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Excimer Formation of Poly(styrenesulfonic acid) and Its Salts in Solution

Yanari, Bovey, and Lumry[1] were the first to suggest that the fluorescence emission from isotactic polystyrene solutions was due to the formation of excimers. Hirayama[2] then showed that the compounds that give rise to excimer fluorescent emission are so structured that the phenyl groups along the main alkane chain are on every other carbon atom so that adjacent phenyl groups could interact electronically. Morawetz discussed fluorescence techniques in polymer chemistry.[3]

Counterions are believed to interact with polyelectrolytes in solution by two principal modes—the short-range interaction of counterion condensation onto the polyion and the long-range ion atmosphere interaction with the polyion.[4–8] Recently, Manning[9,10] introduced another way in which condensed counterions can interact with the polyion, called territorial binding, whereby the fully hydrated counterion may move in an unrestricted and random way along the polyelectrolyte chain. Quantitative correlation of the experimental results with theoretical models has been more easily accommodated for the long-range interactions than for the short-range ones, whose principal measurements include transport, NMR, and several techniques based on volume change.[7,10] Here, we report the application of a technique that could be potentially useful to investigate counterion condensation. Since excimers form with polystyrene in solution,[1] excimer formation should be facilitated for salts of poly(styrenesulfonic acid). Moreover, if counterion condensation depends on the nature of the counterion, the observed excimer spectra should reveal this. Hence, the lithium, sodium, potassium, cesium, magnesium, calcium, strontium, and lanthanum salts of poly(styrenesulfonate) were prepared from the same poly(styrenesulfonic acid) sample and their fluorescent spectra in aqueous solutions were determined.

The sodium poly(styrenesulfonate) sample (NaPSS) used was supplied by Dow Chemical Co. and was found to have a molecular weight of 4.8×10^5, as determined from the intrinsic viscosity in aqueous 0.010 N NaCl solution and the known Mark–Houwink parameters.[11]

The lithium, potassium, cesium, magnesium, calcium, strontium, and lanthanum salts of PSS were prepared by adding excess 1 N HCl to the NaPSS solutions, followed by dialysis, addition of excess amounts of their respective hydroxides, and filtering and dialyzing the LiPSS, KPSS, CsPSS, MgPSS, CaPSS, SrPSS, and LaPSS aqueous solutions. The NaPSS and HPSS solutions were also dialyzed.

Aqueous salt-free and 0.0010, 0.10, and 0.50 N LiCl, NaCl, KCl, CsCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, and $LaCl_3$ aqueous solutions containing 4.0×10^{-3} N LiPSS, NaPSS, KPSS, CsPSS, MgPSS, CaPSS, SrPSS, and LaPSS, respectively, and aqueous 4.0×10^{-3} N HPSS were prepared. The fluorescence spectra of nonnitrogenated and nitrogenated solutions were obtained with a Varian SF-330 spectrofluorometer at an excitation wavelength of 266 nm. Also, the spectra of 4.0×10^{-3} N aqueous solutions of *p*-toluenesulfonic acid and its salts were obtained.

Figure 1 shows the fluorescence spectra of the nonnitrogenated aqueous solutions of HPSS, LiPSS, NaPSS, KPSS, CsPSS, MgPSS, CaPSS, SrPSS, and LaPSS, each solution at the same equivalent concentration of 4.0×10^{-3} N. The spectra are similar and consist of two bands, with maxima at 294 and 324 nm (for the LaPSS solutions these bands were shifted to 298 and 333 nm, respectively), whereas the spectra for the aqueous solutions of monomeric *p*-toluenesulfonic acid and its salts, each solution at the same equivalent concentration as that of the polyelectrolyte solutions, were observed to consist of one band, with a maximum at 287 nm. This is analogous to the results found for atactic and isotactic polystyrenes in cyclohexane, with the spectra maxima at 280 nm for the normal or monomer band and at 331 and 327 nm, respectively, for the excimer or dimer band.[12,13] The spectra for LiPSS, NaPSS, CsPSS, and MgPSS in LiCl, NaCl, CsCl, and $MgCl_2$ solutions, respectively, showed no salt concentration dependence over the range 1.0×10^{-3} to 5.0×10^{-1} N. For KPSS, CaPSS, and SrPSS in KCl, $CaCl_2$, and $SrCl_2$, respectively, illustrated in Figure 2 for SrPSS, the intensity ratios of the excimer to the monomer at their maximum wavelengths were found to increase slightly with increasing salt concentration over the range 1.0×10^{-3} to 5.0×10^{-1} N. The spectra for LaPSS in 0.0010, 0.10, and 0.50 N $LaCl_3$, in Figure 3, not only showed a strong salt concentration dependence but also showed a shift of excimer band from 333 nm from salt-free solution to 354 nm for the 0.50 N salt concentration. Bubbling N_2 through the solutions increased the intensity of both bands of the spectra, as has been observed previously.[1,12,13] For salt-free solutions, the excimer-to-monomer intensity ratios are in the order LaPSS < MgPSS $\simeq$ CaPSS $\simeq$ SrPSS < LiPSS $\simeq$ NaPSS $\simeq$ KPSS $\simeq$ CsPSS $\simeq$ HPSS, which indicates that the condensed Li^+, Na^+, K^+, and Cs^+ ions interact with the sulfonate group via short-range forces in the same manner and to the same extent since their intensity ratios

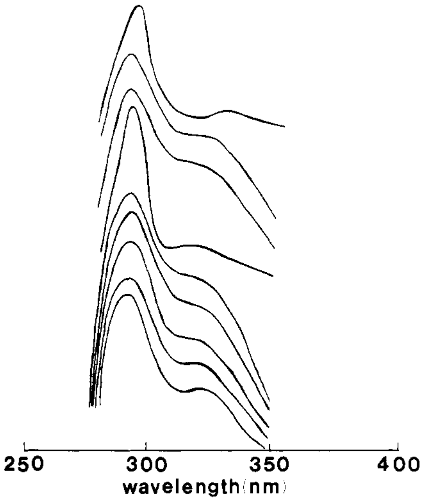

Figure 1. Fluorescence spectra of 4.0×10^{-3} N HPSS, LiPSS, NaPSS, KPSS, CsPSS, MgPSS, CaPSS, SrPSS, and LaPSS in aqueous salt-free solutions from bottom to top, respectively.

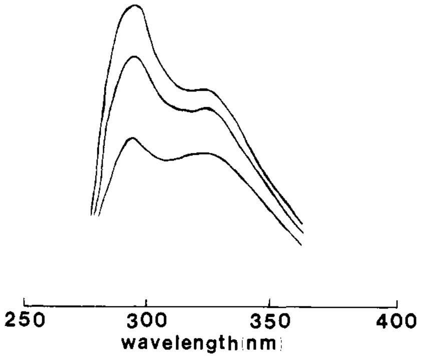

Figure 2. Fluorescence spectra of 4.0×10^{-3} N SrPSS in 0.50, 0.10, and 0.0010 N $SrCl_2$ from bottom to top, respectively.

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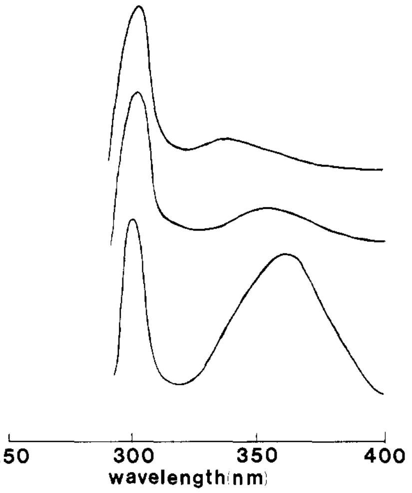

Figure 3. Fluorescence spectra of 4.0×10^{-3} N LaPSS in 0.50, 0.10, and 0.0010 N $LaCl_3$ from bottom to top, respectively.

are identical. This is also true for the divalent ions. It was interesting to note that the ability to form excimer depended on the hydrated radii of the counterions, with the largest hydrated ion, La^{3+}, least capable of excimer formation. For the counterions used here, their hydrated radii can be classified principally as tervalent > divalent > monovalent.[14] While it has been established that the most hydrated alkali metal ion binds least to the poly(styrenesulfonate) polyion,[15-17] it was at first surprising that the alkali metal ions did not bind to poly(styrenesulfonate) in the order generally found, i.e., $Li^+ < Na^+ < K^+ < Cs^+$. However, the type of counterion binding that favors excimer formation is specific inasmuch as it requires binding that causes plane-to-plane contact between the adjacent aromatic rings. Divalent ions in salt-free solutions yielded low excimer-to-monomer ratios than did the alkali metal ions. Each divalent metal ion can bind more readily to both sulfonate groups on adjacent aromatic rings than can alkali metal ions, thereby reducing the coplanarity between adjacent aromatic rings. This is probably due to the larger size of the hydrated divalent ions (Mg^{2+}, Ca^{2+}, and Sr^{2+} are 0.44, 0.42, and 0.42 nm, respectively[14]) as compared to the 0.25 nm between adjacent phenyl rings. Tervalent La^{3+} ion causes the largest reduction in coplanarity since it has the lowest excimer-to-monomer ratio in salt-free solution. It is interesting that the spectrum of a 4.0×10^{-3} N aqueous solution of poly[(vinylbenzyl)trimethylammonium chloride] showed only one band, with a maximum at 316 nm, and no excimer band because of the bulky ionic groups pendant from each phenyl ring.

The excimer-to-monomer ratios were found to be independent of simple salt concentration for LiPSS, NaPSS, CsPSS, and MgPSS. It appears that any change in the conformation of each of these polyelectrolytes due to a change in the ionic strength of the solution does not effect the short-range counterion–polyion interaction. For KPSS, CaPSS, SrPSS, and LaPSS, the excimer-to-monomer ratios were found to increase as the simple salt concentration was increased. This suggests that increased screening of the polyelectrolyte at the higher ionic strengths permits the adjacent phenyl groups to come closer together to form a tighter bond with these larger counterions. Hydrated counterion radii decrease as their concentration increases,[14] thereby, perhaps, facilitating excimer formation.

References and Notes

(1) Yanari, S. S.; Bovey, F. A.; Lumry, R. *Nature (London)* **1963**, *200*, 242.
(2) Hirayama, F. *J. Chem. Phys.* **1965**, *42*, 3163.
(3) Morawetz, H. *Science (Washington, D.C.)* **1979**, *203*, 405.
(4) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(5) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 934.
(6) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 3249.
(7) Manning, G. S. *Annu. Rev. Phys. Chem.* **1972**, *23*, 117.
(8) Manning, G. S. *Biophys. Chem.* **1977**, *7*, 95.
(9) Manning, G. S. *Q. Rev. Biophys.* **1978**, *11*, 179.
(10) Manning, G. S. *Acc. Chem. Res.* **1979**, *12*, 443.
(11) Takahashi, A.; Kato, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 2001.
(12) Longworth, J. W.; Bovey, F. A. *Biopolymers* **1966**, *4*, 1115.
(13) Longworth, J. W. *Biopolymers* **1966**, *4*, 1131.
(14) Erdey-Gruz, T. "Transport Phenomena in Aqueous Solution"; Wiley: New York, 1974; Chapter 5.
(15) Caille, A.; Daoust, H. *J. Polym. Sci., Polym. Symp.* **1974**, *No. 45*, 153.
(16) Tondre, C.; Zana, R. *J. Phys. Chem.* **1971**, *75*, 3367.
(17) Strauss, U. P.; Leung, Y. P. *J. Am. Chem. Soc.* **1965**, *87*, 1476.

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Separation of Two Relaxation Processes in Bulk Polymers Using Photon Correlation Spectroscopy at High Pressures

During the past 20 years the dynamic processes in amorphous polymers have been studied mainly by dielectric relaxation (DR).[1,2] Thus from the shapes of dielectric loss peaks two types of motion, known as α and β motions, have been characterized for a series of polymer melts. These two kinds of motion become indistinguishable and probably display a strong coupling at higher temperatures because of the different temperature dependence of the respective relaxation times τ. The different pressure dependence of τ has led to a fairly good resolution at most temperatures in the dielectric studies.[3-5] In general, the α mode in dielectric relaxation has been assigned mainly to collective motions involving several segments, while the assignment of the β mode to the dynamics of polar side groups seems to be questionable.

Recently, photon correlation spectroscopy has been applied to studies on bulk polymer dynamics with the hope of obtaining additional information, as the two methods monitor the polymer dynamics from a different viewpoint. So far the following polymers have been studied by dynamic light scattering: polystyrene (PS),[6-8] poly(methylphenylsiloxane) (PMPS),[9] poly(propylene glycol) (PPG),[10] and poly(ethyl methacrylate) (PEMA).[11] The experimental correlation functions for most of these polymers have been discussed in terms of local motions involving several chemical segments (α motion). The only exception was PMPS, for which the spectrum was shown to depend on the magnitude of the scattering vector **q**. For PS the observed dynamics have been assigned either to two relaxation processes (α, β)[6,8] or to a single process (α)[7], while the dielectric relaxation data of this polymer show both α and β relaxation processes. This uncertainty was not removed as yet because the light scattering experiments were carried out at constant pressure (1 bar). Thus the experiments were deprived of a valuable means of resolving the time scales. More recently, Patterson et al.[11] performed photon correlation measurements on PEMA and observed an exceptionally broad distribution of re-

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