copolymer of methyl methacrylate and 4-vinylbiphenyl rather than a further exploration of random copolymer systems. We conclude that alternating polymer systems represent an interesting class of copolymers that permit facile down-chain energy transfer, partially as a result of diminished excimer formation rates.

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Registry No. P(4VBP-*alt*-MMA) (copolymer), 82530-42-5; P4VBP (homopolymer), 25232-08-0; CCl_4, 56-23-5.

References and Notes

(1) Nakahira, T.; Sasaoka, T.; Iwabuchi, S.; Kojima, K. *Makromol. Chem.* **1982**, *183*, 1239.
(2) Fox, R. B.; Price, T. R.; Cozzens, R. F.; Echols, W. H. *Macromolecules* **1974**, *7*, 937.
(3) Bai, F. L.; Chang, C. H.; Webber, S. E. *Macromolecules* **1986**, *19*, 588.
(4) Razi Naqvi, K.; Donatsch, J.; Wild, U. P. *Chem. Phys. Lett.* **1975**, *34*, 285.
(5) Berlman, I. B. *J. Phys. Chem.* **1970**, *74*, 3085.
(6) Berlman, I. B. *Energy Transfer Parameters of Aromatic Compounds*; Academic: New York, 1973. For biphenyl self-transfer R_0 = 3.11 Å. For 4-methylbiphenyl R_0 = 6.41 Å.
(7) Abuin, E.; Lissi, E.; Gargallo, L.; Radic, D. *Eur. Polym. J.* **1982**, *18*, 319.
(8) Webber, S. E.; Avots-Avotins, P. E.; Deumié, M. *Macromolecules* **1981**, *14*, 105.
(9) Rembaum, A.; Moacanin, J.; Haack, R. *J. Macromol. Chem.* **1966**, *1*, 657.
(10) Frank, C. W. *J. Chem. Phys.* **1974**, *61*, 2015.
(11) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic: New York, 1965.
(12) Reid, R. F.; Soutar, I. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 231.
(13) Semerak, S. N.; Frank, C. W. *Adv. Polym. Sci.* **1983**, *54*, 33 (see p 75).
(14) Voltz, R.; Laustriat, G.; Coche, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1966**, *63*, 1253.
(15) Heisel, F.; Laustrait, H. *J. Chim. Phys. Phys.-Chim. Biol.* **1965**, *66*, 895.
(16) Pratte, J. F.; Webber, S. E. *Macromolecules* **1984**, *17*, 2116.

Fluorescence of Vinyl Aromatic Polyelectrolytes: Effects of Conformation, Concentration, and Molecular Weight of Sodium Poly(styrenesulfonate)

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ABSTRACT: Conformational behavior of atactic sodium poly(styrenesulfonate) has been investigated by the use of fluorescence spectroscopy. Measurement of the excimer to monomer fluorescence intensity ratio, I_E/I_M, provides information relating to specific conformational populations in vinyl aromatic polymers. The overall size of the polyelectrolyte coils was varied extensively through control of ionic strength of the solvent, and the influence of the overall conformation of the polyelectrolyte on I_E/I_M was monitored. As the shape of the chain changes from a highly extended, rodlike form to a loose coil, I_E/I_M was found to be approximately constant, implying that local bond conformations are almost invariant. Increased molecular weight was found to increase I_E/I_M in a manner that cannot be explained solely on the basis of end effects. The concentration dependence of I_E/I_M was similar to that observed in polystyrene: no effect is seen for $0.01 \leq c \leq 2$ g/L, and above 2 g/L I_E/I_M increases only very gradually. Absorbance spectra were recorded and found to exhibit slight sensitivity to conformational changes.

Introduction

Fluorescence behavior of neutral polymers, containing either naturally present chromophores or fluorescent probes, has been studied in detail by a number of research groups.[2-30] One reason for this interest, particularly for vinyl aromatic polymers, is that fluorescence emission is sensitive to specific local conformations and configurations of the polymer chain. For example, Hirayama[31] demonstrated with low molecular weight analogues of phenyl-containing polymers, such as polystyrene, that intramolecular excimer formation occurs only when the number of carbon atoms separating phenyl rings is equal to three (the "$n = 3$" rule). Later, Bokobza, Jasse, and Monnerie[32] investigated the fluorescence of three polystyrene model compounds (2,4-diphenylpentane, 2,4,6-triphenylheptane, and 2,4,6,8-tetraphenylnonane) and found that isotactic configurations were more favorable for excimer formation than were syndiotactic configurations: the ratio of excimer to monomer fluorescence intensity, I_E/I_M, was up to 20 times higher for the isotactic model compounds than for the syndiotactic compounds. These results have been corroborated in polymeric systems by Longworth[3] and Ishii et al.[4] In the case of isotactic (or meso) diads, excimer formation is associated with the trans–trans conformation. Thus, by measuring I_E/I_M in vinyl aromatic polymers, such as polystyrene, one may probe local conformational behavior, specifically, the presence of trans–trans conformations in isotactic diads along the chain. Excimer fluorescence may occur from trans–trans conformations formed either prior to excitation or by a conformational transformation after excitation. Therefore, we may take advantage of the sensitivity of fluorescence spectroscopy to monitor local polymer behavior. In this paper, we report on local orientations of a polyelectrolyte chain and how these orientations change as the macroscopic dimensions of the coil vary.

There have recently been a number of investigations of fluorescence and absorbance phenomena in aqueous po-

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lyelectrolyte systems using chromophoric probes or labels;[32-47] however, relatively little has been published concerning polyelectrolytes in which each monomer residue is a fluorophore such as poly(styrenesulfonate).[48-50] Often, probes are sensitive to the environment that surrounds them (either hydrophillic or hydrophobic), but they are unable to provide the specific information concerning local orientation of the polyelectrolyte chain that can be obtained from observation of excimer formation. Poly(styrenesulfonate) (PSS) is well suited to an investigation of conformational behavior because it resembles polystyrene; therefore, its behavior may be interpreted on the basis of results established for polystyrene and its model compounds. Additionally, its electrolytic character allows overall conformational transitions of significantly greater magnitude than are possible for an uncharged polymer. These transitions can be induced simply by altering the ionic strength of the solvent.

Recently, two reports on poly(styrenesulfonate) fluorescence were published.[49,50] Turro and Okubo[49] investigated the concentration dependence of I_E/I_M and found that the ratio increased almost twofold over a range of dilute concentrations. Because they focused primarily on the kinetics and mechanism of the fluorescence scheme, they did not elaborate on the influence that concentration has on either the conformation or macroscopic behavior of the polymer chains. No mention of concentration transitions or the molecular weight dependence was made by these authors. Ander and Mahmoudhagh[50] reported on the influence of various inorganic salts on the fluorescence spectra of PSS solutions. They recorded the effects of counterion valence and concentration on the spectra obtained from dilute polymer systems; however, little quantitative information was provided. Again, their study did not elaborate on the influence of polyion molecular weight.

In this paper, we report on the fluorescence behavior of well-characterized PSS over a wide range of molecular weights and under solution conditions ranging from the dilute regime to the bulk. Additionally, the influence of low molecular weight electrolyte is examined over a broad range of ionic strengths, and the information is interpreted based on local conformational arguments. Results of absorbance measurements are also presented.

Experimental Section

Sodium poly(styrenesulfonate) was obtained from Pressure Chemical Co. in narrow molecular weight distribution standards ($M_w/M_n \leq 1.1$) which were generally used without further purification. Information supplied by the manufacturer states that the polymer was prepared by sulfonation of polystyrene standards and was about 90% sulfonated. (One hundred precent sulfonation corresponds to one chargeable sulfonate group per repeat unit.) Fourier transform NMR spectroscopy was used to verify that the polymer was almost completely sulfonated and to establish that substitution occurred almost exclusively in the para position. Polyion molecular weight ranged from 1600 (approximately 8 repeat units) to 1 060 000 (approximately 5800 repeat units) and included 6500, 16 000, 31 000, 65 000, 88 000, 177 000, 354 000, and 690 000. Other chemicals used in this study were of reagent grade and included sodium chloride, sodium sulfate, and *p*-toluenesulfonic acid and were obtained from Allied Chemical, Mallinckrodt, and Matheson Coleman and Bell, respectively.

Solutions were prepared by weighing the salt and polymer, which was dried under vacuum at about 50 °C for at least 24 h, into volumetric flasks and diluting with distilled, deionized water. Ample time (>24 h) was allowed for dissolution.

Absorbance measurements were performed by using an IBM 9410 UV–visible spectrometer and matched high-quality quartz cuvettes with path lengths of 1 and 10 mm. All fluorescence spectra were measured by using a Perkin-Elmer MPF-44A spectrophotometer and high-quality, 10-mm path length, quartz cuvettes. Samples were air equilibrated; a previous study[49] showed that the presence of dissolved oxygen did not affect the fluorescence of this system. For highly concentrated polymer solutions, it was found that acceptable fluorescence spectra were unobtainable with the standard right-angle excitation–emission geometry, presumably due to little transmission of excitation light to the cell center and to self-absorption[11] of fluorescence emission; therefore, a front-surface cell-holding apparatus (excitation–emission angle approximately 30°) was employed. Identical spectra are obtained with either geometric arrangement with dilute solutions.

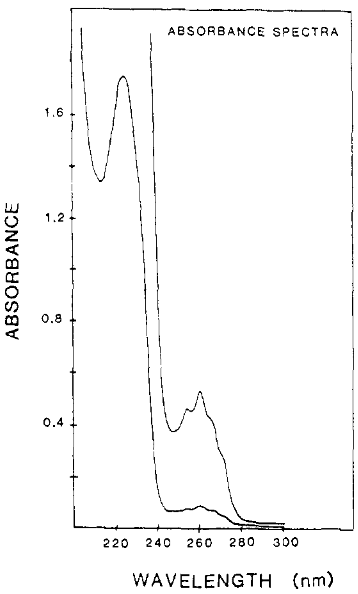

Figure 1. Ultraviolet absorption spectra of aqueous solutions of sodium poly(styrenesulfonate) at concentrations of 0.034 and 0.296 g/L. The polyion molecular weight is 88 000.

Excimer and monomer fluorescence intensities were monitored at wavelengths of 345 and 280 nm, respectively. By comparison with the fluorescence of *p*-toluenesulfonic acid, it is clear that the emission at 345 nm is essentially of pure excimer origin. At a wavelength of 280 nm, there is a slight overlap of excimer and monomer bands, with the excimer band contributing several percent of the emission. No attempt was made to correct for this slight contamination of the monomer by the excimer band.

Usually the emission slit width was kept at 2 nm; however, for very dilute solutions, a wider slit width (up to 5 nm) was used to enhance spectral intensity. It was demonstrated that use of a wider emission slit opening had no effect on the spectra for dilute polymer systems. Excitation of the samples was performed by using UV light of 253.7-nm wavelength and a 5-nm slit opening.

Results and Discussion

The absorption spectrum of NaPSS is shown in Figure 1 and was found to be independent of molecular weight from 6500 to 1.06 × 10^6. The 1600 molecular weight polyion exhibited a slightly higher absorption coefficient; this may be due to the presence of impurities because the sample could not be dialyzed. Molar extinction coefficients at wavelengths of 261.7, 258, and 255.9 nm were determined to be 362, 302, and 313 M^{-1} cm^{-1} independent of concentration through 9 g/L.

The addition of sodium chloride to the aqueous polyelectrolyte system induced either a hyperchromic or hypochromic shift, depending on the amount of salt added. These results, expressed in Figure 2, show a sharp increase of absorbance of several percent upon addition of salt, with a maximum in absorbance occurring at about 0.1 M NaCl. Above 0.1 M NaCl concentration, the absorbance exhibits a continuous decline. These results confirm the findings of Carroll and Eisenberg[51] and strongly suggest the occurrence of local reorientation of phenyl rings on the chain.

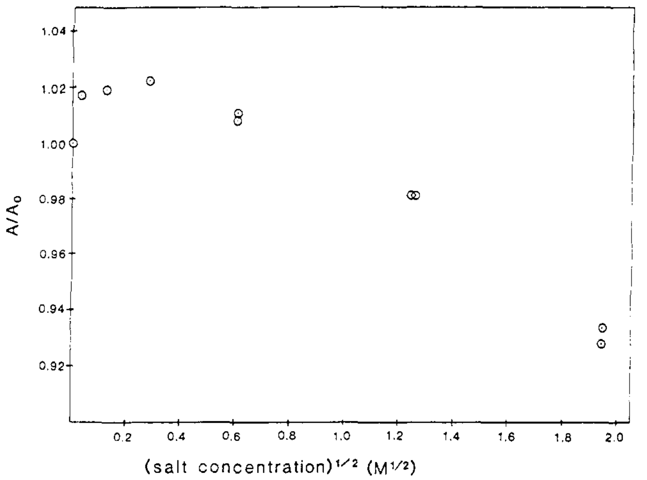

Figure 2. Ratio of absorbance of saline and salt-free solutions of NaPSS as a function of sodium chloride concentration (wavelength = 261.7 nm).

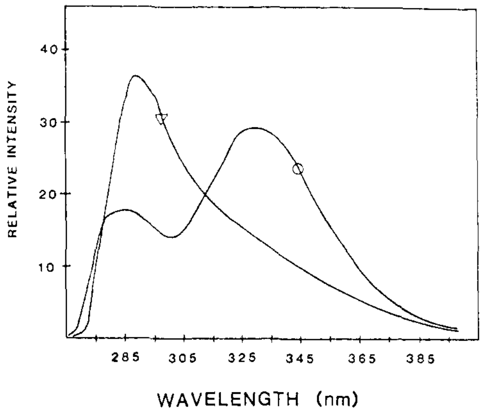

Figure 3. Uncorrected fluorescence spectra of polystyrene in cyclohexane (○) and sodium poly(styrenesulfonate) (▽) in water. The polymers have equal degrees of polymerization (DP = 960) and matched optical density ($A_{253.7}$ = 1.234).

Fluorescence spectra as recorded for PSS and polystyrene with equal degrees of polymerization and equal optical densities are reproduced in Figure 3. Although these spectra have not been corrected for instrument response, it is clear from comparison of spectral shape that excimer formation in the sulfonated system is greatly diminished, presumably due to local electrostatic repulsions and steric effects. It is noted that a corrected spectrum of either polymer would exhibit more substantial long-wavelength (excimer) emission than these spectra.

Figure 4 depicts fluorescence spectra of several NaPSS samples of varying molecular weight at a concentration of 0.5 g/L along with a monomeric analogue, *p*-toluenesulfonic acid (*p*-TSA). The change in spectral shape with molecular weight is clearly manifested as a broadening of the monomer peak and gradual extension into a long-wavelength tail. This spreading of the emission spectrum is evidence suggesting the existence of the fluorescing excimer species. The presence of an isoemissive point[31] near 316 nm indicates that excimers are in fact formed in dilute aqueous NaPSS systems. The locations of the monomer and excimer peaks have been determined to be 287 and 325 nm, respectively.[52] Both of these peaks are shifted relative to their counterparts in polystyrene, where monomer and excimer peaks occur at 283 and 335 nm, respectively.

The excimer to monomer fluorescence intensity ratio is shown in Figure 5 for a range of molecular weights of PSS. No comparable data for a polyelectrolyte system have been

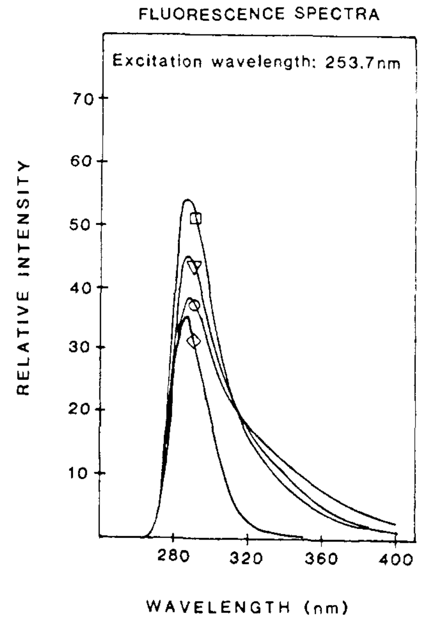

Figure 4. Fluorescence spectra of NaPSS with polyion molecular weights of 1060000 (○), 31000 (▽), and 16000 (□) and the fluorescence spectrum of *p*-toluenesulfonic acid (◇). Polymer concentration is 0.5 g/L.

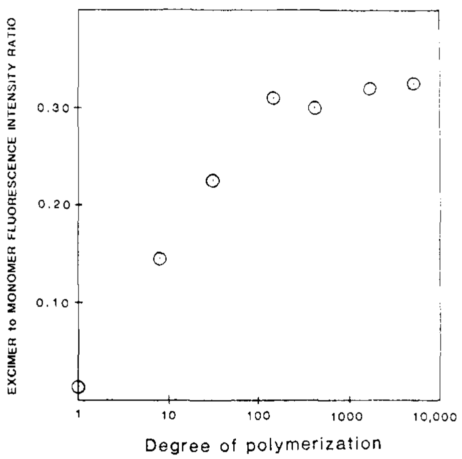

Figure 5. Excimer to monomer fluorescence intensity ratio for 0.5 g/L solutions of *p*-TSA and various molecular weights of NaPSS.

previously published; however, these data display a trend similar to that observed in polystyrene,[7] specifically, strong molecular weight dependence of I_E/I_M at low molecular weight and reduced dependence at higher molecular weight. Clearly, enhanced excimer fluorescence and the associated reduction in monomer fluorescence with increasing molecular weight is responsible for the changes described. The increase in I_E with molecular weight becomes less pronounced above 31000 daltons (degree of polymerization 170) for a number of possible reasons. Unquestionably, one factor is that a phenyl unit at the terminus of the polymer chain has only one vicinal neighbor with which to form an excimer while a nonterminal phenyl unit has two neighboring phenyl units with which to form an excimer. Thus, an increase in the relative number of chain ends in the system would be expected to diminish the intensity of excimer fluorescence. Another factor relevant to the excimer fluorescence efficiency of the end units of a vinyl polymer is the increased mobility and rotational freedom that the chain ends possess. The influence of the factors listed above, referred to as end effects, has been quantified in general by Nishijima et al.[53]

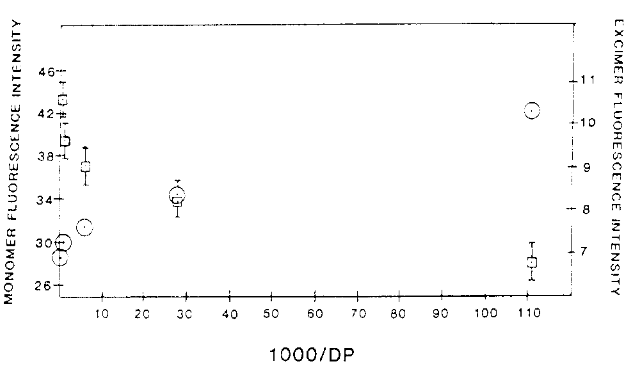

Figure 6. Dependence of uncorrected excimer (□) and monomer (○) fluorescence intensities on reciprocal degree of polymerization of NaPSS.

The relative intensities of excimer and monomer fluorescence can be expressed as[53]

$$I_E = nK\phi_E[1 - (2X/N)(1 - p)] \quad (1)$$

$$I_M = n\phi_M[(1 - K) + (2X/N)K(1 - p)] \quad (2)$$

where K is the probability that an excimer will form from a single chromophore, ϕ_E and ϕ_M are the quantum efficiencies of the excimer and monomer species, respectively, X is the number of phenyl units that are subjected to some end effect on any given chain, n is the total number of chromophores present, N is the degree of polymerization, and p is the fractional end-effect parameter.

From this type of analysis, a linear dependence of I_E and I_M on the reciprocal degree of polymerization is expected. Obviously, Figure 6 demonstrates that a linear relationship is not obtained; therefore, we conclude that end effects are not the sole cause of the observed molecular weight dependence of fluorescence in PSS. Because end effects are not sufficient for explanation of the molecular weight dependence found in other polymers such as polystyrene,[7] it is not surprising that they are not entirely responsible for the dependence discovered here. Another factor that has been postulated as contributing to the fluorescence behavior in polystyrene includes energy migration,[4,11,16,17,54] and it may also be operative in PSS.

It is further noted that the molecular weight dependence of I_E/I_M is not associated with intermolecular excimer formation at higher molecular weights. The likelihood of intermolecular excimer formation is negligible because the concentration at which these spectra were measured is low enough to ensure large average separation between chains. Proximate alignment of chromophores from different polymer chains may result in the formation of intermolecular excimers; however, at a concentration of 0.05% polymer, even fully extended rods of PSS would not overlap until their molecular weight exceeded ~40 000. Because the change in I_E/I_M occurs predominantly prior to attainment of this molecular weight, it is clear that chain overlap and intermolecular excimer formation are not the primary sources of excimer fluorescence for the results in Figures 3–6.

The concentration dependence of PSS fluorescence has also been examined. I_E/I_M increases with concentration and shows only a gradual increase over a broad range, demonstrating that there is no obvious indication of the onset of chain overlap and, hence, no demarcation of the semidilute solution regime boundary. No concentration dependence is observed at low concentrations, $0.01 \leq c \leq 2$ g/L. The trend seen here is similar to that seen in polystyrene[7] but slightly different from that reported by Turro and Okubo.[49] However, most of the concentrations that Turro and Okubo tested were substantially lower than those examined here. Their results and the results of the present study are in general agreement over the small range where the concentrations in the two studies coincide.

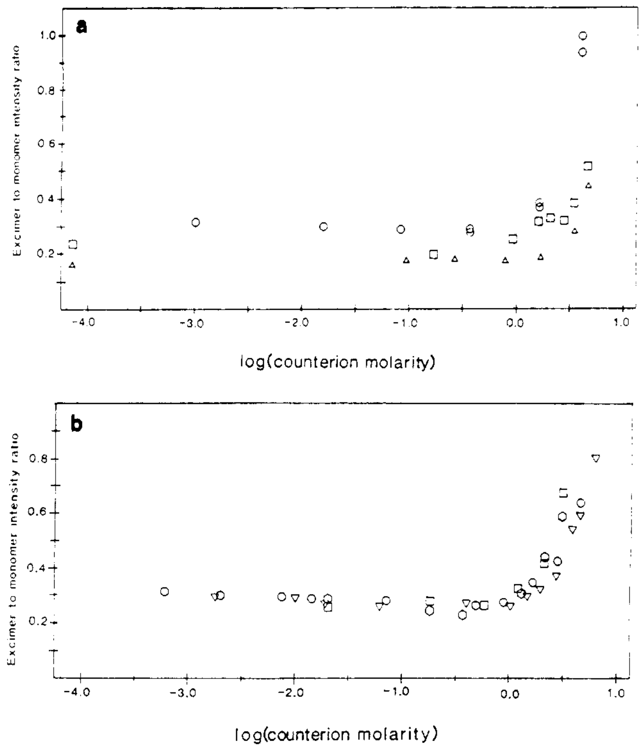

Figure 7. (a) I_E/I_M for various molecular weights of PSS in saline (NaCl) solutions: (△) 1600 daltons; (□) 6500 daltons; (○) 88 000 daltons. (b) I_E/I_M for 31 000 molecular weight PSS at concentrations of 2.0 g/L in NaCl (○) and Na_2SO_4 (○) and 0.5 g/L in NaCl (□) and Na_2SO_4 (▽).

The region where we observe the onset of increase in I_E/I_M extends from about 2 to 5 g/L and is apparently independent of molecular weight. Thus, the critical overlap concentration, c^*, is not discernible via fluorescence measurement in this system. Scaling arguments[55] suggest that the point of overlap scales as $c^* \sim N/l^3$, where N is the degree of polymerization and l is the contour length of the chain. Such arguments imply that c^* would vary, in salt-free solutions, by 4 orders of magnitude over the range of molecular weights studied. The locations of the transitions observed show no such variation.

A number of other factors may contribute to the increase in I_E/I_M with polyion concentration. Clearly, in concentrated solutions, the possibility of intermolecular excimer formation cannot be discounted. Although scaling laws suggest[56] that the number of intermolecular contacts per unit volume should depend on concentration as $c^{5/4}$, such a dependence of I_E/I_M is not observed. Nevertheless, it is well-known that neutral polymer chains interpenetrate and contract with increasing concentration,[57] and similar effects have been reported in polyelectrolyte systems.[58] Increased concentration and the contraction that occurs might facilitate intermolecular and intramolecular energy migration and remote excimer formation and may even affect vicinal excimer formation through variation in local conformational structure. Although remote intramolecular excimer formation has been shown to be negligible in polystyrene systems, mutual affinity of aromatic moieties might be more pronounced due to hydrophobic interactions present in the aqueous PSS system.

To further examine the impact of coil size and conformation on the fluorescence spectra of PSS, the solution environment was modified to induce chain contraction through the addition of low molecular weight electrolyte.

Variation of I_E/I_M with simple salt concentration is displayed in Figure 7 for several molecular weights of PSS. The most striking feature of Figure 7 is the dramatic increase in I_E/I_M demonstrated by solutions of high ionic strength. In these solutions, where the salt concentration exceeds 100 g/L, the fluorescence mechanism itself might be affected by the substantial change in the environment to which chromophores are exposed. A more subtle and probably more important feature of the effect that salt has on I_E/I_M in NaPSS solutions is the absence of any significant change from the salt-free solution to solutions with a salt concentration of about 1 M. In salt-free solutions, PSS molecules are expected to adopt highly extended conformations; in solutions with ionic strength of 1 M, viscosity measurements[59,60] and light scattering studies[59,61] have demonstrated that the molecules assume coiled conformations. For example, Takahashi, Kato, and Nagasawa[59] have determined the parameters K and a in the Mark–Houwink equation $[\eta] = KM^a$ to be 1.86×10^{-4} dL/g and 0.64, respectively, for NaPSS solutions in 0.5 M NaCl. These values are close to those obtained for polystyrene in ethylbenzene ($K = 1.76 \times 10^{-4}$ dL/g, $a = 0.68$),[62] which is known to be in a coiled conformation. As the salt concentration is increased, continued reduction in coil size will occur until the Θ dimensions are reached.

Surprisingly, I_E/I_M, or, equivalently, the relative number of trans–trans conformations of isotactic diads (excimers),[63] is affected little by the large overall conformational change that occurs in going from salt-free conditions to moderately high salt concentrations. This experimental evidence qualitatively supports the implication of Flory's rotational isomeric state scheme[64] that a relatively minor variation in local conformational populations is required to cause substantial change in overall chain dimensions. Moreover, it establishes the relative invariance of bond orientations over an even greater conformational range than originally discussed by Flory.[64] The observation that I_E/I_M is relatively insensitive to salt addition up to about 1 M salt is also consistent with NMR experiments by Schaefer[65] and SAXS experiments by Nagasawa[66] that indicate that the local conformation of poly(carboxylic acids) is insensitive to electrostatic effects. A slight decline in I_E/I_M is discernible in Figure 7 and might be evidence of a nominal decrease in the number of trans–trans conformations that accompanies the contraction of the polymer from a rodlike state.

Conformational effects may also be postulated in explanation of the profound increase in I_E/I_M with increased salt concentration. Allegra et al.[67] calculated the unperturbed dimensions of sodium polyacrylate with variable fractions of meso and racemic diads in the chain and accounted not only for skeleton interactions but also for electrostatic counterion effects. Their results suggest that these polyions will assume a somewhat expanded form even in high ionic strength media. If PSS molecules behave in a similar fashion, then the excimer-forming trans–trans conformation of meso diads might actually be favored to occur at very high salt concentrations. A similar undertaking by Aylward,[48] who modeled isotactic poly(styrenesulfonic acid), corroborates this interpretation and indicates that there is a high probability of finding meso diads in excimer conformations in solutions with high ionic strengths. Although the observed changes in I_E/I_M may be predicted by these conformational energy calculations, the influence of solvent environment should not be completely disregarded. Interestingly, however, the fluorescence spectrum of the monomeric analogue p-TSA was unaffected by the addition of salt.

Additional fluorescence and absorbance experiments performed on NaPSS in mixed solvents have revealed some noteworthy results. The ternary system NaPSS–water–methanol exhibits hypochromic absorption behavior and peculiar fluorescence behavior. I_E/I_M passes through a distinct minimum before increasing substantially in solutions with high methanol concentrations. Similar findings have been discovered in dioxane–water and glycerol–water systems.

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Registry No. p-TSA, 104-15-4; NaCl, 7647-14-5; Na_2SO_4, 7757-82-6.

References and Notes

(1) (a) Department of Chemical Engineering. (b) Departments of Chemical Engineering and Materials Science and Engineering and the Materials Research Center.
(2) Vala, M. T.; Haebig, J.; Rice, S. A. *J. Chem. Phys.* **1965**, *43*, 886.
(3) Longworth, J. W. *Biopolymers* **1966**, *4*, 1131.
(4) Ishii, T.; Handa, T.; Matsunaga, S. *Macromolecules* **1978**, *11*, 40.
(5) Aspler, J. S.; Guillet, J. E. *Macromolecules* **1979**, *12*, 1082.
(6) Frank, C. W.; Gashgari, M. A. *Macromolecules* **1981**, *14*, 1558.
(7) Torkelson, J. M.; Lipsky, S.; Tirrell, M. *Macromolecules* **1981**, *14*, 1601.
(8) Johnson, G. E.; Good T. A. *Macromolecules* **1982**, *15*, 409.
(9) Frank, C. W.; Fitzgibbon, P. D. *Macromolecules* **1982**, *15*, 733.
(10) Gelles, R.; Frank, C. W. *Macromolecules* **1982**, *15*, 1486.
(11) Torkelson, J. M.; Lipsky, S.; Tirrell, M.; Tirrell, D. A. *Macromolecules* **1983**, *16*, 326.
(12) Ng, D.; Yoshiki, K.; Guillet, J. E. *Macromolecules* **1983**, *16*, 568.
(13) Loutfy, R. O. *Macromolecules* **1983**, *16*, 678.
(14) Pekcan, O.; Winnik, M. A.; Gan, L.; Croucher, M. D. *Macromolecules* **1983**, *16*, 699.
(15) Li, X.-B.; Winnik, M. A.; Guillet, J. E. *Macromolecules* **1983**, *16*, 992.
(16) Phillips, D.; Roberts, A. J.; Soutar, I. *Macromoleclules* **1983**, *16*, 1593.
(17) Phillips, D.; Roberts, A. J.; Rumbles, G.; Soutar, I. *Macromolecules* **1983**, *16*, 1597.
(18) Hargreaves, J. S.; Webber, S. E. *Macromolecules* **1984**, *17*, 235.
(19) Winnik, M. A.; Li, X.-B.; Guillet, J. E. *Macromolecules* **1984**, *17*, 699.
(20) Semerak, S. E.; Frank, C. W. *Macromolecules* **1984**, *17*, 1148.
(21) Torkelson, J. M.; Tirrell, M.; Frank, C. W. *Macromolecules* **1984**, *17*, 1505.
(22) Hargreaves, J. S.; Webber, S. E. *Macromolecules* **1984**, *17*, 1741.
(23) Abia, A. A.; Burkhart, R. D. *Macromolecules* **1984**, *17*, 2739.
(24) Kauffmann, H. F.; Weixelbaumer, W.-D.; Buerbaumer, J.; Schmoltner, A.-M.; Olaj, O. F. *Macromolecules* **1985**, *18*, 104.
(25) Watanabe, A.; Matsuda, M. *Macromolecules* **1985**, *18*, 273.
(26) Hargreaves, J. S.; Webber, S. E. *Macromolecules* **1985**, *18*, 734.
(27) Kim, N.; Webber, S. E. *Macromolecules* **1985**, *18*, 741.
(28) Bednar, B.; Li, Z.; Huang, Y.; Chang, L.-C. P.; Morawetz, H. *Macromolecules* **1985**, *18*, 1829.
(29) Ren, X.-X.; Guillet, J. E. *Macromolecules* **1985**, *18*, 2012.
(30) Viovy, J. L.; Frank, C. W.; Monnerie, L. *Macromolecules* **1985**, *18*, 2606.
(31) Hirayama, F.; Lipsky, S. *J. Chem. Phys.* **1969**, *51*, 1939.
(32) Bokobza, L.; Jasse, B.; Monnerie, L. *Eur. Polym. J.* **1977**, *13*, 921.
(33) Stork, W. H. J.; deHasseth, P. L.; Schippers, W. B.; Kormeling, C. M.; Mandel, M. *J. Phys. Chem.* **1973**, *77*, 1772.
(34) Stork, W. H. J.; Van Boxsel, J. A. M.; de Goeij, A. F. P. M.; deHasseth, P. L.; Mandel, M. *Biophys. Chem.* **1974**, *2*, 127.
(35) Jung, Ch.; Heckner, K.-H. *Chem. Phys.* **1977**, *21*, 227.
(36) Erny, B.; Muller, G. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 4011.
(37) Yamagishi, A.; Watanabe, F. *J. Phys. Chem.* **1981**, *85*, 2129.
(38) Okubo, T.; Turro, N. J. *J. Phys. Chem.* **1981**, *85*, 4034.
(39) Turro, N. J.; Okubo, T. *J. Am. Chem. Soc.* **1982**, *104*, 2985.
(40) Turro, N. J.; Okubo, T. *J. Phys. Chem.* **1982**, *86*, 1535.

(41) Nagata, I.; Okamoto, Y. *Macromolecules* **1983**, *16*, 749.

(42) Ortona, O.; Vitagliano, V.; Sartorio, R.; Costantino, L. *J. Phys. Chem.* **1984**, *88*, 3244.

(43) Chu, D.-Y.; Thomas, J. K. *Macromolecules* **1984**, *17*, 2142.

(44) Sassoon, R. E.; Aizenshtat, Z.; Rabani, J. *J. Phys. Chem.* **1985**, *89*, 1182.

(45) Szentirmay, M. N.; Prieto, N. E.; Martin, C. R. *J. Phys. Chem.* **1985**, *89*, 3017.

(46) Strauss, U. P.; Schlesinger, M. S. *J. Phys. Chem.* **1978**, *82*, 1627.

(47) Bednar, B.; Morawetz, H.; Shafer, J. A. *Macromolecules* **1985**, *18*, 1940.

(48) Aylward, N. N. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 373.

(49) Turro, N. J.; Okubo, T. *J. Phys. Chem.* **1982**, *86* 1485.

(50) Ander, P.; Mahmoudhagh, M. K. *Macromolecules* **1982**, *15*, 213.

(51) Carroll, W. R.; Eisenberg, H. *J. Polym. Sci. Part A* **1966**, *4*, 599.

(52) The location of the excimer peak has been determined by using a Spex spectrofluorimeter, which has a much higher sensitivity to fluorescence above 300 nm than the Perkin-Elmer spectrofluorimeter used in the rest of this study.

(53) Nishijima, Y.; Mitani, K.; Katayama, S.; Yamamoto, M. *Rep. Prog. Polym. Phys. Jpn.* **1973**, *13*, 421.

(54) Klopffer, W. *Spectrosc. Lett.* **1978**, *11*, 863.

(55) de Gennes, P.-G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 1461.

(56) Odijk, T. *Macromolecules* **1979**, *12*, 688.

(57) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.

(58) Nierlich, M.; Boue, F.; Lapp, A.; Oberthur, R. *J. Phys. (Les Ulis, Fr.)* **1985**, *46*, 649.

(59) Takahashi, A.; Kato, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 2001.

(60) Fuoss, R. M.; Strauss, U. P. *J. Polym. Sci.* **1948**, *3*, 602.

(61) Eisenberg, H. *J. Chem. Phys.* **1966**, *44*, 137.

(62) Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*; Wiley: New York, 1975.

(63) At moderately high salt concentrations, the polymer chains have considerable excluded volume even though they are contracted relative to the salt-free case. In polystyrene systems with excluded volume, any energy migration is expected to occur along the backbone of the chain and does not involve long-range interactions.[17] Thus as energy migration should be essentially unaffected by the overall conformational change, I_E/I_M may be interpreted simply in terms of the the relative number of trans–trans conformations of isotactic diads.

(64) Flory, P. *Macromolecules* **1974**, *7*, 381.

(65) Schaefer, J. *Macromolecules* **1971**, *4*, 98.

(66) Muroga, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 1576, 1580.

(67) Allegra, G.; Bruckner, S.; Crescenzi, V. *Eur. Polym. J.* **1972**, *8* 1255.

Photophysical Investigations of the Interactions of Phospholipids and a Pyrene-Substituted Poly(acrylic acid) in Dilute Solutions

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ABSTRACT: Fluorescence spectra of a pyrene-substituted poly(acrylic acid) (1) were measured in the presence of dipalmitoylphosphatidylglycerol (DPPG) at pH values of 4 and 7 to investigate the interactions between 1 and phospholipids. These photophysical investigations showed that at pH 4 mixed micelles of 1 and phospholipids were formed with the incorporation of 1 in the hydrophobic core of the mixed micelle. The measurements of fluorescence decay and quenching of fluorescence by nitromethane in solutions of 1 and DPPG also supported this model for the interactions of 1 and phospholipids. These results were in agreement with a calorimetric investigation of the interactions between phospholipids and poly(acrylic acid) derivatives (Tirrell, D. A.; Takigawa, D. Y.; Seki, K. *Ann. N.Y. Acad. Sci.* **1985**, *446*, 237). The effects of head group and temperature on the interactions of 1 and phospholipids were also investigated.

Investigations of the interactions of phospholipids and synthetic polymers could be expected to play important roles in the pursuit of scientific knowledge of the structures and functions of biological macromolecules and membranes. These investigations are also of importance for the synthesis of novel functional polymers for reactions in organized media and to mimic the functions of biological molecules. Tirrell and co-workers[1,2] have investigated the interactions of a variety of synthetic polymers and phospholipids in aqueous solutions. Photophysical techniques have been extensively used in the investigations of the structure and functions of synthetic and biological macromolecules.[3] Photophysical properties of the pyrene chromophore covalently bound to poly(acrylic acid) (PAA) have been used by Turro and Arora[4] to investigate the inter- and intrapolymer interactions in dilute aqueous solutions of PAA and complementary polymers. Intrachain interactions of pyrene groups in pyrene-substituted PAA (1) investigated by measurements of fluorescence spectra, fluorescence lifetimes, and quenching of fluorescence were found to be useful probes for inter- and intramolecular interactions in solutions of 1 and complementary polymers. Intramolecular excimer formation in bichromophoric pyrene-substituted compounds has been used to investigate structures and functions of phospho-

Table I
Definitions and Significance of the Photophysical Parameters of Pyrene Obtained from Emission and Excitation Spectra of 1

symbol	definition	significance
I_M/I_E	ratio of intensities of monomer (0,0) and excimer fluorescence	reflects intrachain interactions of pyrene groups
λ_E	wavelength corresponding to maximum in the excimer emission	environment and orientation of pyrene groups involved in excimer formation affect the value of λ_E
P_M	peak-to-valley ratio for the (0,0) transition in the ^1L_a band in the excitation spectrum viewed at 380 nm	reflects interactions of isolated (non-excimer-forming) pyrene groups
P_E	peak-to-valley ratio for the (0,0) transition in the ^1L_a band in the excitation spectrum viewed at 480 nm	reflects interactions of excimer-forming pyrene groups

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