References and Notes

(1) Registered trademark of E. I. du Pont de Nemours and Co., Inc. for its perfluorinated membrane products.
(2) Grot, W. G. F.; Munn, G. E.; Walmsley, P. N. Paper presented at the 141st National Meeting, The Electrochemical Society, Houston, May 7-11, 1972.
(3) Grot, W. G. F. *Chem.-Ing.-Tech.* **1972**, *44*, 167; **1975**, *47*, 617.
(4) Grot, W. G. F. U.S. Patent 3 969 285, 1976.
(5) Hsu, W. Y.; Barkley, J. R.; Meakin, P. *Macromolecules* **1980**, *13*, 198.
(6) Gierke, T. D. Paper presented at the 152nd National Meeting, The Electrochemical Society, Atlanta, Oct 10-14, 1977.
(7) Yeo, S. C.; Eisenberg, A. *J. Appl. Polym. Sci.* **1977**, *21*, 875.
(8) Hus, W. Y.; Gierke, T. D. *Macromolecules* **1982**, *15*, 101.
(9) Brown, R. G. *J. Chem. Phys.* **1964**, *40*, 2900.
(10) Bates, T. W.; Stockmayer, W. H. *Macromolecules* **1968**, *1*, 17.
(11) Bates, T. W.; Stockmayer, W. H. *Macromolecules* **1968**, *1*, 12.
(12) Pao, Y.-H.; Bjorklund, R. F. *J. Appl. Phys.* **1960**, *31*, 1925.
(13) D'Ilario, L.; Giglio, E. *Acta Crystallogr., Sect. B* **1964**, *30*, 372.
(14) Corradini, P.; Guerra, G. *Macromolecules* **1977**, *10*, 1410.
(15) Krimm, S. *Fortschr. Hochpolym. Forsch.* **1960**, *2*, 51.
(16) The equivalent weight is the mass of a dry perfluorosulfonic acid ionomer in grams required to neutralize 1 equiv of base.
(17) A linear base line is employed to correct for the background. The measured absorbance is the peak-to-base line value.
(18) $C < 1$ is most likely due to different absorptivities, arising from different symmetries, of the normal and reversed helical states. For example, the cis and gauche states of 2,3-difluoropropene have very different microwave and far-IR absorptivities (cf.: English, A. D.; Scharpen, L. H.; Ewool, K. M.; Strauss, H. L.; Harris, D. O. *J. Mol. Spectrosc.* **1976**, *60*, 210).
(19) According to ref 9, eq 3 can still be fitted to the low-T data of PTFE except near the 19 and 30 °C transitions. The formation energy E_d, however, is larger than the corresponding value at high T. This suggests that helix reversals still exist but are less numerous at low T. See also ref 21.
(20) Gierke, T. D., unpublished results.
(21) Martin, G. M.; Eby, R. K. *J. Res. Natl. Bur. Stand., Sect. A* **1968**, *72*, 467.
(22) Clark, E. S.; Muus, L. T. *Z. Kristallogr.* **1962**, *117*, 119.
(23) Hyndman, D.; Origlio, G. F. *J. Appl. Phys.* **1960**, *31*, 1849.
(24) Clark, E. S. *J. Macromol. Sci., Phys.* **1967**, *B1*, 795.
(25) See, for example: Kjems, J. K.; Steiner, M. *Phys. Rev. Lett.* **1978**, *41*, 1137. Krumhansl, J. A.; Schrieffer, J. R. *Phys. Rev.* **1975**, *11*, 3535.
(26) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. Lett.* **1979**, *42*, 1698.
(27) For a general discussion of solitons, see: Bishop, A. R.; Krumhansl, J. A.; Trullinger, S. E. *Physica (The Hague)* **1980**, *1*, 1.
(28) Currie, J. F.; Krumhansl, J. A.; Bishop, A. R.; Trullinger, S. E. *Phys. Rev. B* **1980**, *22*, 477.
(29) Kasowski, R. V.; Hsu, W. Y.; Caruthers, E. B. *J. Chem. Phys.* **1980**, *72*, 4896.
(30) Mansfield, M. L. *Chem. Phys. Lett.* **1980**, *69*, 383. See also: Mansfield, M. L.; Boyd, R. H. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1227.
(31) Skinner, J. L.; Wolynes, P. G. *J. Chem. Phys.* **1980**, *73*, 4022.
(32) IR spectra reported here, however, only track the number density of solitons (and antisolitons) but not their motion.
(33) DeLeonardis, R. M.; Trullinger, S. E. *Phys. Rev. B.* **1983**, *27*, 1867. I am grateful to Prof. Trullinger for a preprint and several helpful discussions.

Investigation on Ion Binding in Synthetic Polyelectrolyte Solutions Using Rare Earth Metal Fluorescence Probes[1]

Isao Nagata and Yoshiyuki Okamoto*

Department of Chemistry and Polymer Research Institute, Polytechnic Institute of New York, Brooklyn, New York 11201.

Received August 20, 1982

ABSTRACT: The rare earth metal fluorescence probe technique was applied for the elucidation of the binding of metal ions to polyelectrolytes. We have observed that the presence of synthetic polyelectrolytes such as poly(sodium acrylate) (PAA) and poly(sodium ethenesulfonate) (PVS) enhances considerably the fluorescence intensity of the Tb^{3+} ion in aqueous solution. This result was accounted for by the fact that the Tb^{3+} ion was bound to asymmetrically arranged polyanions. The formation of a unique asymmetric environment surrounding the Tb^{3+} ion led to the increased transition probability for the fluorescence, and the resulting fluorescence of the Tb^{3+} ion was greatly enhanced. With poly(sodium methacrylate) and poly(sodium styrenesulfonate), the fluorescence intensity of the Tb^{3+} ion did not increase appreciably. When the methyl and phenyl groups were attached to the polymer chain, the polymer became less flexible and the multidentate complex formation between the Tb^{3+} ion and carboxylate or sulfonate became more difficult. When the Tb^{3+} ion solutions were titrated with Li-, Na-, K-, and Rb-PAA salts, the fluorescence intensity of the Tb^{3+} ion increased sharply over a small range of the PAA salt concentration and reached a constant value at higher concentration. We calculated the binding constants, K (M^{-1}), of these PAA alkali salts with the Tb^{3+} ion and found them to be 300, 390, 500, and 610, respectively, in the presence of Li, Na, K, and Rb. This order was attributed to the competition reaction between Tb^{3+} and alkali metal ions for the binding to polyacrylate. Addition of a large excess of NaCl to the solution of the PAA-Na salt and Tb^{3+} increased the fluorescence intensity of the Tb^{3+} ion. This result indicated that the electrostatic repulsion of the polymer chain was reduced by addition of NaCl and then the polymer became more compact. Such contraction would facilitate the multidentate complex formation of the Tb^{3+} ion with the carboxylate group. When EDTA was added to the solution of the PAA-Tb^{3+} complex, the fluorescence of the Tb^{3+} ion was drastically decreased and this result suggested that EDTA binds Tb^{3+} much more strongly than PAA.

Introduction

The extremely low activity coefficients of counterions in polyelectrolyte solutions are attributed to two types of association of counterions to polyions. One type of binding is referred to as "diffuse" or "ion atmosphere binding", where the counterions are localized in the area of the polyelectrolyte domain due to the large electrostatic forces and have some mobility. Another type of binding is "site binding", where the counterions are attracted to specific sites of the polyions through the formation of the complex.[2]

Positive evidence for site binding has been accumulated from studies of dialysis equilibrium,[3] dilatometric measurements,[4] UV spectroscopy,[5,6,19] and potentiometric titrations of synthetic polyelectrolytes. Site binding of counterions to biological polymers has been studied by NMR,[7] fluorescence,[8] and dichroism measurements.[8]

There has been a great stimulation of interest in the absorption and fluorescence of rare earth metal ions in

0024-9297/83/2216-0749$01.50/0

solution because of their possible use as lasers. In an effort to obtain stronger fluorescence, two general approaches appear possible. The first involves the addition of an agent to the solution, usually an organic ligand, which will absorb energy and transfer it to the rare earth ion. An alternative method is to enhance the absorption and fluorescence of the rare earth ion itself by suitable changes in its environment. Since the transitions involved, e.g., ${}^5D_0 \rightarrow {}^7F_2$ in the case of Eu^{3+} ion, are forbidden by the Laporte selection rule, they depend for their intensity largely on the degree of asymmetry in the environment. Hence the formation of a unique asymmetric environment surrounding the rare earth ion should lead to a marked enhancement of the fluorescence, primarily due to the increased transition probability for fluorescence.

It has been observed that the fluorescence intensities of Tb^{3+} or Eu^{3+} ions are greatly enhanced when they are bound to thermolysin[10] or to nucleic acid.[11] We also observed that the presence of synthetic polyelectrolytes enhances considerably the fluorescence intensity of Tb^{3+} ion in aqueous solution. This result suggests that Tb^{3+} ion is bound to asymmetrically arranged polyanions. In this report, we have studied the effect of the structure of polyelectrolytes and the nature of counterions on the fluorescence enhancement of Tb^{3+} ion.

Experimental Section

Materials. Poly(acrylic acid) (MW = 250000) and poly(sodium styrenesulfonate) (MW = 500000) were purchased from Polysciences Inc. Methacrylic acid was polymerized by free radical initiator (AIBN) in methanol at 60 °C. The polymer obtained was purified repeatedly by precipitation from methanol solution with ethyl ether. Poly(sodium ethenesulfonate) was prepared by the polymerization of sodium ethenesulfonate (obtained from Polysciences Inc.) using ammonium persulfate and sodium bisulfite as initiators at 5 °C.[12] The polymer obtained was purified by precipitation from aqueous solution with methanol. The polymer was dried at reduced pressure at 70 °C for 1 day.

The molecular weights of poly(methacrylic acid) and poly(sodium ethenesulfonate) were determined to be 200000 and 16000, respectively, using viscosity measurements in methanol at 26 °C[13] and in 1 M NaCl solution at 32.4 °C.[14] Sodium ethanesulfonate was purchased from Pfaltz and Bauer. Terbium chloride ($TbCl_3 \cdot 6H_2O$) was purchased from Ventron and used without further purification.

Fluorescence Measurements. A Perkin-Elmer Model MPF-44B fluorescence spectrophotometer was used for the measurement of the fluorescence intensities of Tb^{3+} solutions. The temperature was controlled at 25 °C. The fluorescence intensities were measured in a nitrogen atmosphere. Tris(hydroxylmethyl)methylamine solutions were tried. However, the buffer solutions interfered with the interaction between the Tb^{3+} ion and the polyelectrolytes.[15] Thus the pH of each sample was adjusted within ±0.2 by addition of dilute alkali hydroxide aqueous solution. The fluorescence intensity (emission at 545 nm) was recorded with excitation at 315 nm for carboxylate compounds. The excitation for sulfonates was at 295 nm.

Results and Discussion

The excitation and emission spectra of Tb^{3+} ion in the presence of poly(acrylic acid) (PAA) and the absence of the polymer are shown in Figure 1. The emission spectra were obtained under excitation at 315 nm. The fluorescence intensity of Tb^{3+} was considerably enhanced in the presence of the polymer.

Fluorescence intensities of Tb^{3+} ions in the presence of poly(acrylic acid), acetic acid, and ethylenediaminetetraacetic acid (EDTA) as a function of Tb^{3+} ion concentration were also measured. Typical data are plotted in Figure 2. A sharp increase in the fluorescence intensity was observed over a small range of Tb^{3+} concentration in the presence of PAA at high pH. This tendency was similar to the results of Strauss and Begala, who studied the binding of silver ion with PAA using the potentiometric titration technique.[16] Fluorescence intensities of the Tb^{3+} ion in the presence of poly(sodium ethenesulfonate) (PVS) increased moderately, as compared with those in PAA (Figure 3). On the other hand, the fluorescence intensities of the Tb^{3+} ion in the presence of acetic acid, EDTA, and sodium ethanesulfonate did not show appreciable enhancement.

To confirm these observations further, we titrated the solution of Tb^{3+} (0.5×10^{-3} and 1.0×10^{-3} M) with Na-PAA salt at pH 8 (Figure 4). The fluorescence intensities of the Tb^{3+} ion were found to be initially increased and reached a constant value at higher polymer concentrations.

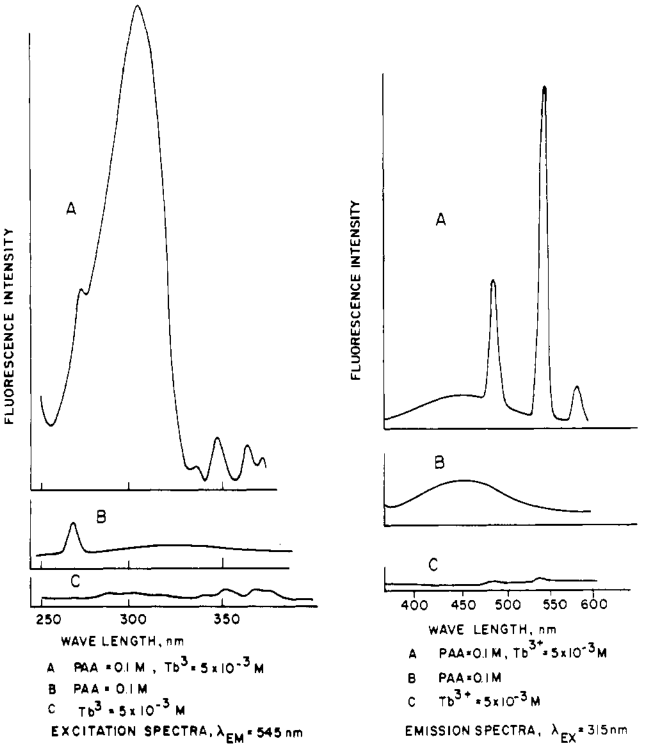


Figure 1. (Left) Excitation spectra of Tb^{3+} ion. (Right) Emission spectra of Tb^{3+} ion.

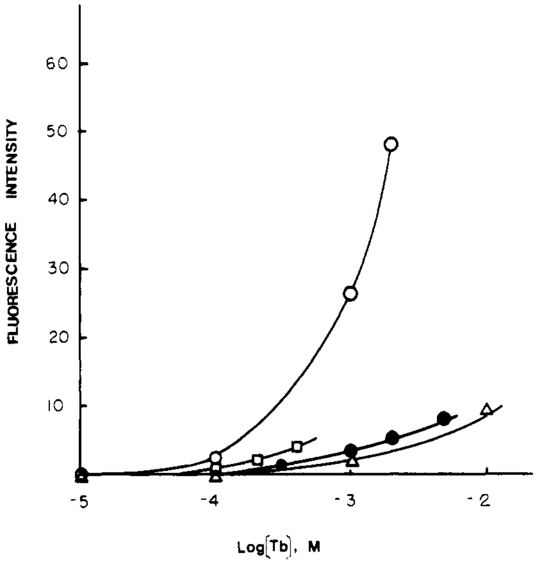


Figure 2. Fluorescence intensities of the Tb^{3+} ion in the presence of various acids at 25 °C: (○) poly(acrylic acid), 6×10^{-2} M, pH 8.5; (□) poly(acrylic acid), 6×10^{-2} M, pH 4.5; (△) ethylenediaminetetraacetic acid, 6×10^{-2} M, pH 8.9; (●) acetic acid. Emission at 545 nm; excitation at 315 nm.

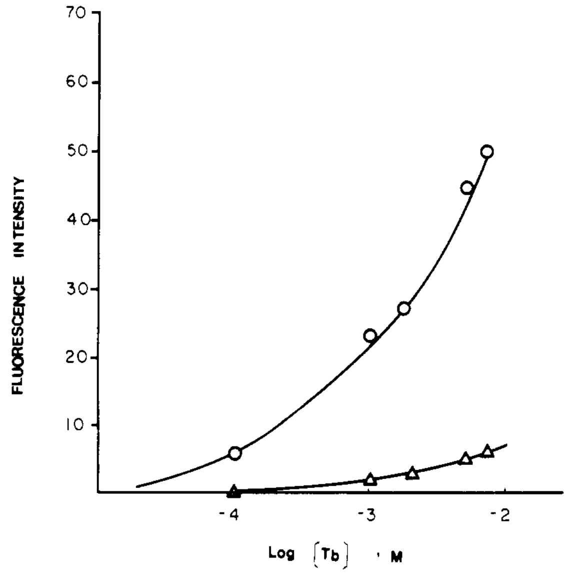


Figure 3. Fluorescence intensities of Tb^{3+} ion in the presence of 6×10^{-2} M poly(sodium ethenesulfonate), pH 8.5 at 25 °C: (○) poly(sodium ethenesulfonate); (△) sodium ethenesulfonate. Emission at 545 nm; excitation at 295 nm.

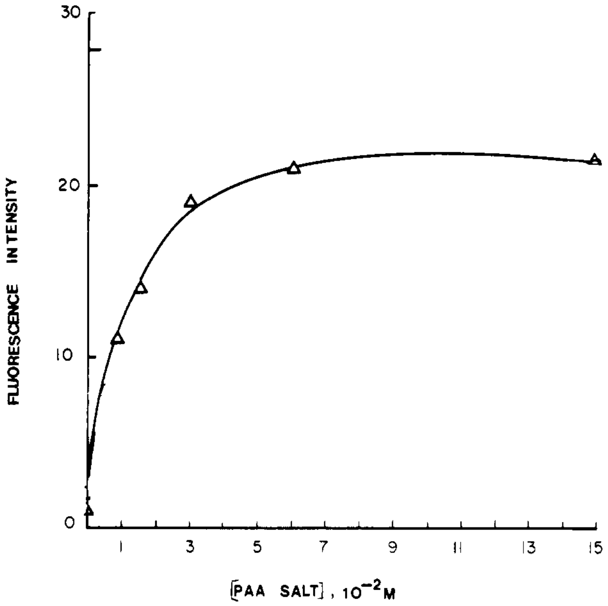


Figure 4. Relationship between fluorescence intensities of Tb^{3+} and concentration of poly(sodium acrylate) at pH 8.0, 25 °C. $[Tb^{3+}] = 1.0 \times 10^{-3}$ M.

However, when the Tb^{3+} ions were added to the solution of poly(sodium methacrylate) (PMA), only moderate enhancement of the fluorescence intensity was observed. A large increase in the Tb^{3+} fluorescence intensity was also found with Na-PVS, when compared to the effect of its monomeric analogue, sodium ethanesulfate (Figure 5). With poly(sodium styrenesulfonate) (PSS), the intensity did not increase appreciably. These results indicate that the trivalent Tb^{3+} ion forms the complex with polyanions such as PAA and PVS, not only due to a strong electrostatic force of polyelectrolytes, but also with locally concentrated ligand groups.[3] As a result of the complex formation of Tb^{3+} with randomly located carboxylate or sulfonate groups, the Tb^{3+} ion was coordinated asymmetrically with these groups and the fluorescence intensity of Tb^{3+} was greatly enhanced.

In order to study the effect of counterions on the binding behavior of the Tb^{3+} ion with PAA we titrated the Tb^{3+} solutions with Li-, K-, and Rb-PAA salts. The fluorescence intensity of Tb^{3+} was increased as was observed with the Na-PAA salt and reached a constant value at higher polymer concentration. However, the degree of increase in fluorescence intensity was found to depend on the counterion. Thus we calculated the binding constant of these alkali PAA salts with the Tb^{3+} ion using a method similar to that reported by Eldridge and Treloar.[6] The binding constant, K, is defined by

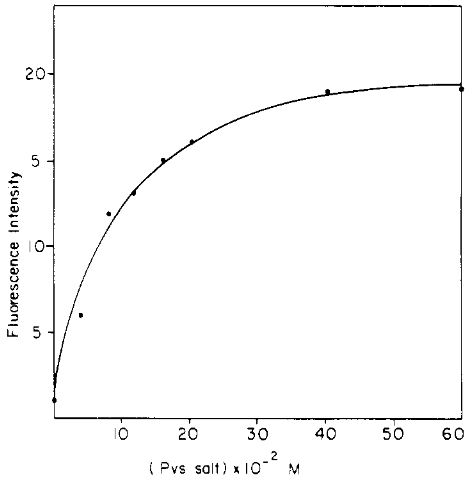


Figure 5. Relationship between fluorescence intensities of Tb^{3+} ion and concentration of poly(sodium ethenesulfonate) at pH 8.0, 25 °C. $[Tb^{3+}] = 0.5 \times 10^{-3}$ M.

$$K = \frac{M_b}{(M_t - M_b)(\frac{1}{3}P_t - M_b)} \tag{1}$$

where M_t, M_b, and P_t are the total Tb^{3+} ion, bound Tb^{3+}, and polymer concentrations, respectively. The value $^1/_3$ is used assuming that three carboxyl groups are bound to one Tb^{3+} ion.[20]

Since $P_t \gg M_b$, eq 1 can be simplified as follows:

$$\frac{1}{\frac{1}{3}P_tK} + 1 = \frac{M_t}{M_b} = \frac{1}{f} \tag{2}$$

where f is the fraction of the Tb^{3+} ion bound to polyacrylate over all the Tb^{3+} ion presented. The value of f was estimated from the observed fluorescence intensity at any polyacrylate concentration divided by the fluorescence intensity at polyacrylate concentrations where the intensity reached a constant value, so that it may be assumed that all Tb^{3+} ions are bound to polyacrylates.

When $1/f$ is plotted as a function of reciprocal polymer concentration (Figure 6), straight lines with the intercept of 1 were obtained. The binding constants K (M^{-1}) were calculated from the slope and are as follows: Li, 300; Na, 390; K, 500; Rb, 610. From the foregoing K values, it can be observed that the Tb^{3+} binding constant with polyacrylate increases with increasing size of the alkali metal ions. The association constants of carboxylate with alkali metal ions are in the order Li > Na > K.[4] Trivalent ions are generally associated strongly with carboxylates as compared with univalent ions.[18] The order of the Tb^{3+} binding constant obtained may be attributed to the competition reaction between Tb^{3+} and alkali metal ions for the binding to polyacrylates. Thus, in the presence of the weakly bound K^+, the binding constant for Tb^{3+} with polyacrylate is higher than when Li^+ or Na^+ competes with Tb^{3+}.

The complex formation of polyanions with metal ions usually results in an intramolecular coordination (cooperative bonding), which leads to contraction of the polymer chain.[15] Thus the flexibility of polyanions must be an important factor for the complex formation. When methyl

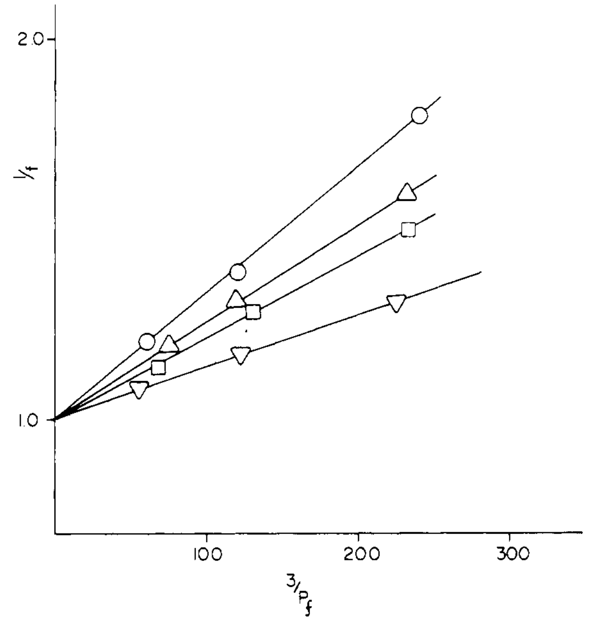


Figure 6. $1/f$ vs. polymer concentration at 25 °C: (○) PAA-Li; (△) PAA-Na; (□) PAA-K; (▽) PAA-Rb. $[Tb^{3+}] = 1.0 \times 10^{-3}$ M, pH 8.0.

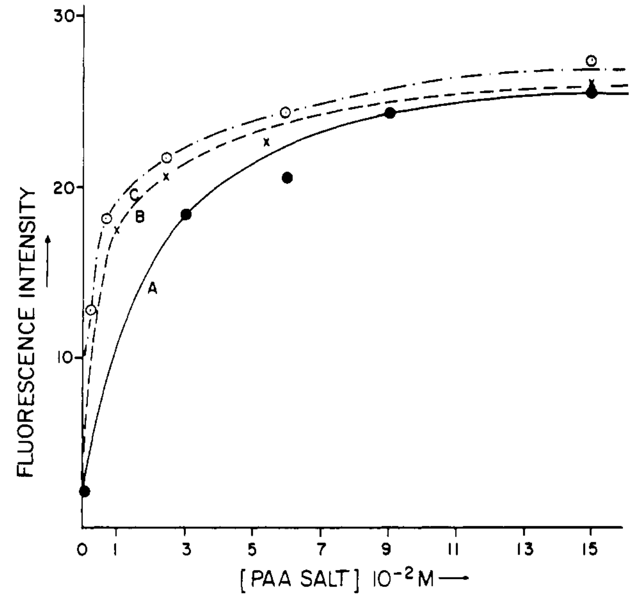


Figure 7. Effect of sodium chloride on the fluorescence intensities of Tb^{3+} ion: (●) [NaCl] = 0; (×) [NaCl] = 0.5 M; (⊙) [NaCl] = 1.0 M. pH 8, 25 °C, $[Tb^{3+}] = 0.5 \times 10^{-3}$ M.

and phenyl groups were attached in the polymer chain, the polymer became less flexible and multidentate complex formation between the Tb^{3+} ion and carboxylate or sulfonate became more difficult. Thus the differences observed between PAA and PMA and between PVS and PSS in the fluorescence intensity of Tb^{3+} indicated that PMA and PSS did not form strong complexes with the Tb^{3+} ion. A similar tendency was also reported in the interaction between dyes and polyelectrolytes[17] and also in the dilatometric study of alkali salts of polymeric acids.[4]

Addition of a large excess of NaCl to the solution of the PAA-Na and Tb^{3+} produced an increase in the fluorescence intensity of the Tb^{3+} ion (Figures 7 and 8). This may have been unexpected since the addition of excess Na^+ ion should replace Tb^{3+} from the carboxylate–Tb^{3+} complex. On the other hand, an increase in the ionic strength reduced the electrostatic repulsion between the ionic charges of the chain, leading to chain contraction. Such a contraction of the polymer chain would facilitate the multidentate complex formation of Tb^{3+} with the carboxylate groups. The latter factor was clearly dominant in this system. When a strong chelating agent such as EDTA was added to the solution of the PAA-Tb^{3+} complex, the fluorescence intensity of the Tb^{3+} ion was drastically decreased as shown in Figure 9. The addition of sodium acetate to the solution was found to increase slightly the fluorescence intensity. This result showed that EDTA binds Tb^{3+} ion much more strongly than PAA. The EDTA-Tb^{3+} may form a rather symmetrical coordination complex and the resulting fluorescence intensity is relatively weak. The slight increase in the fluorescence intensity in the presence of sodium acetate is accounted for by a similar effect as in the case of the addition of NaCl.

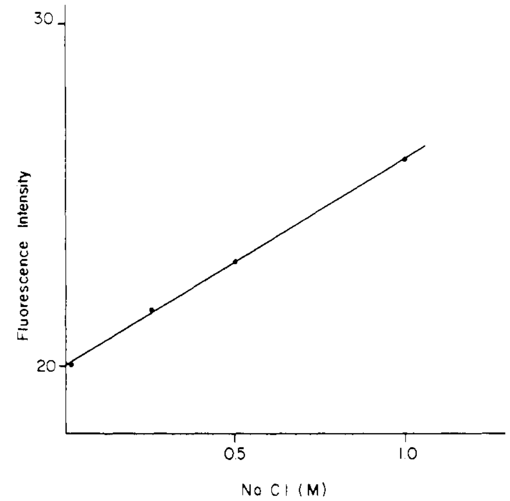


Figure 8. Effect of sodium chloride on the fluorescence intensities of the Tb^{3+} ion in the PAA-Na system at pH 8, 25 °C. [PAA-Na] = 1.5×10^{-2} M, $[Tb^{3+}] = 1.0 \times 10^{-3}$ M.

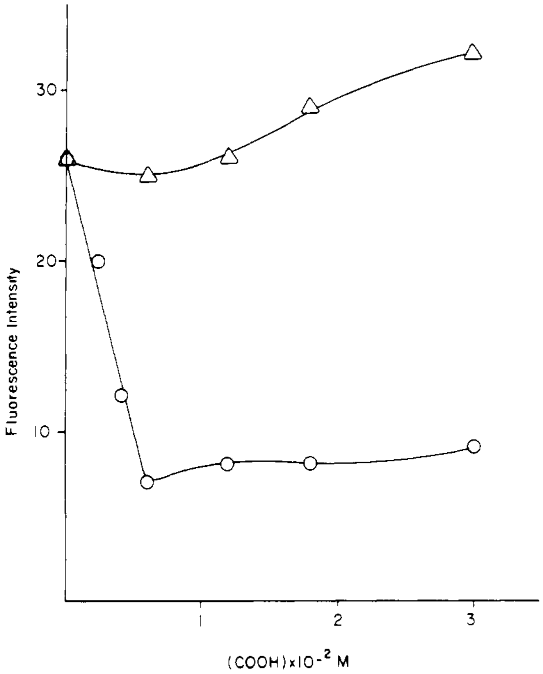


Figure 9. Effect of CH_3COONa and EDTA on the fluorescence intensities of Tb^{3+} ion in the PAA-Na system at pH 8, 25 °C: (△) CH_3COONa added; (○) EDTA added.

Acknowledgment. This work was supported by a generous grant from the National Science Foundation under Polymers Program Grant DMR-09764. We thank Professor H. Morawetz for many helpful discussions and

we also thank Miss Rosa Li for her assistance in measuring some fluorescence spectra.

Registry No. Sodium polyacrylate, 9003-04-7; poly(sodium ethenesulfonate), 9002-97-5; sodium polymethacrylate, 54193-36-1; lithium polyacrylate, 25656-42-2; potassium polyacrylate, 25608-12-2; rubidium polyacrylate, 39936-29-3; poly(acrylic acid), 9003-01-4; acetic acid, 64-19-7; sodium ethanesulfonate, 5324-47-0; EDTA, 60-00-4; PSS, 62744-35-8; $TbCl_3$, 10042-88-3; NaCl, 7647-14-5.

References and Notes

(1) Rare Earth Metal Containing Polymers, 8.
(2) (a) Rice, S. A.; Nagasawa, M. "Polyelectrolyte Solutions"; Academic Press: New York, 1961; Chapter IX. (b) Miller, M. L. "The Structure of Polymers"; Reinhold: New York, 1966; Chapter 12.
(3) Kotliar, A. M.; Morawetz, H. *J. Am. Chem. Soc.* **1955**, *77*, 3692.
(4) Strauss, U. P.; Leung, Y. P. *J. Am. Chem. Soc.* **1965**, *87*, 1476.
(5) Walls, F. T.; Gill, S. J. *J. Phys. Chem.* **1954**, *58*, 1128.
(6) Eldridge, R. J.; Treloar, F. I. *J. Phys. Chem.* **1970**, *74*, 1446.
(7) Eisinger, T.; Estrup, F. F.; Shulman, R. G. *J. Chem. Phys.* **1965**, *42*, 43.
(8) Regani, H.; Friedman, H. *J. Chem. Soc., Chem. Commun.* **1973**, 432.
(9) Gallagher, R. K. *J. Chem. Phys.* **1964**, *41*, 3061.
(10) Horrocks, W. D., Jr.; Holmquist, B.; Vallee, B. L. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4764.
(11) Wolfson, J. M.; Kearns, D. R. *Biochemistry* **1975**, *14*, 1436.
(12) Breslow, D. S.; Kutner, A. *J. Polym. Sci.* **1958**, *27*, 295.
(13) Wederhorn, N. M.; Brourn, A. R. *J. Polym. Sci.* **1952**, *8*, 651.
(14) Eisenberg, H.; Woodside, D. *J. Chem. Phys.* **1962**, *36*, 1844.
(15) Kaneko, M.; Tsuchida, E. *Macromol. Rev.* **1980**, *16*, 467.
(16) Strauss, U. P.; Begala, A. J. In "Ions In Polymers"; Eisenberg, A., Ed.; American Chemical Society: Washington, D.C., 1980; Adv. Chem. Ser. No. 187.
(17) Shirai, M.; Nagatsuka, T.; Tanaka, M. *Makromol. Chem.* **1977**, *178*, 37.
(18) Kolat, R. S.; Powell, J. E. *Inorg. Chem.* **1962**, *1*, 293.
(19) Morawetz, H. *J. Polym. Sci.* **1955**, *17*, 1442.
(20) Soresson, A. *Acta Chem. Scand.* **1958**, *12*, 165.

Phase Behavior of Polystyrene, Poly(2,6-dimethyl-1,4-phenylene oxide), and Their Brominated Derivatives

Roger P. Kambour,* John T. Bendler, and Richard C. Bopp

Polymer Physics and Engineering Branch, Corporate Research and Development, General Electric Company, Schenectady, New York 12301. Received August 3, 1982

ABSTRACT: Polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PXE) have been brominated selectively to produce in each case a series of copolymers and ultimately two new homopolymers. Limits of miscibility of the copolymers with the homopolymers have been defined in terms of the copolymer compositions in 11 unique binary, ternary, and quaternary blend series. Segment–segment χ values have been derived from an interpretation of the binary blend miscibility limits in the Flory–Huggins framework and used to predict ternary blend results successfully. Relative segment–segment repulsion inside copolymers is seen to be an important driving force for mixing frequently.

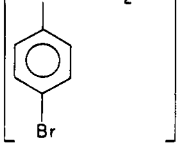
Introduction

Miscibility in polymer–polymer blends is a subject of widespread theoretical as well as practical interest currently. In the past decade or so the number of blend systems that are known to be miscible has increased considerably.[1] Moreover, a number of systems have been found that exhibit upper or lower critical solution temperatures, i.e., complete miscibility only in limited temperature ranges.[1–6] Modern thermodynamic theories have had limited success to date in predicting miscibility behavior in detail.[7] These limitations have spawned a degree of pessimism regarding the likelihood that any practical theory can be developed that can accommodate the real complexities that nature has bestowed on polymer–polymer interactions.

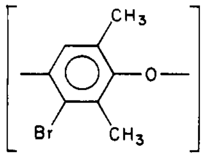
The purpose of this paper is fourfold: first, to describe several related polymer blend systems that are convenient for experimental and theoretical studies of miscibility limits; second, to show how classical Flory–Huggins segmental interaction parameters can be derived from these miscibility limits; third, to show to what extent these parameters are true constants, i.e., to what extent they are useful in predicting the miscibility characteristics of other blend systems containing the same segment pairs; and fourth, to highlight, for blends containing copolymers, the importance to blend miscibility of the segment–segment interactions internal to the copolymer itself.

Experimental Procedures

The subject blends were made from polystyrene (PS), poly(2,6-dimethyl-1,4-phenylene oxide), trivially named poly(xylenyl ether) (PXE), and their brominated derivatives. Both parent resins can be easily and controllably brominated in solution up to one bromine per repeat unit without the need for adding a catalyst. (Experimental conditions used: (a) For PXE, $CHCl_3$ as solvent; stoichiometric liquid bromine added; absence of light: 3–6-h reaction time.[8] For PS, nitrobenzene as solvent; ca. 5/4 stoichiometric liquid bromine added; absence of light; 1-day reaction time. The latter reaction is sluggish; unreacted bromine at the end of the reaction period was titrated with pentene before the polymer was precipitated.) The bromine substitution occurs in each case in one position on the aromatic ring only and, due to deactivation, once only on each ring. Thus, in the case of complete bromination two new homopolymers are formed, poly(*p*-bromostyrene) and poly(3-bromo-2,6-dimethyl-1,4-phenylene oxide):



PBr$_1$S



PBr$_1$XE

Lesser degrees of bromination result in random copolymers of (a) styrene with *p*-bromostyrene, coded PBr$_x$S and, (b) xylenyl