption chromatography, using cyclohexane as eluent and alumina as adsorbant. The ratio of length to the diameter of the column was 5:1. It was then sublimed under vacuum at 40 °C.

P2VN was prepared by 2,2'-azobis(isobutyronitrile) (AIBN)-initiated radical polymerization of purified 2VN monomer in degassed benzene solution at 60 °C. The P2VN was purified by threefold precipitation from benzene into methanol and then freeze-dried. The molecular weight (osmotic) was $M_n = 90\,400$.

Poly(2-vinylnaphthalene-*co*-2-vinylnaphthalenesulfonic acid) (SP2VN) was prepared by sulfonation of P2VN with chlorosulfonic acid ($ClSO_3H$) as the sulfonating agent in 1:1 $CCl_4$–dichloromethane solution. The temperature of the P2VN–$CHCl_3$ solution was 0 °C during the addition of $ClSO_3H$. The reaction temperature was controlled at 0 °C for 35 min and at 25 °C for 35 min. The SP2VN was precipitated in ether and washed several times with ether before drying in a circulating-air oven at 40 °C.

Benzene (Caledon, ACS reagent grade) (for polymerization of P2VN and freeze-drying) was purified by reflux over $P_2O_5$ overnight and fractionally distilled. Chloroform (Caledon, ACS reagent grade) (for sulfonation of P2VN) was shaken with concentrated $H_2SO_4$, washed with water, and then distilled over $CaCl_2$. Tetrahydrofuran (THF, Caledon, ACS reagent grade) and 2-methyltetrahydrofuran (MTHF, Aldrich) were refluxed over $LiAlH_4$ overnight and then distilled. Methanol and diethyl ether (Caledon, ACS reagent grade) were used as received. Water was threefold distilled over NaOH and $KMnO_4$.

**Polymer Characterization.** The degree of sulfonation was measured by titration of an aqueous SP2VN solution with 0.01 N NaOH solution, using phenolphthalein as indicator. The degree of sulfonation for the polymer used in this work was 77%. Sulfonation is expected to occur primarily in the 8-position on the naphthalene ring based on previous work on substituted naphthalenes.[6]

Infrared spectra of P2VN and SP2VN were recorded on a Perkin-Elmer Model 337 grating infrared spectrometer in a KBr pellet. The SP2VN showed a reduction in the 740–810-$cm^{-1}$ band for aromatic protons and the appearance of bands at 1045 and 1130–1230 $cm^{-1}$ after sulfonation. The latter were consistent with the strong vibrational bands of S=O in the $SO_3H$ group normally located at 1030–1070 and 1160–1200 $cm^{-1}$. The reduction of the 740–800-$cm^{-1}$ band attributed to the $\gamma$ vibration mode of aromatic CH was due to the decrease of the hydrogen atoms on the naphthyl group and to changes in the symmetry of the aromatic ring as a result of sulfonation.

The number-average molecular weight of the polymer was estimated to be 8400, based on osmotic pressure determination in methanol. The reduction in molecular weight was due to fractionation of the product during isolation. Only the lower molecular weight fractions were water soluble.

**Ultraviolet Spectra.** The UV absorption spectra of P2VN and SP2VN were measured with a Pye-Unicam 1800 UV spectrometer. The results are shown in Figures 1 and 2. The UV spectrum of P2VN in solution showed some change after sulfonation. The absorption maximum of P2VN in THF at 276 nm was red-shifted to 280 nm in THF–$CH_3OH$ and 282 nm in $H_2O$ or NaOH–$H_2O$ and the extinction coefficient reduced. The absorption band of P2VN at 319 nm was red-shifted to about 323 nm for all solutions. The vibrational structure of the main absorption peaks was also broadened.

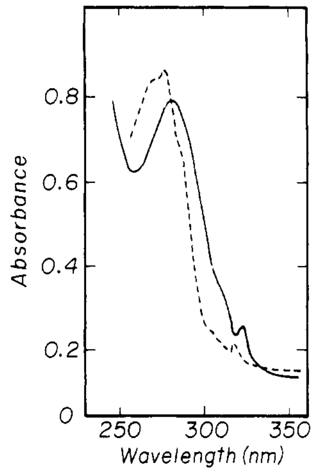

Figure 1. Ultraviolet absorption spectra of (—) SP2VN (1.45 × $10^{-4}$ M) in THF–$CH_3OH$ (4:1) and (- - -) P2VN (2.8 × $10^{-4}$ M) in THF.

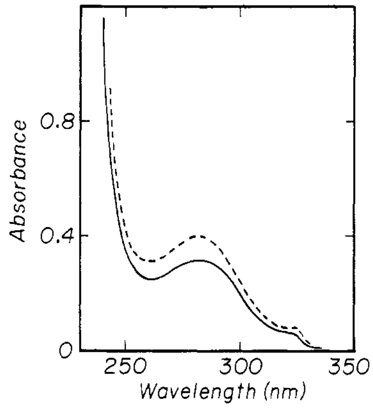

Figure 2. Ultraviolet absorption spectra of (—) SP2VN (9.0 × $10^{-5}$ M) in $H_2O$ and (- - -) SP2VN (7.3 × $10^{-5}$ M) in 0.25 N NaOH.

**Transient Measurements of Fluorescence Decay.** All solutions were degassed with five freeze–pump–thaw cycles before sealing in Pyrex test tubes. Concentrations were ca. 2 × $10^{-3}$ M. The fluorescence decay curves were measured with a single-photon-counting apparatus of standard design.[7] Two 10-$\mu$m slits were used at both the entrance and exit of the monochromator for reduction of scattered light. The samples were excited at 310 nm for measurement of the emission at >450 nm. They were excited at 290 nm for measurement of the emission at 330 nm. The lamp profile was recorded by scattering off a ludox scattering solution. The nonlinear iterative deconvolution technique was used to fit the decay curves.[8]

## Results and Discussion

**Ultraviolet Spectra.** The UV spectrum of SP2VN is similar to that of P2VN except for a slight red-shift in the absorption bands in the UV spectrum. This is the usual effect of a polar medium on the absorption spectrum of a vinyl aromatic polymer. This is illustrated in Figure 1 for P2VN, where the addition of methanol to the THF solvent shifts the absorbance maxima for naphthalene normally at 276 and 319 nm by about 5 nm to 281 and 323 nm, respectively, for the SP2VN polymer. An additional red-shift of 1–2 nm is observed when SP2VN is dissolved in water or dilute NaOH, as shown in Figure 2. This could also be attributed to the presence in the polymer of the strongly polar sulfonated naphthalene groups.

**Fluorescence Emission.** The partial sulfonation of P2VN leads to a polymer with rather unusual luminescence

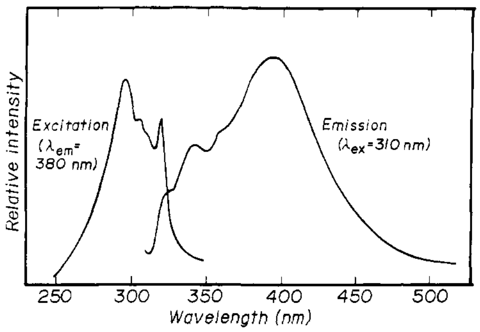

**Figure 3.** Fluorescence emission and excitation spectra of P2VN ($6.5 \times 10^{-3}$ M in THF) at 22 °C.

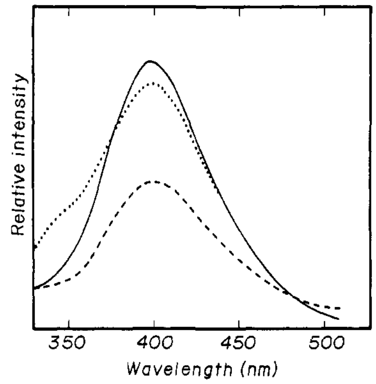

**Figure 4.** Fluorescence emission spectra of SP2VN ($4.8 \times 10^{-3}$ M) on 310-nm excitation at 22 °C: (···) in THF–$CH_3OH$ (4:1); (---) in $H_2O$; (—) in NaOH–$H_2O$ (pH 13).

characteristics, particularly when dissolved in aqueous media. The major differences between the sulfonated polymer and P2VN occur in the luminescence spectra. For example, the excitation and emission spectra for P2VN in THF solution are shown in Figure 3. Although the excimer emission with $\lambda_{max}$ 403 nm dominates the emission, there is still evidence for naphthalene monomer emission with peaks at 335, 342, and 360 nm in the spectrum. SP2VN is not soluble in THF but does dissolve in a mixture of 4:1 THF–methanol. In this solvent, as shown in Figure 4, only a trace of monomer emission is observed, while in water and dilute NaOH the emission appears to be almost entirely from the excimer. This would be consistent with the pseudomicellar model proposed by Guillet and Rendall[2] for the conformation of such polymers in aqueous solution, where the water forces the aromatic groups into closer proximity. The higher emission intensity of the polymer in dilute NaOH solution is reproducible and may be related to the higher absorbance noted in Figure 2 for alkaline solutions of the polymer. The excitation spectrum (Figure 5) for the 400-nm excimer band is similar in all three solvents except for the higher intensity in dilute alkali noted previously and corresponds to a monomeric naphthalene absorption. The excitation peak at 322 nm in 4:1 THF–methanol is shifted to 332 nm in water and dilute NaOH. *It is apparent that the conformation of the polymer in aqueous media favors either a higher number of excimer sites per chain or a more rapid transfer of excitation energy to them.*

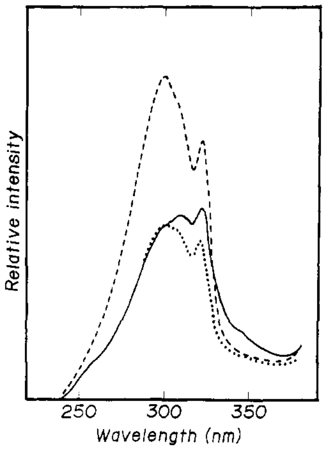

**Figure 5.** Fluorescence excitation spectra of the excimer band at 400 nm from SP2VN in solution at 22 °C: (—) in THF–$CH_3OH$ (4:1); (···) in $H_2O$; (---) in NaOH–$H_2O$.

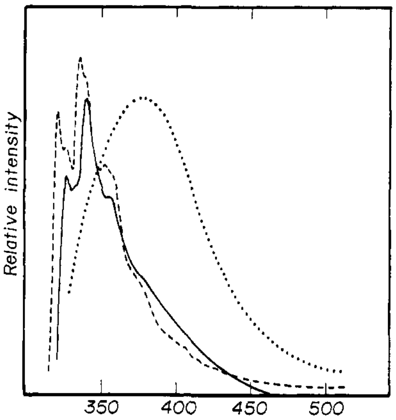

**Figure 6.** Fluorescence emission spectra at 77 K ($\lambda_{ex}$ 310): (···) SP2VN solid glass in $H_2O$; (—) SP2VN solid glass in THF–$CH_3OH$ (4:1) ($4.8 \times 10^{-3}$ M); (---) P2VN in THF–$CH_3OH$ ($6.5 \times 10^{-3}$ M).

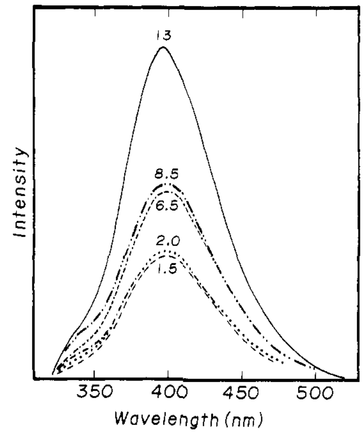

**Figure 7.** Fluorescence emission from SP2VN in aqueous solution at 22 °C: (---) 2.0 N $H_2SO_4$, pH < 2.0; (···) 0.2 N $H_2SO_4$, pH = 2.0; (-·-) 0.02 N $H_2SO_4$, pH ~ 3; (·---·) $H_2O$, pH = 6.5; (··--··) 0.02 N NaOH, pH = 8.5; (—) 0.2 N NaOH, pH > 13.

Further differences occur in the fluorescence spectra at 77 K. Figure 6 shows the emission spectra of P2VN and SP2VN in an organic glass as compared with an aqueous solution. Although these are not clear glasses at this temperature, the effects are unmistakable. In organic media P2VN and SP2VN both show emission primarily from naphthalene "monomer", with a very small excimer component. The water solution of SP2VN when frozen, however, shows almost exclusively excimer emission. Presumably the aqueous medium causes a very high concentration of excimer sites to be formed which do not require molecular motion to be completed. The intensity of the excimer emission varies considerably with the pH of the aqueous solution, even at 22 °C, as shown in Figure 7. Maximum excimer emission is shown under alkaline conditions (pH > 13) and the minimum for pH < 2. This

Table I
Monomer Emission Decay from P2VN and SP2VN

| sample | solvent | $\lambda_{ex}$ | $\lambda_{em}$ | $A_1$ | $A_2$ | $A_3$ | $\tau_1$ | $\tau_2$ | $\tau_3$ | $\chi^2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| P2VN | MTHF | 290 | 330 | 0.26 | 0.01 | <0.01 | 1.67 | 7.22 | 47.1 | 1.56 |
| SP2VN | MTHF-$CH_3OH$ (1:3) | 290 | 330 | 0.31 | 0.02 | <0.01 | 0.86 | 4.77 | 34.5 | 1.58 |
| SP2VN | $H_2O$ | 290 | 330 | 0.65 | <0.01 | <0.01 | 0.33 | 9.44 | 40.0 | 1.72 |
| SP2VN | 0.25 N NaOH | 290 | 330 | 0.29 | 0.01 | <0.01 | 0.59 | 5.33 | 35.9 | 1.78 |

Table II
Excimer Fluorescence Decay Parameters

| sample | solvent | $\lambda_{ex}$ | $\lambda_{em}$ | $A_1$ | $A_2$ | $A_3$ | $\tau_1$ | $\tau_2$ | $\tau_3$ | $\chi^2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| P2VN | MTHF | 310 | >450 | 0.08 | 0.12 | 0.09 | 7.27 | 30.8 | 85.2 | 1.31 |
| SP2VN | MTHF-$CH_3OH$ | 310 | >450 | 0.27 | 0.02 | 0.01 | 0.19 | 8.52 | 55.0 | 1.57 |
|  | $H_2O$ | 310 | >450 | 0.07 | 0.04 | 0.02 | 3.67 | 13.4 | 31.3 | 0.99 |
|  | 0.25 N NaOH | 310 | >450 | 0.07 | 0.05 | 0.02 | 3.51 | 14.9 | 33.5 | 1.29 |

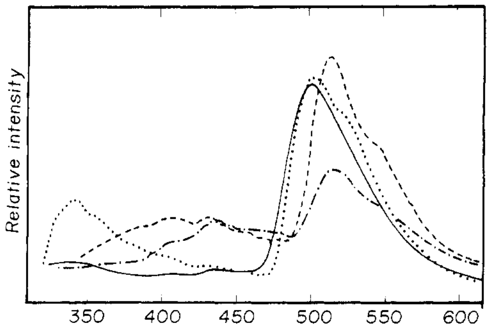

**Figure 8.** Phosphorescence and delayed emission spectra of SP2VN solid glass at 77 K on 310-nm excitation (4.8 × $10^{-3}$ M): (---) in NaOH-$H_2O$ (0.125 N); (···) in THF-$CH_3OH$ (4:1); (-·-) in $H_2O$. (—) P2VN in THF.

is presumably because preferred conformations for excimer formation occur at high pH, although it is not possible to quantify this without further measurements of the actual conformations that occur under various conditions.

**Phosphorescence and Delayed Emission.** Even more dramatic differences occur in the delayed emission from SP2VN. Figure 8 compares the delayed emission of P2VN in THF with that from SP2VN in 4:1 THF-methanol. The latter shows the normal phosphorescence emission with $\lambda_{max}$ 500 nm, but a significantly increased delayed emission ($\lambda_{max}$ 330 nm) attributable to naphthalene monomer, as compared with the unsulfonated polymer. However, when SP2VN is dissolved in water or dilute NaOH, almost all of the delayed emission is from the excimer with $\lambda_{max} \sim$ 400 nm and an additional species with $\lambda_{max}$ 435 nm as yet unidentified. Furthermore, the phosphorescence peak is red-shifted about 12 nm from 503 to 515 nm. All of these results are consistent with the occurrence of a large number of excimer sites in SP2VN in aqueous solution. The identity of a second excimer species cannot be substantiated from these measurements alone. However, it might be expected that excimers may form between an unsubstituted naphthalene and a naphthalenesulfonate, or possibly two of the latter might show emission red-shifted from the normal excimer due to the highly polar character of the sulfonate group.

Measurements of the intensity of the delayed emission as a function of the phosphorescence intensity are shown on a log-log plot in Figure 9 for SP2VN in dilute NaOH and in THF-methanol. The slopes are 1.9 and 1.6, respectively, reflecting the biphotonic character of the delayed fluorescence (P type) emission.

**Transient Measurements. Monomer Decays.** Measurement of the decay of naphthalene monomer emission were made by procedures described previously. The decays for both monomer and excimer could not be fitted with double exponentials of the type used with the Birks kinetic scheme. Accordingly, triple-exponential fits were used[9,10] of the form

$$i(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$$

Values of the various parameters for naphthalene monomer emission from P2VN in various solvents are summarized in Table I.

Although it is not always possible to associate each lifetime with a distinct emission species, Phillips et al.[11,12] have associated $\tau_1$ for P2VN with the decay of monomer species to form excimer via energy transfer and rotational transfer, $\tau_2$ with the lifetime of naphthalenes trapped in conformations unable to form excimers or participate in energy transfer, and $\tau_3$ with naphthalene emission from monomer created by dissociation of the excimer. The $A$ values relate to the relative contributions of the various emissions. From Table I it is clear that sulfonation of P2VN leads to a substantial reduction in the lifetime $\tau_1$ of the monomer species (from 1.6 to 0.86 ns) in organic solution and a still further reduction in dilute NaOH ($\tau_1$ = 0.59 ns) and water ($\tau_1$ = 0.33 ns). This would be consistent with the more rapid formation of excimers in aqueous media and with a more rapid and efficient population of these by energy migration and trapping in the micellar conformation that is proposed for these polymers.

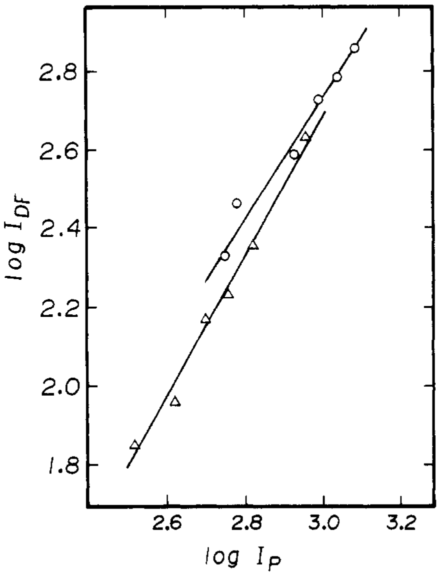

**Figure 9.** Intensity of delayed emission ($I_{DF}$) as a function of phosphorescence intensity ($I_P$) for SP2VN in (△) dilute NaOH and (○) in THF-methanol (4:1) ($c$ = 4.8 × $10^{-3}$ M; $T$ = 77 K).

Table II summarizes data on the decay of the excimer emission ($\lambda$ > 450 nm). Again, a triexponential fit is required. However, a major difference between P2VN and

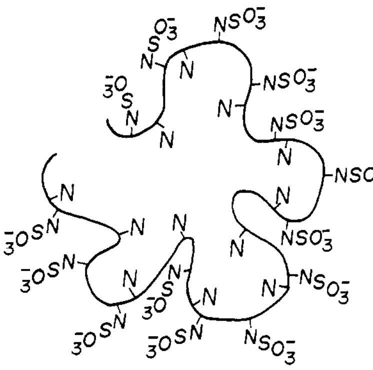

**Figure 10.** Proposed hypercoiled conformation for SP2VN in aqueous solution.

SP2VN is the much more rapid decay of the excimer emission in the latter. For P2VN in THF, $\tau_1$ is 7.3 ns, whereas in SP2VN in THF–MeOH, $\tau_1$ is only 1.2 ns and accounts for most of the observed decay. In aqueous solution, the excimer decays are more normal, with components described by lifetimes of about 3.5, 14, and 32 ns for both water and dilute NaOH. However, all of the measurements on SP2VN show that the lifetime of the excimer is shorter for the major decay parameters than for P2VN. Since there is little evidence for extensive dissociation of the excimer back to "monomer" and the emission intensities for P2VN are comparable, it seems likely that the higher polarity of the aqueous medium may increase $k_{FD}$, the rate constant for emission from the excimer, thus causing a more rapid decay of the excimer species.

In experiments of this kind, it is usually not possible to assign lifetimes from multiexponential fits to particular excimer species. In our previous studies on similar polymers in organic solution, we have shown that excimer dissociation is slow relative to emission and so the simple Birks mechanism does not apply. Furthermore, partially sulfonated P2VN will have a large variety of possible excimer sites, including those between two sulfonated N units, those between two unsulfonated N groups, and those between a sulfonated and unsulfonated N moiety. Further complexities are introduced due to configurational effects involving meso and racemic diads.[13] Conceivably in this case the excimer emission might result from as many as six emitting species.

## Discussion

The photophysical phenomena observed in aqueous solutions of SP2VN are all consistent with the existence of a hypercoiled structure for the polymer, as proposed by Holden et al.[1] and Guillet and Rendall[2] for other polyelectrolytes containing large aromatic chromophores. The difference in this case is that both the interior "core" and the exterior ionized layer will contain naphthalene groups. A structure such as that shown in Figure 10 is envisaged, where the unsulfonated naphthalene chromophores are clustered in the interior, while the sulfonated groups are on the exterior. The hydrophobic bonding of the internal unsubstituted naphthalene groups may bring them into very close proximity (~3–4 Å), thus giving a high concentration of excimer sites. Photon energy absorbed anywhere in the polymer chain would undergo rapid singlet energy migration to these sites, and excimer emission would result. The much higher ratio of excimer to monomer emission for SP2VN in water compared to organic solvents, where one might expect a closer approximation to a random coil conformation, is consistent with the idea that either the conformation shown in Figure 10 is more compact, thus bringing the chromophores closer together and increasing the efficiency of energy migration, or the conformation provides more excimer-forming sites (or both).

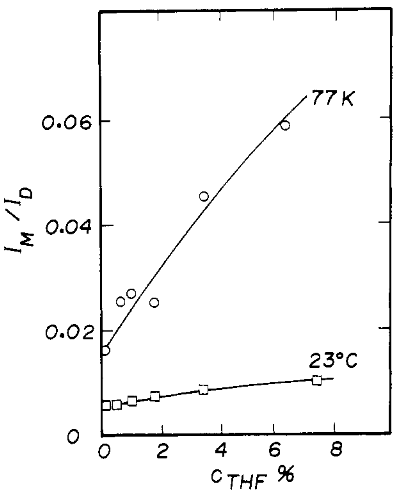

**Figure 11.** Ration of monomer to excimer emission $I_M/I_D$ for aqueous solutions of SP2VN as a function of THF concentration.

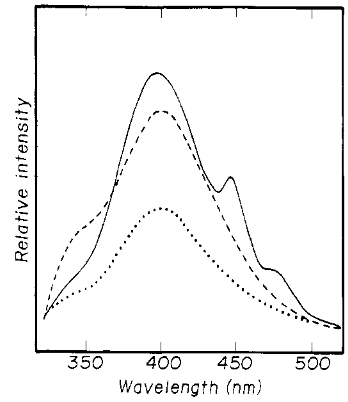

**Figure 12.** Fluorescence emission from SP2VN solutions after treatment with an ether solution of perylene ($\lambda_{ex}$ = 310 nm, $T$ = 22 °C, $c$ = 4.8 × $10^{-3}$ M): (—) 0.125 N NaOH; (···) $H_2O$; (---) THF–$CH_3OH$ (4:1).

Further evidence for the proposed structure of the polymer in aqueous solution was obtained by addition of small amounts of THF to the aqueous solution of SP2VN. The THF might be expected to be absorbed preferentially in the hydrophobic core, thus causing some expansion of the polymer coil. Figure 11 shows that there is a significant increase in the ratio of emission intensity of the monomer to that of the excimer ($I_M/I_D$) even when quite small amounts of organic solvent are added, both for measurements at 23 °C and for those at 77 K. This is consistent with a reduction in the density of aromatic groups in the core, which is responsible for the high efficiency of excimer trapping and emission.

In an additional series of experiments it was shown that other large aromatic chromophores could, under certain circumstances, be trapped in the hydrophobic core of the polymer coil. A dilute solution of perylene in diethyl ether was tumbled with an aqueous solution of SP2VN overnight. The ether was then separated and the aqueous solution pumped several hours under vacuum to remove dissolved ether. The solution was then centrifuged and decanted. The luminescence results are shown in Figure 12.

Strong emission bands at 450 and 480 nm characteristic of perylene are visible in the SP2VN solution in dilute NaOH both when excited directly and when the naphthalene is excited at 310 nm. Under these conditions the aqueous solution of SP2VN at pH 6 did not absorb any perylene, although some evidence of trapping was obtained in subsequent experiments using higher concentrations of perylene. The concentration of perylene was estimated to be $1.4 \times 10^{-6}$ M by UV absorption measurements. No perylene was found dissolved in water treated with ether solutions of perylene in control experiments. When SP2VN was dissolved in THF–methanol along with $1.5 \times 10^{-6}$ M perylene, no perylene emission was observed when the naphthalene groups in the polymer were excited at 310 nm, although direct excitation of the perylene at 330 nm showed the expected emission. Thus, we conclude that only in the dilute NaOH solution is the perylene trapped in proximity to the naphthalene groups so that efficient energy transfer can occur. In organic solution at these concentrations the traps are apparently uniformly dispersed in solution rather than concentrated in the pseudomicellar structure of the polymer.

In conclusion, it appears possible to design aromatic polyelectrolytes from polymers containing both hydrophobic and hydrophyllic groups, which under appropriate conditions of pH and ionic strength will hypercoil to form pseudomicellar conformations in aqueous solution. These conformations will reversibly trap hydrophobic organic molecules in the interior of the polymer coil. If these molecules have the correct photophysical characteristics, as in the case of naphthalene and perylene, the trap can be selectively excited by light absorbed only by the naphthalene groups. Presumably the excitation reaches the trap via singlet energy migration and transfer. This represents a novel application of the antenna effect in synthetic polymers.

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**Registry No.** Perylene, 198-55-0.

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# Fluorescence and Energy Migration in 4-Vinylbiphenyl Homopolymer and Alternating and Random Copolymers of 4-Vinylbiphenyl with Methyl Methacrylate

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ABSTRACT: The fluorescence properties of random and alternating copolymers of 4-vinylbiphenyl and methyl methacrylate are compared with those of a model polymer with ca. 1 mol % 4-vinylbiphenyl (remainder methyl methacrylate) and the homopolymer of 4-vinylbiphenyl. For the alternating copolymer there is no excimer fluorescence, unlike the random copolymer. The singlet energy migration constant ($\Lambda_S$) was estimated by the method of comparative fluorescence quenching. It was found that $\Lambda_S$ is larger for the alternating copolymer than for the random copolymer (ca. $1.1 \times 10^{-5}$ and $3 \times 10^{-7}$ cm$^2$/s, respectively). $\Lambda_S$ is estimated to be 0 for the homopolymer. These values are smaller than values for the corresponding naphthalene copolymers.

## Introduction

It is well-known that energy migration along polymer chains can be terminated via excimer formation. Introducing bulky groups[1] on the chromophore is an effective way to reduce excimer formation; however, the energy transfer rate may also be reduced. Fox and co-workers noted in their early polymer photophysical experiments that alternating naphthalenic polymers exhibited little or no excimer fluorescence.[2] Our previous studies on alternating copolymers of 2-vinylnaphthalene with methyl methacrylate and methacrylic acid demonstrated not only that excimer formation was essentially eliminated but also that energy transfer rate was still significant.[3] This report is an extension of this previous study. The nonplanar molecule[4,5] biphenyl was selected to make an alternating copolymer. The Förster self-transfer distance is very small for this chromophore, ca. 3.11 Å.[6]

Singlet energy migration rates were estimated for the homopolymer and the alternating and random copolymers by the method of comparative quenching.[8] In contrast to the interpretation of Abuin et al.[7] no singlet energy migration was observed in the homopolymer, and the average energy migration distance ($L_S$) for the alternating copolymers was larger than that of the random copolymers, similar to the results of our previous study.[3] We will return to this point in the Discussion.

## Experimental Section

**A. Materials and Polymerization.** The starting materials for sample preparation were 4-vinylbiphenyl (4VBP) (COC), ethylaluminum sesquichloride ($Et_2AlCl \cdot EtAlCl_2$) (Aldrich), and methyl methacrylate (MMA) (J. T. Baker). 4VBP was purified[9] by chromatographic adsorption on alumina from a 2:1 (v/v) benzene–*n*-hexane solution and recrystallized from methanol, mp

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