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# Studies of the Antenna Effect in Polymer Molecules. 13. Preparation and Photophysical Studies of Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene)

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ABSTRACT: Copolymerization of 2-vinylnaphthalene with sodium styrenesulfonate yields the water-soluble polymer, poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS–VN). Luminescence emission studies have shown that PSSS–VN exhibits hypercoiling in aqueous media. Because excimer formation in PSSS–VN has been found to be an intramolecular process, the ease of populating excimer sites was used as a measure of the polymer conformation. The efficiency of excimer formation is much lower in methanol, in which the polymer is expected to display a conformation closer to a random coil, than in aqueous solution. An increase in the ionic strength of the solution resulted in an increase in the efficiency of excimer formation. The polarity of the interior of the polymer core has been found to be considerably lower than the surrounding water. This enables the solubilization of large hydrophobic compounds. Energy transfer from electronically excited pendant naphthalene groups to the solubilized probe can induce photochemical reactions of the probe.

## Introduction

A recognition of the importance of the photocatalytic activity of natural "antenna pigments", such as chlorophyll in photosynthesis, leads to the question whether such a process can be mimicked in the laboratory. This explains the growing interest in the synthesis and studies of the properties of synthetic polymers displaying the "antenna effect". The first "antenna polymers" consisted of a sequence of pendant aromatic groups with a small number of low-energy traps located either at the end of the polymer chain or randomly distributed along the backbone of the polymer.[1–6] Recently, efforts to create modified antenna systems have been undertaken.[7–11] The polymers consist of hydrophobic and hydrophilic groups. Such polyampholytes have been shown to form a "pseudo-micellar" conformation in dilute aqueous solution. This conformation not only enhances the efficiency of energy transfer to the covalently attached trap but also has been shown to solubilize large hydrophobic compounds. The solubilized molecules can then act as energy traps.

The present paper reports the results of studies of the photophysical properties of the novel "antenna type" polyelectrolyte poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS–VN). The goal of these studies was to determine the conformation of the polymer in aqueous solution on the basis of its photophysical properties.

## Experimental Section

**Materials.** Commercial 2-vinylnaphthalene (2VN, Aldrich) was purified by adsorption chromatography, using cyclohexane as eluent and alumina as adsorbant. The purity of the compound (99.5%) was confirmed by gas chromatography.

Commercial sodium styrenesulfonate (SSS, Du Pont) was purified by recrystallization from a 9:1 (v/v) mixture of methanol and water, followed by two recrystallizations from pure methanol (Caledon, Spectro grade).

Poly(sodium styrenesulfonate-*co*-2-vinylnaphthalene) (PSSS–VN) was prepared by 2,2′-azobis(isobutyronitrile) (AIBN) initiated radical polymerization of SSS and 2VN monomers in degassed dimethyl sulfoxide (DMSO) solution. The polymerization was carried out for 21 h at 60 °C. The resulting polymer was then precipitated with 1-butanol, filtered, washed three times with diethyl ether, and dried in a vacuum oven at 40 °C. The polymer was dissolved in water, exhaustively dialized (Fisher, cellulose tubing, cutoff 12000–14000 g $mol^{-1}$) against deionized water, and freeze-dried.

DMSO, 1-butanol, and diethyl ether (all Caledon, ACS reagent grade) were used without further purification. Distilled water was passed through a deionizer and subsequently filtered through a trace organic removal cartridge (Norganic, Millipore). Ethyl alcohol (anhydrous, Aldrich), spectral grade acetone (Aldrich), and spectral grade methanol (Caledon) were used without further purification. All solvents used in polarity studies were spectroscopic quality and were used as received.

9,10-Dimethylanthracene (DMA) (Aldrich, 99%) and 10-nonadecanone (Calbiochem) were recrystallized three times from ethyl alcohol. 1-Pyrenecarboxaldehyde (PCA) (Aldrich, 98+%) was recrystallized three times from spectral grade methanol. 8-Anilino-1-naphthalenesulfonic acid ammonium salt (ANS) (Aldrich) was recrystallized three times from distilled water.

The polymer solutions were prepared by using deionized water. The ionic strength of the system was adjusted by adding a sodium chloride solution.

**Procedures. Polymer Characterization.** Elemental analysis (Galbraith Laboratories, Inc.) was used to determine the composition of the polymer. The polymer consists of 60 mol % 2VN and 40 mol % SSS (66.3% C, 5.62% H, 7.34% S, 12.68% O, 8.07% Na). From the high-speed meniscus depletion method of Yphantis[12] (Beckman Model E analytical ultracentrifuge), the weight-average molecular weight, $\bar{M}_w$, of the polymer was determined to be 310000. By application of the simple copolymerization model the values of the reactivity ratio were determined to be 1.0 and 0.32 for 2VN and SSS, respectively. The solubility of the polymer in water was found to be about 6 g $dm^{-3}$ at room temperature. The polymer is also soluble in DMSO, DMF, THF, and methanol.

**Steady-State Spectra.** Steady-state emission and excitation spectra were recorded at room temperature on a Spex Fluorolog-2 fluorescence spectrometer. Emission spectra were corrected for the wavelength dependence of the detector response by using an internal correction function provided by the manufacturer.

**Transient Measurements of Fluorescence Decay.** The fluorescence decay curves were measured by using a single-photon-counting apparatus. The solutions were degassed with five freeze–pump–thaw cycles before sealing in quartz tubes. The samples were excited at 280 nm, and emissions at 330 nm for monomer and 450 nm for excimer were measured. The lamp profiles for monomer and excimer decay were obtained by use of reference compounds with lifetimes of 1.10 and 1.47 ns, respectively. The nonlinear iterative deconvolution technique was used to fit the decay curves.

**Viscosity Measurements.** The viscosity of the polymer solutions was measured with the automatic viscometer described previously.[13] The values of the intrinsic viscosity and effective hydrodynamic volume of PSSS-VN in aqueous solution at different ionic strengths were determined by the method described elsewhere.[14]

**Solubilization of Probes.** Solubilization of DMA and 10-nonadecanone in aqueous polymer solution was achieved by slowly

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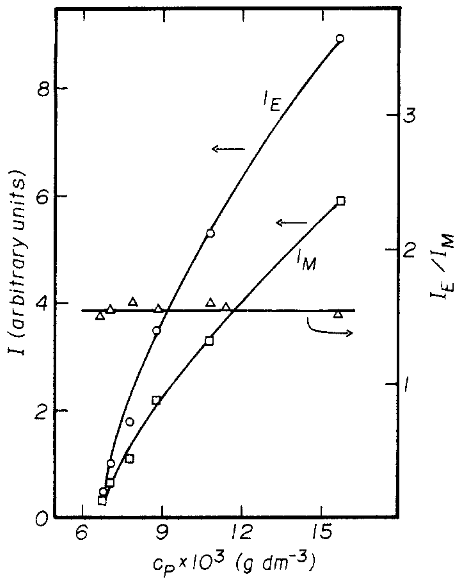


**Figure 1.** Dependence of the monomer ($I_M$) and excimer ($I_E$) intensity and the ratio of the excimer-to-monomer emission ($I_E/I_M$) on polymer concentration in aqueous solution.

injecting microliter quantities of probe dissolved in acetone and ethyl alcohol, respectively, into milliliter quantities of polymer solution. The mixture was shaken for 5 min and allowed to equilibrate in the dark for 2–4 h.

Solubilization of oxygen in the aqueous polymer solution was achieved by first saturating the solution with oxygen at defined oxygen pressures in the gas phase and then equilibrating for 4 h.

## Results and Discussion

**Steady-State Emission Spectra.** As was shown in the previous paper of this series,[11] the emission spectrum of PSSS–VN in aqueous solution consists of two bands. The shorter wavelength structured band ($\lambda_{max}$ = 335 nm) was assigned to monomer emission, and the longer wavelength band ($\lambda_{max}$ = 382 nm) was attributed to excimer fluorescence. The fluorescence excitation spectrum of PSSS–VN in aqueous solution has been shown to match that of the absorption spectrum. The shape of the excitation spectrum in the 250–480-nm spectral range, monitored at different emission wavelengths, has been found to be nearly identical. None of the spectra displayed the additional excitation bands indicating the formation of ground-state dimers.

Figure 1 shows the dependence of the monomer and excimer intensity as well as the ratio of excimer to monomer emission on the polymer concentration. As expected, an increase in the polymer concentration results in an increase of the monomer and excimer fluorescence intensity. It should be stressed, however, that within experimental error no change in the $I_E/I_M$ ratio with polymer concentration was observed. This fact shows that excimer formation in an aqueous solution of PSSS–VN is strictly an intramolecular process.

It has been found that the relative efficiency of excimer formation, measured as a ratio of $I_E/I_M$, in PSSS–VN is solvent dependent, being the highest in water solution. Figure 2 shows the dependence of $I_E/I_M$ on the mole fraction of water $x_{H_2O}$ in methanol–water solutions. An increase in the mole fraction of water in the range $0 < x_{H_2O} < 0.7$ results in a small decrease in the ratio of excimer to monomer emission. A further increase in the mole fraction of water ($x_{H_2O} > 0.7$) yielded a rapid increase in the $I_E/I_M$ ratio. A similar type of dependence was observed for various mixtures of DMSO and water. It is known that excimer emission in polymer solutions does not depend on the viscosity of the pure solvent. Two general reasons can thus be considered as responsible for the observed effect: (1) the change in the lifetimes of the emitting species for different solvent composition and (2) the solvent-induced changes in the conformation of the macromolecular coil. Transient measurements (see below) have shown that the excimer lifetimes are the same in methanol and water, while the monomer fluorescence lifetimes are longer in aqueous solutions of PSSS–VN. Thus differences in the lifetimes cannot explain the observed phenomena. Generally, the polarity of the solvent is not believed to be responsible for changes in the efficiency of excimer formation in polymer solutions.[15] It seems that the situation is slightly different for aqueous solutions of PSSS–VN. On the basis of the reactivity ratios, one can assume that the PSSS–VN copolymer consists of approximately a random arrangement of pendant hydrophobic naphthalene groups and hydrophilic styrenesulfonate units. The conformation of such a polymer is expected to be highly dependent on the polarity of the solvent. The considerable difference in the values of the dielectric constants of methanol ($\epsilon$ = 32.63) and water ($\epsilon$ = 78.54)[16] may thus lead to a different conformation of PSSS–VN in the two solvents. The much higher efficiency of excimer formation in water compared to that in methanol or DMSO indicates that PSSS–VN adopts a compact conformation that favors excimer formation in aqueous solution. It seems that the pseudomicellar model proposed by Guillet et al.[7-9] for similar types of polymers may be applied to describe the conformation of PSSS–VN in aqueous solution. The hydrophobic–hydrophilic interactions between water and PSSS–VN lead to the formation of a polymer core with naphthalene groups clustered in the interior. The naphthalene chromophores are thus much closer together than would be expected for the expanded polymer chain. This increases the probability of excimer formation.

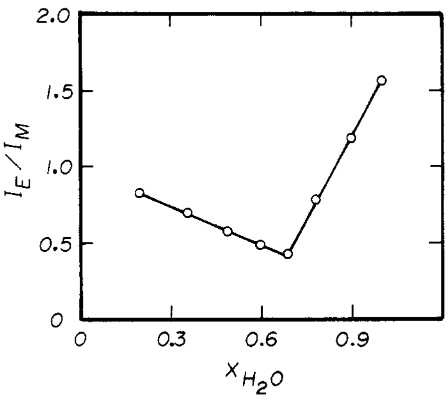


**Figure 2.** Dependence of the efficiency of excimer formation in PSSS–VN ($c_p$ = 0.01 g dm$^{-3}$, given as a ratio $I_E/I_M$) on the mole fraction of water in methanol–water solutions.

Studies of the effect of ionic strength on the efficiency of excimer formation in aqueous solutions of PSSS–VN support the above findings. It is well-known that a change in the ionic strength of the aqueous polymer solution will alter the dimensions of the macromolecular coil. Figure 3 shows the dependence of $I_E/I_M$ (curve a) and effective hydrodynamic volume of the polymer coil ($V_{eff}$), measured by intrinsic viscosity (curve b), on the ionic strength of the aqueous polymer solution. As expected, an increase in the ionic strength resulted in a gradual decrease in the dimensions of the polymer coil. Interestingly, the relative efficiency of excimer formation decreased slightly in the ionic strength region $2 \times 10^{-6}$–$2.5 \times 10^{-2}$. A further increase in the ionic strength, up to $I = 1$, produced a rapid increase

**Table I**
**Monomer and Excimer Emission Decays for PSSS-VN in Aqueous and Methanol Solutions**

| sample | solvent | $\lambda_{ex}$, nm | $\lambda_{em}$, nm | $A_1$ | $A_2$ | $A_3$ | $\tau$, ns | $\tau$, ns | $\tau$, ns | $\chi^2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| PSSS-VN | $H_2O$ | 280 | 320 | 0.22 | 0.21 | 0.01 | 16.8 | 43.4 | 91.5 | 1.1 |
| PSSS-VN | $H_2O$ | 280 | 450 | 0.06 | 0.03 | | 36.3 | 91.2 | | 1.38 |
| PSSS-VN | MeOH | 280 | 320 | 0.68 | 0.12 | <0.01 | 10.0 | 26.7 | 77.0 | 1.03 |
| PSSS-VN | MeOH | 280 | 450 | 0.38 | 0.25 | | 36.2 | 94.5 | | 1.02 |

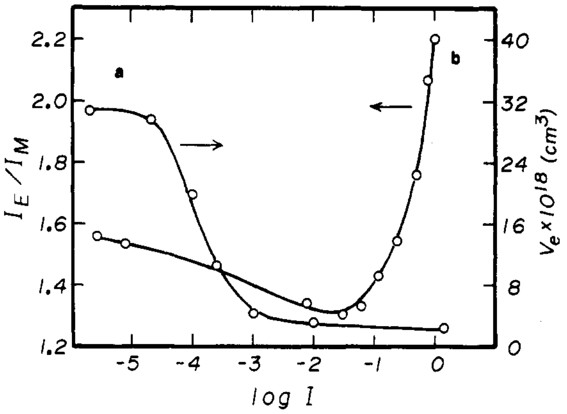


**Figure 3.** Dependence of the relative efficiency of excimer formation ($I_E/I_M$, curve a) and the effective hydrodynamic volume of the polymer coil ($V_{eff}$, curve b) on the ionic strength of the solution (log $I$).

in the ratio of $I_E/I_M$. Hence, the first 4 orders of magnitude increase in the ionic strength resulted in a very pronounced decrease in the dimensions of the polymer coil but had little effect on the photophysical properties of the polymer. The slight decrease in the values of $I_E/I_M$ for contraction of the polymer core may be due to a change in the spatial orientation of the naphthalene groups, which lowers the probability of forming the sandwich conformation needed for excimer formation. It was observed, however, that below a "critical volume" ($V_{eff} = 3 \times 10^{-18}$ cm$^3$) a slight decrease in the effective hydrodynamic volume of the polymer coil yielded a rapid increase in the relative efficiency of excimer formation. This phenomenon may be explained by assuming that at low values of the ionic strength, excimer formation in PSSS-VN occurs mainly between nearest neighbors, while at high ionic strength, nonnearest neighbors can participate to a greater extent in excimer formation. Considering that excimer formation requires proximity (3-4 Å) and proper spatial orientation between two chromophores, one can easily visualize why such a process becomes effective at a defined value of $V_{eff}$. It seems that the effect of ionic strength on the photophysical properties of PSSS-VN supports the suggestion of a pseudomicellar conformation for the copolymer in aqueous solution.

Figure 4 shows the steady-state fluorescence spectrum of a PSSS-VN film at room temperature. The spectrum displays only excimer emission attributed to both intermolecular and intramolecular excimer formation.

**Transient Measurements.** Fluorescence decay of PSSS-VN for both monomer and excimer was measured in water and methanol solution by the single photon counting method. The fluorescence decays in aqueous solution were very similar to those observed in methanol. The decays could not be fitted with the double exponentials of the type used in the Birks kinetic scheme.[17] Accordingly, for monomer decay, triple-exponential fits of the form presented below were used:

$$i(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) \qquad (1)$$

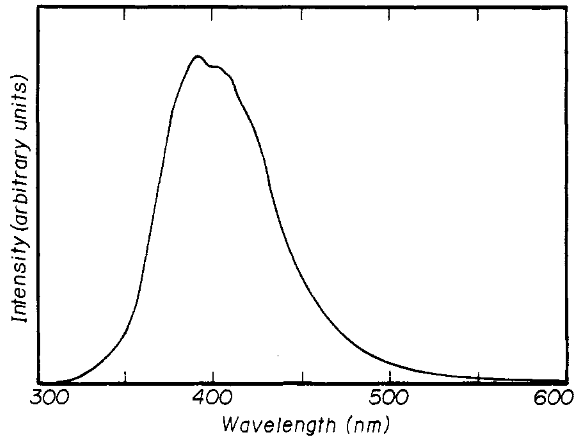


**Figure 4.** Fluorescence spectrum of a film of PSSS-VN at room temperature ($\lambda_{ex}$ = 280 nm).

The excimer fluorescence decay was found to be best fitted to a double-exponential equation of the type

$$i(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \qquad (2)$$

It should be stressed that both of the excimer components are decay components. An excimer-rising component was not observed under the experimental conditions. This indicates that excimer formation in PSSS-VN occurs very rapidly. (Excimer is formed in less than a 1 ns, which is the experimental limit of the equipment used.) The above observation is in agreement with the results for other polymers consisting of pendant naphthalene chromophores.[18,19] For example, the very rapid rate of excimer formation for copolymers of 2-vinylnaphthalene and maleic acid in aqueous solution has been attributed to the existence of preformed excimer sites in the polymer. It has been suggested that the excitation energy can migrate along the polymer backbone until a preformed excimer site is reached.[18] Table I lists the parameters characterizing monomer and excimer decays of PSSS-VN in aqueous and methanol solution. Although it is not possible to associate each lifetime with a distinct emitting species, the component characterized by the longest lifetime ($\tau_3$) in the monomer decay is probably due to overlap between monomer and excimer fluorescence. This conclusion is in agreement with the results obtained previously for studies of the quenching of PSSS-VN fluorescence by 2-undecanone.[10] 2-Undecanone solubilized in an aqueous solution of PSSS-VN selectively quenched monomer emission but the long decay component of the monomer emission was not affected. Additionally, the excimer decays were found to be identical in the presence and absence of 2-undecanone. The above data indicated that excimer sites do not dissociate in the time scale of the experiment. The existence of two excimer decay components for PSSS-VN may be explained by the similarity of the decay profile observed for poly(2-isopropenylnaphthalene).[19] Itagaki and Guillet[19] explained the observed double-exponential decay (also without a rising component) as connected with the existence of two types of excimers: a wholly overlapping excimer ("normal" excimer) and a partially overlapping excimer ("second" excimer).

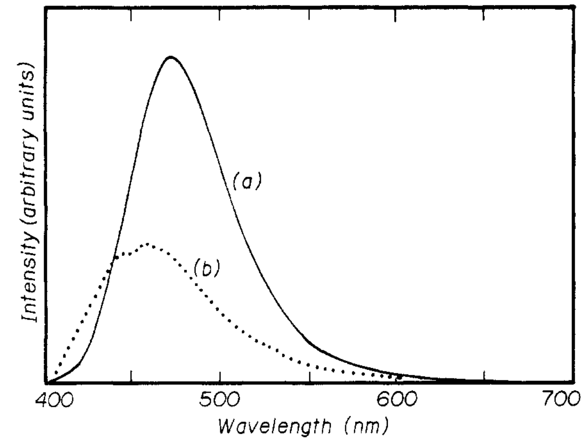
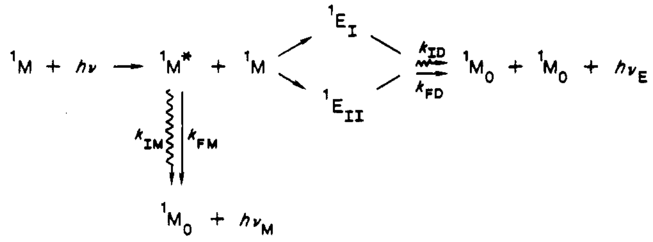


**Figure 5.** Fluorescence spectrum of 1-pyrenecarboxaldehyde in water (a) and PSSS–VN aqueous solution (b) ($c_{pol} = 1 \times 10^{-5}$ M).

On the basis of studies of the steady-state and transient fluorescence of PSSS–VN in aqueous solution, the following kinetic scheme of the most important photophysical processes occurring in the system can be proposed



where $^1M$ and $^1M^*$ are the pendant naphthalene monomer group and $^1E_I$ and $^1E_{II}$ stand for the "normal" and "second" excimer.

**Polarity of the Polymer Core Microenvironment.** Because PSSS–VN adopts a pseudomicellar conformation in aqueous solution, one would expect the presence of hydrophobic naphthalene groups clustered in the interior of the polymer core to lead to the formation of specific microenvironments dispersed throughout the aqueous phase. The polarity of these microdomains should be different from that in the water phase. Changes in the absorption and emission characteristics of dyes solubilized in the interior of micelles of low molecular weight are commonly used to describe the polarity of these environments. The spectral changes are usually correlated to solvent polarity parameters such as the dielectric constant ($\epsilon$) for a series of solvents. From a suitable solvent property and on the basis of the characteristic absorption and emission spectrum of the dye solubilized in the micelle, the polarity of the microdomain can be estimated. The method based on changes in the fluorescence spectrum is more sensitive than that using the absorption.

8-Anilino-1-naphthalenesulfonic acid ammonium salt (ANS) and 1-pyrenecarboxaldehyde (PCA) were used to study the polarity of the microenvironment of the polymer core created in an aqueous solution of PSSS–VN. These dyes exhibit a change in the quantum yield of fluorescence and in the position of the fluorescence maximum on solvent polarity.[20,21] In both cases a red shift in the position of the fluorescence maximum is observed with an increase in the polarity of the medium. The fluorescence quantum yield of ANS decreases with an increase in the dielectric constant of the solvent, equal to 0.64 in 2-propanol and 0.0020 in water solution.[20] The fluorescence quantum yield of PCA changes in the opposite direction from 0.07 in 2-propanol to 0.42 in water solution.[22] Figure 5 shows the fluorescence spectrum of PCA in water and in an aqueous solution of PSSS–VN ($c_p = 1 \times 10^{-5}$ M). It can be observed that the maximum of the fluorescence band of PCA is blue-shifted and the intensity is considerably lower in the polymer solution than that observed in water. Figure 6 shows the dependence of the position of maximum fluorescence of PCA on the dielectric constant of the solvents. The position of the fluorescence maximum of the dye solubilized in an aqueous solution of PSSS–VN ($c_p = 1 \times 10^{-5}$ M) is also marked on the graph. A comparison of the relative fluorescence intensity and position of the fluorescence maximum of the dyes in the solvents used and in polymer solution leads to the conclusion that the polarity of the polymer core microenvironment is close to that of methanol. The above observation provides additional support for a pseudomicellar conformation of PSSS–VN in aqueous solution.

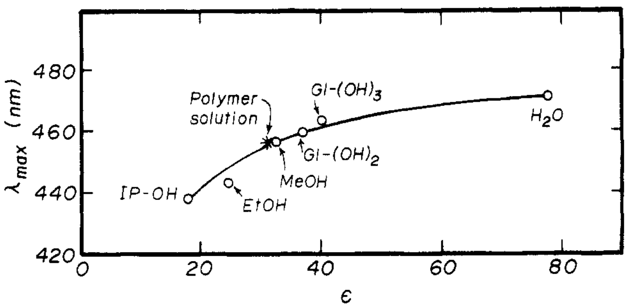


**Figure 6.** Dependence of the position of the fluorescence maximum of 1-pyrenecarboxaldehyde on the dielectric constant ($\epsilon$) of various solvents and the position of the fluorescence maximum of PCA in polymer solution (*).

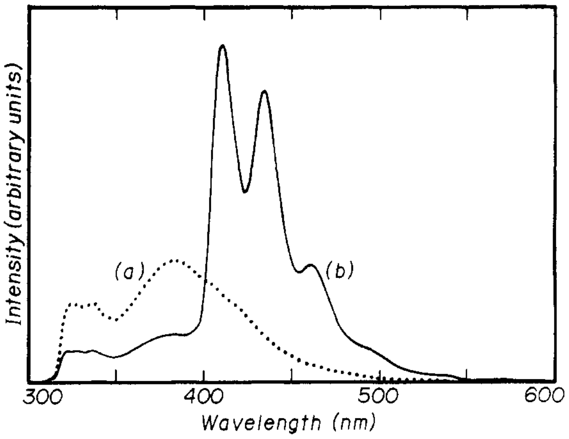


**Figure 7.** Steady-state fluorescence spectrum of PSSS–VN ($c_p$ = 0.01 g dm$^{-3}$) in aqueous solution (a) and emission spectrum of the polymer containing solubilized DMA ($c_{DMA}^{tot} = 2 \times 10^{-6}$ M) (b) ($\lambda_{ex}$ = 280 nm).

**Solubilization of Hydrophobic Compounds and Energy Transfer in the PSSS–VN Photozyme.** Figure 7 shows the steady-state fluorescence spectrum of PSSS–VN in aqueous solution (curve a) and the fluorescence spectrum of the PSSS–VN photozyme containing solubilized 9,10-dimethylanthracene (DMA) (curve b). A comparison of the spectra shows that solubilization of DMA results in a decrease of the naphthalene emission and the appearance of DMA fluorescence in the 400–490-nm spectral region. This decrease in emission is due to energy transfer from pendant naphthalene chromophores to the DMA molecules. A comparison of the fluorescence excitation spectrum of PSSS–VN (Figure 8, curve a) and PSSS–VN + DMA (Figure 8, curve b) also leads to the same conclusion. Similar results have been obtained for several other polynuclear aromatic compounds (PNA) solubilized in aqueous solutions of PSSS–VN.[11] It was

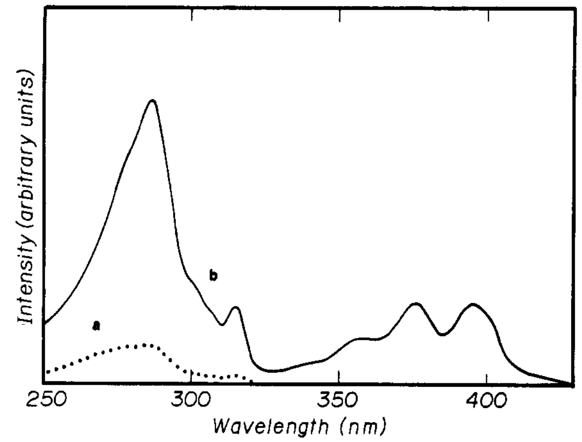


**Figure 8.** Fluorescence excitation spectra of PSSS–VN in aqueous solution (a) and photozyme containing solubilized DMA (b) ($\lambda_{em}$ = 440 nm).

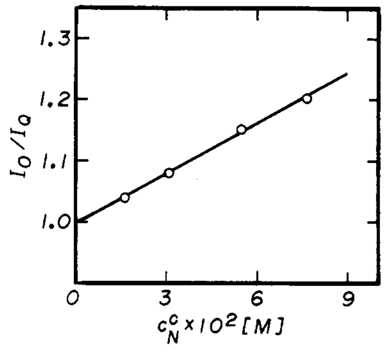


**Figure 9.** Stern–Volmer plot of the ratio of fluorescence intensities ($I_O/I_Q$) in the absence ($I_O$) and presence of quencher ($I_Q$) versus concentration of 10-nonadecanone in the polymer core microphase.

shown that electronic energy transfer from polymeric naphthalene chromophores to PNA compounds occurs according to the long-range Förster mechanism.[11]

It has been observed that some large sparingly water-soluble aliphatic ketones such as 2-undecanone or 10-nonadecanone quench the fluorescence of PSSS–VN in aqueous solution, due to solubilization of the ketone molecules in the photozyme. The concentration of the ketone in the polymer pseudophase can be calculated by the method described previously.[14] Figure 9 shows a plot of $I_O/I_Q$ for polymer fluorescence quenching versus concentration of 10-nonadecanone in the photozyme. The quenching process obeys the Stern–Volmer kinetic equation. Thus the singlet–singlet energy-transfer process from excited pendant naphthalene groups in PSSS–VN to the ketone molecules seems to occur via a diffusion-controlled collisional mechanism. The occurrence of this short-range energy-transfer process in PSSS–VN provides additional evidence that the ketone molecule is actually being trapped in the interior of the polymer core.

Figure 10 illustrates the dependence of $I_O/I_Q$ on the oxygen pressure in the gas phase above the aqueous PSSS–VN solution. As one would expect, oxygen deactivates the excited polymeric naphthalene groups. Oxygen is known to quench organic compounds in their electronically excited states via a diffusion-controlled collisional process.[17] The deactivation of the naphthalene chromophores in the polymer core interior results in the formation of singlet oxygen. This conclusion is based on studies of the photooxygenation of several polynuclear aromatic compounds that are known to be singlet oxygen acceptors.[11]

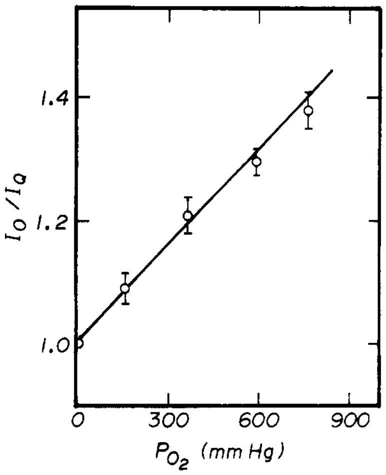


**Figure 10.** Plot of the ratio of the total polymer fluorescence intensities ($I_O/I_Q$) in the absence ($I_O$) and presence of quencher ($I_Q$) versus oxygen pressure.

## Conclusions

The photophysical phenomena presented above indicate that PSSS–VN in aqueous solution adopts a pseudomicellar conformation. The hydrophobic–hydrophilic interaction between water and pendant naphthalene groups induces the formation of a polymer core with naphthalene groups oriented toward the interior. The increase in the ionic strength of the solution, resulting in a decrease of the dimension of the polymer core, enhanced the efficiency of excimer formation. This indicates that the chromophores are close enough to form excimer, not only between nearest neighbors but also between nonnearest neighbors. PSSS–VN in methanol solution displayed a lower efficiency of excimer formation. This can be explained by taking into account the fact that the polymer is expected to adopt a conformation closer to a random coil.

The interior of the polymeric pseudomicelle formed in an aqueous solution of PSSS–VN has been found to be more hydrophobic than the surrounding water. The polarity of this microenvironment was estimated to be close to that of methanol. This explains the ability of PSSS–VN to solubilize large hydrophobic compounds. The pendant excited naphthalene chromophores can act as energy donors and transfer energy to solubilized compounds. The energy-transfer process can occur according to the long-range resonance Förster mechanism or diffusion-controlled collisional process, depending on the type of compound solubilized. The transferred energy may induce photochemical reactions of solubilized compound.

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**Registry No.** (PSSS)(VN) (copolymer), 115468-37-6; PCA, 3029-19-4; DMA, 781-43-1.

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# Dielectric Properties and Cocrystallization of Mixtures of Poly(butylene terephthalate) and Poly(ester–ether) Segmented Block Copolymers

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ABSTRACT: Measurements of the complex permittivity were used to assess the amorphous phase miscibility in blends of poly(butylene terephthalate) (PBT) and several poly(ester–ether) (PEE) segmented block copolymers. In addition, complex plane parameters were determined for the component polymers and certain blends and their variation with hard segment content or blend composition is discussed. It was found that larger hard segment (tetramethylene terephthalate) content in the segmented block copolymers favors increased amorphous phase miscibility and cocrystallization. Thermal analysis and morphological evidence point to extensive cocrystallization in PEE-84/PBT mixtures.

## Introduction

In the past several years there has been considerable interest in polymer blends in which one or more of the component polymers are capable of crystallizing. Particularly intriguing examples are mixtures based on poly(butylene terephthalate) (PBT) and various poly(ester–ethers) (PEE) segmented block copolymers. The poly(ester–ethers) under consideration are comprised of a poly(tetramethylene oxide) "soft" segment and a "hard" segment that is chemically identical with PBT (i.e., tetramethylene terephthalate (4GT)). Since it has been demonstrated that the crystalline unit cell structure and interplanar spacings of PBT and the PEE segmented copolymers are identical,[1] it would seem possible that, given the opportunity (i.e., that there is at least some limited miscibility in the melt), the PEE hard segment and PBT would cocrystallize in the blended state to give labile intermolecular cross-links.

Although a rather large number of papers have appeared concerning crystallization, morphology, and solid-state properties of both PBT (e.g., ref 2–4) and the PEE segmented copolymers (e.g., ref 5–9), little attention has focused on blends of these two polymers. The one exception is a relatively recent study by Shih[10] in which mixtures of PBT and a PEE block copolymer containing 59 wt % 4GT (soft segment molecular weight of 1000 g/mol) were found to be immiscible at compositions from 10–90% PBT. The resulting blends contained four phases, two amorphous and two crystalline. In the present paper we report our initial findings on the phase behavior of mixtures of PBT and poly(ester–ether) segmented block copolymers containing a range of hard-segment concentrations. Particular attention is paid to the dielectric properties of the copolymers and blends. We show that amorphous phase miscibility increases as 4GT concentration in the block copolymer increases and that extensive cocrystallization appears to occur in blends containing the high 4GT content copolymer.

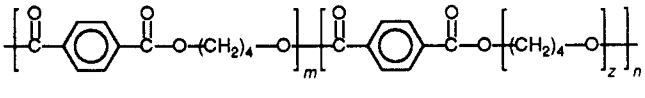
**Table I**
**Characteristics of PBT and Segmented Block Copolymers**

| designation | hard seg (4GT), wt % | $T_g$, °C | $T_m$, °C | $W_c$, % | av 4GT seg length |
|---|---|---|---|---|---|
| PEE-44 | 44[a] | −40 | 146 | 13 | 5 |
| PEE-58 | 58 | −30 | 198 | 19 | 8 |
| PEE-84 | 84 | ~30 (br) | 214 | 26 | 31 |
| PBT | 100 | 60 | 223 | 31 | |

[a] Also contains ~7 wt % isophthalate residues.

## Experimental Section

**Materials.** The PBT used in our experiments was provided by General Electric (Valox 310) and is reported to have a number-average molecular weight of ca. 33 000 g/mol. The poly(ester–ethers) were obtained from E. I. du Pont de Nemours and Co. and had overall molecular weights of 25–30 000 g/mol. The three copolymers used in our experiments have the general chemical structure



The characteristics of the copolymers and PBT can be seen in Table I. The 4GT contents range from 44 to 84 wt % (80–97 mol %) as determined from $^1$H NMR. NMR also showed that PEE-44 contained ~7 wt % isophthalate residues. If one assumes a most probable distribution (random polymerization), then the average 4GT segment length can be estimated and this is found

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