

## LETTERS

### Intramolecular Excimer Formation in Aqueous Solutions of Sodium Poly(styrenesulfonate)

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Monomer and excimer emissions are observed in aqueous solutions of sodium poly(styrenesulfonate). The excimer-to-monomer emission intensity ratios ( $I_E/I_M$ ) are between 1 and 2.1 and increase with polymer concentration. From measurements of  $I_E/I_M$  and the lifetimes of these emissions, the rate constants for excimer formation, dissociation, and radiative and nonradiative deactivation processes, and the quenching constants with  $\text{CoSO}_4$  and  $\text{NaNO}_2$ , are estimated. The contributions of the regular configurational alignment of the hydrophilic and hydrophobic moieties of the polymer and the electrostatic interactions between monomer units are suggested to be the main factors controlling excimer formation.

#### Introduction

Aromatic vinyl polymers in solution often show excimer emission similar to that for intramolecular excimers of low molecular weight bichromophores such as 1,3-diarylpropane.<sup>2</sup> For example, in polystyrene, monomer and excimer emission bands appear around 285 and 330 nm,

and the position of these bands is insensitive to the solvent used. This result suggests that the excimer emission is intramolecular, i.e., due to interaction of pendant phenyl groups on the same polymer backbone. However, reports on excimer formation in aqueous media are very rare.<sup>3</sup> We report here the observation of significant intramolecular excimer formation between phenyl groups of sodium poly(styrenesulfonate) in aqueous media. It is anticipated that studies of this phenomenon may afford knowledge of the stereochemical association of other polyelectrolytes such as biological polymers that will be transferable toward an understanding of the biological functions such as enzymatic catalytic effects.

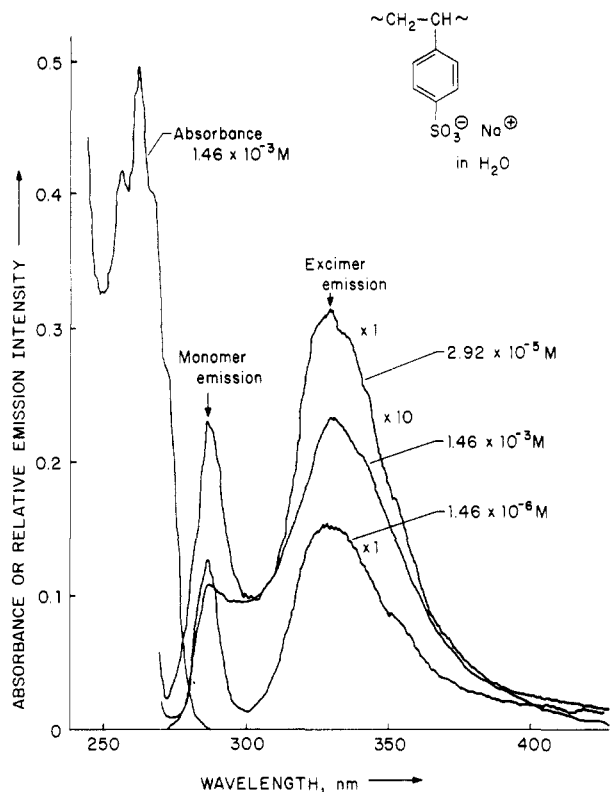
#### Experimental Section

**Materials.** Sodium poly(styrenesulfonate) (NaPSS) was

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**Figure 1.** Fluorescence and absorption spectra of aqueous NaPSS solutions excited at 260 nm. The readings at (X) are not as accurate because of a contribution from scattering.

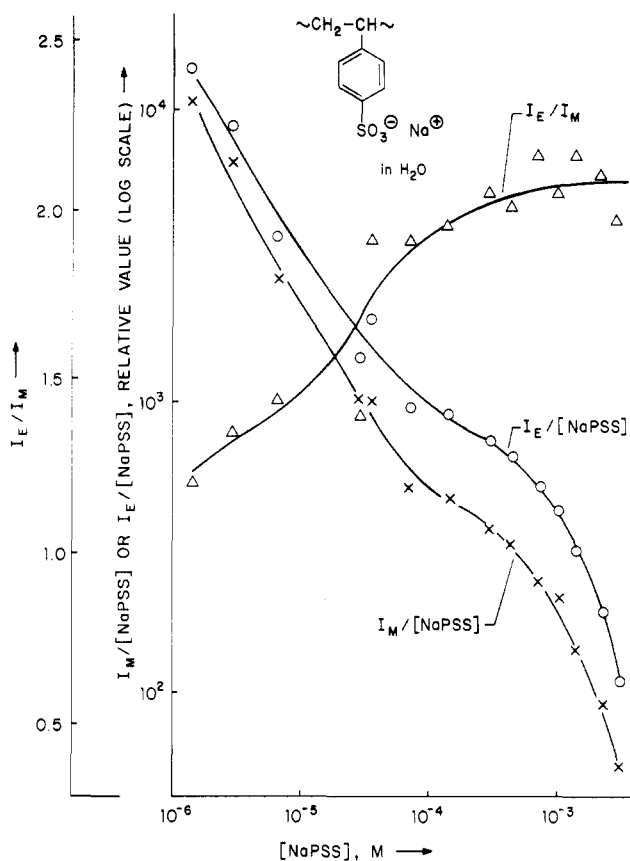
a gift of Dr. H. Gregor. The sample was purified by dialysis against deionized water for 2 weeks followed by ion exchange with columns of ion-exchange resins. After determination of the acid concentration, the solution was neutralized with sodium hydroxide. The molar extinction coefficient at 262 nm was  $403 \text{ M}^{-1} \text{ cm}^{-1}$ .

For the preparation of aqueous sample solutions, deionized water was distilled further. Most sample solutions were bubbled with nitrogen gas (Linde, oxygen-free grade) 5–10 min prior to emission analysis. Oxygen gas (Airdyne Ind., New York) was used.

**Spectroscopic Measurements.** Fluorescence spectra were obtained with a Hitachi-Perkin-Elmer MPF-2A or a SPEX fluorolog spectrophotometer. A Cary 118 spectrophotometer was employed to obtain the absorption spectra. Fluorescence decays were measured by the single-photon counting technique. The details of the high-pressure cell were described in a previous paper.<sup>4</sup>

## Results

Figure 1 displays the emission and absorption spectra of NaPSS in aqueous media. The emission spectra consist of two bands. The shorter wavelength band ( $\lambda_{\text{max}} = 285 \text{ nm}$ ) is assigned to monomer emission, and the larger wavelength band ( $\lambda_{\text{max}} = 330 \text{ nm}$ ) is assigned to excimer emission. Even at low concentration of NaPSS,  $1 \times 10^{-6} \text{ M}$ , the excimer band is clearly discernible. The emission spectra of aqueous solutions of NaPSS are very similar to those of polystyrene in organic solvents.<sup>2d,g,l,m,5-7</sup> As is seen in Figure 1, the two emission bands begin to overlap with



**Figure 2.**  $I_E/I_M$  ( $\Delta$ ),  $I_E/[\text{NaPSS}]$  (O), and  $I_M/[\text{NaPSS}]$  (X) as a function of NaPSS concentration. Monomer and excimer peaks are located at 285 and 330 nm, respectively.

each other as the polymer concentration increases.

Since the separation of the monomer and excimer bands becomes difficult at high polymer concentration ( $>5 \times 10^{-5} \text{ M}$ ), the values of  $I_M$ ,  $I_E$  and  $I_E/I_M$  at higher concentrations contain comparatively large experimental errors, probably  $\pm 20\%$ . Intrinsic emission intensities of monomer and excimer ( $I_M/[\text{NaPSS}]$  and  $I_E/[\text{NaPSS}]$ ) decreased with polymer concentration. This means that the emission quantum yield also decreases with the concentration. However, the ratio of  $I_E/I_M$  increased from 1.2 to 2.1 with increasing polymer concentration, and saturation in  $I_E/I_M$  was observed at high concentrations. The decrease in emission quantum yield may be correlated with the aggregation of phenyl groups via hydrophobic interaction in aqueous media. A hypochromic effect was also observed for NaPSS from absorbance measurements. The total sum of quantum yield of the monomer and excimer emissions was 0.037 ( $[\text{NaPSS}] = 1 \times 10^{-3} \text{ M}$ ), estimated by using quinine sulfate as a quantum yield standard.<sup>8</sup> This value is lower than that of the corresponding monomer, sodium toluenesulfonate (0.071). The emission intensities of both monomer and excimer components were not reduced in oxygen-saturated solutions at all.

The lifetimes obtained for the monomer and excimer of NaPSS are displayed in Figure 3 as a function of polymer concentration. The values were only slightly sensitive to the polymer concentration. The values at high concentrations are 2.5 and 5.2 ns for the monomer and excimer, respectively. The lifetimes were the same whether the solutions were purged with nitrogen gas or with oxygen gas.

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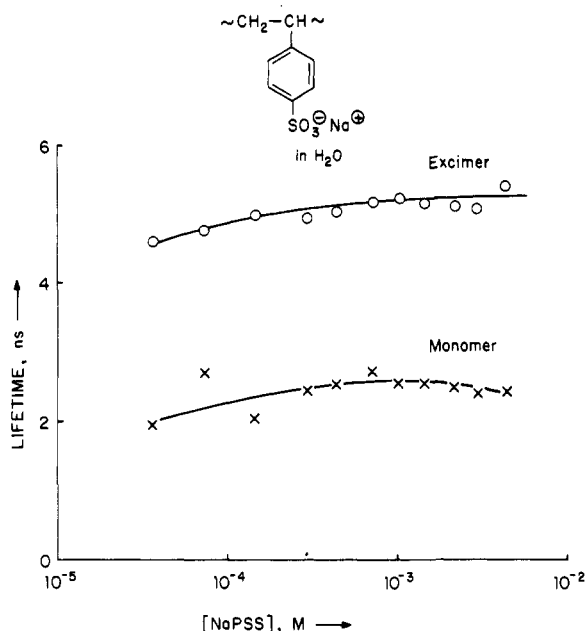
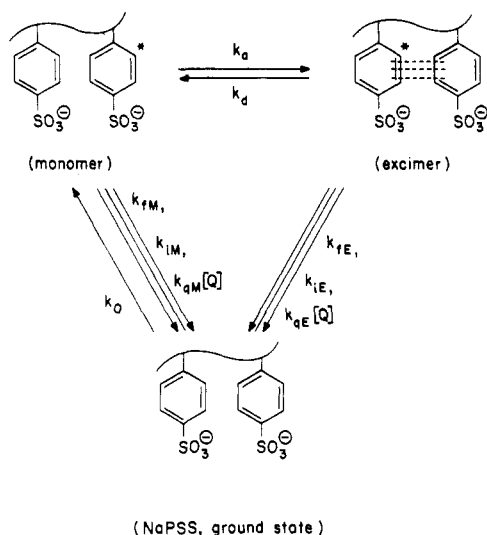


Figure 3. Excimer lifetimes (O, at 330 nm) and monomer emission (X, at 285 nm) as a function of NaPSS concentration.

#### Scheme I



#### Discussion

A kinetic scheme for NaPSS excimer formation is given in Scheme I. This scheme is analogous to that employed to analyze intramolecular excimer formation in polystyrene;  $k_a$  and  $k_d$  are the rate constants of excimer formation and dissociation, and  $k_{fE}$ ,  $k_{iE}$ , and  $k_{qE}$  indicate the rate constants of excimer fluorescence, internal quenching, and external quenching of the excimer. The parameters  $k_{fM}$ ,  $k_{iM}$ , and  $k_{qM}$  are the corresponding rate constants for the monomer. The value of  $k_{qE}$  was determined from Stern-Volmer type plots<sup>9</sup> as  $3 \times 10^{11}$  and  $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  when  $\text{CoSO}_4$  and  $\text{NaNO}_2$  were used as quenchers. The values of  $k_{qM}$  with  $\text{CoSO}_4$  and  $\text{NaNO}_2$  were  $5 \times 10^{10}$  and  $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The monomer emission was more difficult to quench than that of the excimer. The magnitude of  $k_{qE}$

TABLE I: Kinetic Data for NaPSS Excimer at 25 °C

$k_a/\text{s}^{-1}$	$1.9 \times 10^9$	$k_{iE}/\text{s}^{-1}$	$1.9 \times 10^8$
$k_d/\text{s}^{-1}$	$2.5 \times 10^6$	$k_{qE}/(\text{M}^{-1} \text{ s}^{-1})$	$3 \times 10^{11}$
$k_{fE}/\text{s}^{-1}$	$1.1 \times 10^7$		

with cationic quencher ( $\text{Co}^{2+}$ ) seems to be in the range of diffusion-controlled quenching, whereas that with anionic quencher ( $\text{NO}_2^-$ ) is substantially below the diffusion-controlled rate. The difference in  $k_{qE}$  values may be explained in terms of a strong electrostatic attraction ( $\text{Co}^{2+}$ ) or repulsion ( $\text{NO}_2^-$ ) between the macroions and the quencher ions.

The rate parameters for intramolecular excimer formation were estimated from the steady-state kinetics given by Klopffer et al.<sup>10</sup> Sodium toluenesulfonate (NaTS) was used as a low molecular weight analogue of NaPSS. The fluorescence quantum yield and lifetime of NaTS were 0.071 and 1.5 ns in pure water. The parameters obtained for the aqueous NaPSS solution system (Table I) are similar in magnitude to those of polystyrene in organic solvents.<sup>21,2,10c</sup> However, we should note that the association constant for excimer formation is larger than those for polystyrene (50 for atactic PS and 150 for isotactic PS).<sup>21,m</sup> As is understood from its chemical structure, NaPSS has both *hydrophilic* parts (sulfonate ions and their gegenions) and *hydrophobic* parts (main chain of the hydrocarbon and phenyl groups). Furthermore, there exists a strong repulsive interaction between the monomeric ions. These factors may encourage a regular configurational alignment (or the stacking) of phenyl groups in aqueous media. The structures in Scheme I are not intended to depict any detailed knowledge of the local polyelectrolyte structure that is required for excimer formation. Excimer formation may be a dynamic process in which two closely positioned monomer units that are in a favorable condition for excimer formation are excited by an energy migration mechanism. We should note that this kind of regular stacking is significant only for polymer systems. Thus, no excimer was observed for the low molecular weight analogue of NaPSS, i.e., NaTS. The relatively high quantum yield of NaPSS emission (0.037) compared with those PS (0.01–0.02)<sup>3a,10c</sup> may be also explained by the same effect.

From the quenching experiments, it is clear that the monomer and excimer emissions are quenched to a different degree. Thus, monomer fluorescence from NaPSS may arise from excited side groups which have been created mainly by direct absorption of light. Energy migration may then occur competitively with monomer emission, and excimer sites may be more exposed for attack by quenchers. The dissociation of excimers may not contribute to the observed monomer emission.<sup>10c</sup> However, the contribution from cooperative dissociation is not completely excluded at present. For this problem further experiments are now in progress in our laboratory.<sup>11</sup>

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