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Fluorescence as a Probe for Examining Salt Group Association of Sulfonated Polystyrene Ionomers in Tetrahydrofuran

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ABSTRACT: Salt group association in sulfonated polystyrene ionomers with different counterions ((SP)Me) was studied over a wide range of concentrations in tetrahydrofuran (THF) by a fluorescence molecular probe technique. It was found that the tendency to form intra-chain associations in the dilute solution regime decreases in the order (SP)Zn > (SP)Na > SPS, where (SP)Zn is the zinc salt, (SP)Na is the sodium salt, and SPS is the sulfonic acid form of the ionomer. The critical concentration, when inter-chain associations become important, decreases in the order polystyrene ~ SPS ~ (SP)Na ≫ (SP)Zn. Some speculations about the structure of the salt group associations are presented on the basis of the monomer–excimer fluorescence data from (SP)Me solutions.

Introduction

Solutions of ionomers in nonpolar solvents have been the subject of a number of investigations in recent years. It has been found that ionomers associate strongly in the dilute and semidilute regimes in such solvents.[1–5] This association, which increases with increasing concentration, leads to a stable gelation of the ionomer solution at high concentrations. Such behavior takes place even at very low concentrations of salt groups in the ionomers, as low as 2–3 mol %. Because of this behavior, ionomers at low concentrations can be used for viscosification of oils at high temperatures.[3]

The effect of salt group association was discussed first by Lundberg in the context of viscosity experiments.[1,2] He found that in very dilute solutions in a nonpolar solvent, like tetrahydrofuran (THF), the viscosity of the ionomer is much less than that of the unmodified polymer precursor. At higher concentrations (approximately at the coil overlap concentration), there is a crossover of the viscosity curves between the ionomer and its precursor. This was attributed to a balance between intra- and inter-chain associations of the salt groups.

The association of ionomer coils through salt group interactions was examined subsequently by light scattering.[6–8] It was found[7] that in a dilute solution of sodium-sulfonated polystyrene ionomer in xylene the single-chain dimensions of the ionomer coil are 20% smaller than the single-chain dimensions of unmodified polystyrene with the same molecular weight. In the semidilute concentration regime of the same ionomer solution, increasing ionomer concentration is accompanied by an increase of the molecular weight of the aggregates and a decrease of the second virial coefficient.[8]

Very important information concerning the structure of salt group associates was obtained by a neutron scattering examination of the ionomer solutions.[9–11] It was shown that, in THF, the dimensions of individual sodium sulfonate polystyrene ionomer coils are independent of ionomer concentration in the semidilute regime, while the degree of coil aggregation increases rapidly.[9] Later, the same conclusions were reached for the same ionomer with a different content of salt groups,[11] and they were extended to the zinc-neutralized sulfonated polystyrene ionomer.[11] Unfortunately, at present, there is no available information about the structure of the ionomer aggregates and their behavior in the dilute regime of ionomer solutions much below the crossover concentration. Progress in this area is limited by the small number of available methods that are sensitive to associations in the dilute regime of ionomer solutions.

The objective of the present investigation is to examine salt group association of ionomers with different counterions over a wide range of concentrations. We applied fluorescent molecular probe techniques, which are sensitive enough to extend into the dilute solution regime.

Experimental Section

Materials. Sulfonated polystyrene ionomers with different counterions, based on anionically polymerized polystyrene (PS), with $\bar{M}_w$ = 115 000 and narrow molecular weight distribution, $M_w/M_n \sim 1.05$, were used in the investigation. Sulfonation levels of the samples are given in Table I.

The samples were synthesized and characterized by Dr. R. D. Lundberg as described in ref 6. 1,3,6,8-Pyrenetetrasulfonic acid tetrasodium salt ((PTS)Na), was used as the probe in the fluorescence measurements. It was obtained from Eastman Kodak Co. Tetrahydrofuran was used as the solvent in all experiments. Twice distilled water was used as a solvent for (PTS)Na.

Sample Preparation. Polymer solutions were prepared volumetrically by using magnetic stirrers for agitation. Stock solutions were stirred about 24 h to get complete dissolution and then were used for serial dilution. Ionomer–polymer prediluted solutions (2 mL in THF) were mixed with (PTS)Na (0.002 mL in H_2O) in a cell suitable for the fluorescence measurements. The ionomer–polymer solution concentration range was from 10^{-4} to 10^{-1} mol/L. The probe concentration was kept constant at 5.4 × 10^{-7} mol/L.

Measurements. Fluorescence spectra measurements from the ionomer–polymer solutions were carried out at 360- and 378-nm excitation wavelengths on a Perkin-Elmer MPF-66 spectrofluorometer at room temperature. Excimer–monomer maximum values of fluorescence intensities were observed as a function of ionomer concentration at 500 and 409 nm, respectively.

Excimer–monomer maximum values of fluorescence intensities from ionomer solutions were defined as

$$\Delta I_{ex/mon} = I_{ex/mon}(\text{ionomer} + (\text{PTS})\text{Na}) - I(\text{background})$$

$$I(\text{background}) = I_{ex/mon}(\text{PS} + (\text{PTS})\text{Na}) \text{ or } I_{ex/mon}(\text{ionomer})$$

Results and Discussion

Application of the Fluorescence Molecular Probe Technique for Examining Ionomer Behavior in Non-

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Table I

coun- terion	*m*, mol %	desig- nation	coun- terion	*m*, mol %	desig- nation
H	4.47	SPS	Zn	1.78	(SP)Zn
Na	1.35	(SP)Na		4.20	
	2.80				

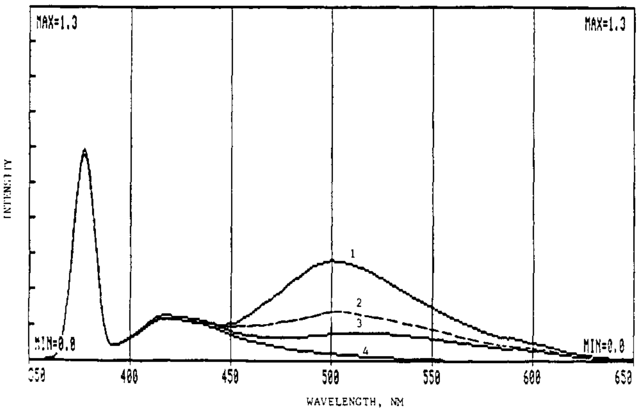

Figure 1. Fluorescence spectra: (SP)Na (m = 2.80%)-THF-(PTS)Na (1); (SP)Na (1.35%)-THF-(PTS)Na (2); PS-THF-(PTS)Na (3); (SP)Na (1.35 and 2.8%)-THF (4). $C \sim 1 \times 10^{-4}$ M. λ_{ex} = 378 nm.

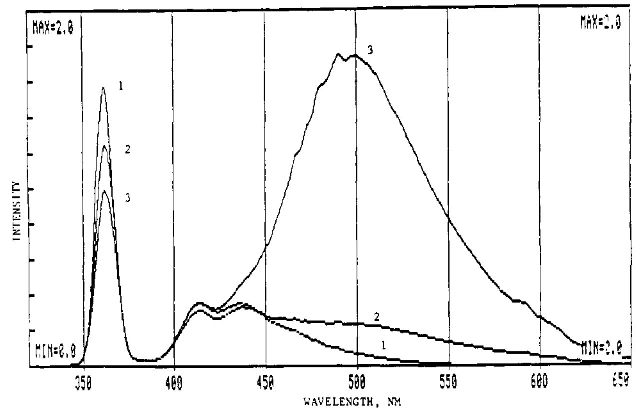

Figure 2. Fluorescence spectra: THF (1); (PTS)Na-THF (2); THF-(PTS)Na/CH_3OH mixture = 1.100 (3). λ_{ex} = 360 nm.

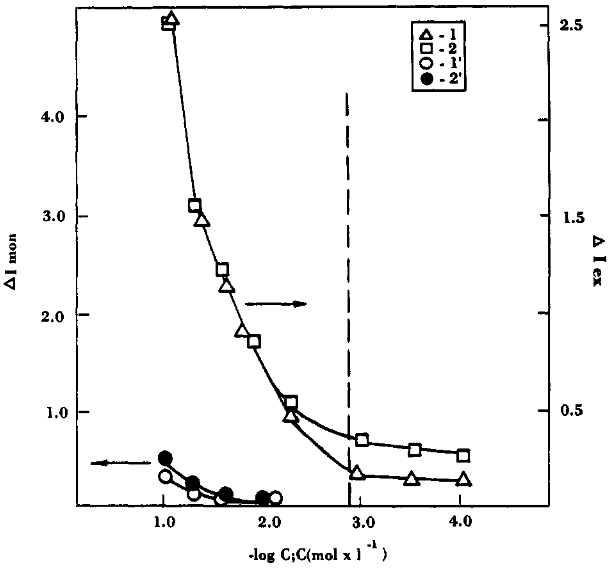

Figure 3. Excimer and monomer fluorescence intensities of the mixtures (SP)Na (m = 1.35%)-THF-(PTS)Na (1 and 1′) and (SP)Na (m = 2.8%)-THF-(PTS)Na (2 and 2′) as a function of the ionomer concentration. λ_{ex} = 360 nm; λ_{em} = 500 nm (excimer); λ_{em} = 409 nm (monomer). The dashed line is the overlap concentration separating the dilute and semidilute regimes.

polar Media. It is well-known that the aromatic molecule (PTS)Na, which is quite soluble in polar solvents, produces a strong concentration-dependent monomer or excimer fluorescence in such solvents. Also[1,2] sulfonated polystyrene ionomers have a strong tendency to associate through salt group interactions, and this results in intra- and interchain aggregates depending on the concentration regime. If it is possible to mix a small amount of (PTS)Na dissolved in a very small amount of a polar solvent, like water, with the ionomer solution in THF, one can expect solubilization or localization of the (PTS)Na molecules in the ionic aggregates, and thus, the excimer-monomer fluorescence of (PTS)Na should be observable and provide a probe for the structure of the aggregates. For example, the fluorescence intensity and its nature, excimer or monomer, should be a function of the dimensions of the ionic aggregates and their structures. If this postulate is correct, one can apply this approach for testing inter- and intrachain association behavior. In the next section, we will consider and discuss the results that can be obtained by such a technique.

Salt Group Association Behavior of Sulfonated Polystyrene Ionomers with Different Counterions in THF Solvent. In this section, we will analyze the solution behavior of polystyrene sulfonated ionomers with H^+, Na^+, and Zn^{2+} counterions over a wide range of concentrations and with different contents of salt groups. The absorption spectra of the (PTS)Na probe in THF solution and in the mixtures with PS and SPNa coincide; e.g., there is no influence of the polymer on the (PTS)Na absorption spectrum in THF. The fluorescence spectra of the PS, (SP)Na-(PTS)Na solutions at $\lambda_{max/ex}$ = 360 nm are shown in Figure 1. One can see that the fluorescence spectrum of the (SP)Na (m = 1.35%)-(PTS)Na mixture, curve 2, shows more intensive fluorescence at λ_{max} = 500 nm than the PS-(PTS)Na mixture (PS-(PTS)Na mixture has the same fluorescence intensity at 1×10^{-4} mol/L^{-1}, as (PTS)Na itself in THF). This characteristic fluorescence corresponds to the excimer fluorescence, which normally is clearly manifested at the same wavelength region for pyrene solutions.[12,13] Excimer fluorescence of (PTS)Na is the fluroescence of two or more excited (PTS)Na molecules that form coplanar sandwich-like structures, affording the maximum π orbital overlap and interchromophore separation of 3-3.7 Å.[10] This is the so-called dynamic complex, which appears as a result of diffusional collisions of (PTS)Na molecules. The excimer fluorescence intensity increases with increasing (SP)Na salt group content, curves 1 and 2 in Figure 1. In order to prove that this fluorescence is characteristic of excimer formation from this particular probe, we have obtained fluorescence spectra from THF-(PTS)Na mixtures (H_2O + CH_3OH), Figure 2. The appearance of strong fluorescence at λ_{max} = 500 nm in this mixture correlates well with the known excimer formation phenomena for pyrene-based molecules in alcohol and water-alcohol solutions.[13]

Excimer and monomer maximum values of the fluorescence intensities from (SP)Na-(PTS)Na mixtures with m = 1.35 and 2.8% are presented in Figure 3 over a wide range of (SP)Na concentrations. Monomer fluorescence of (PTS)Na comes from isolated excited (PTS)Na molecules. The excimer fluorescence intensity does not change in the dilute regime and increases sharply in the semidilute regime. Monomer fluorescence of (PTS)Na appears at high concentrations of the ionomer and its quite weak. An increase in the salt group content of (PS)Na leads to an increase of excimer fluorescence only at intermediate concentrations and to an increase in monomer fluorescence at high concentrations as shown in Figure 3. The situation is quite different for the SPS. Excimer fluorescence from

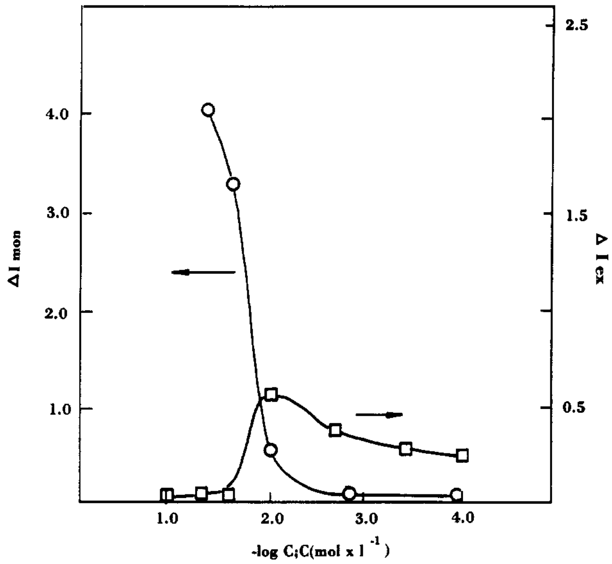

Figure 4. Excimer and monomer fluorescence intensities of the mixture SPS (m = 4.47%)-THF-(PTS)Na as a function of ionomer concentration. λ_{ex} = 360 nm; λ_{em} = 500 nm (excimer); λ_{em} = 409 nm (monomer).

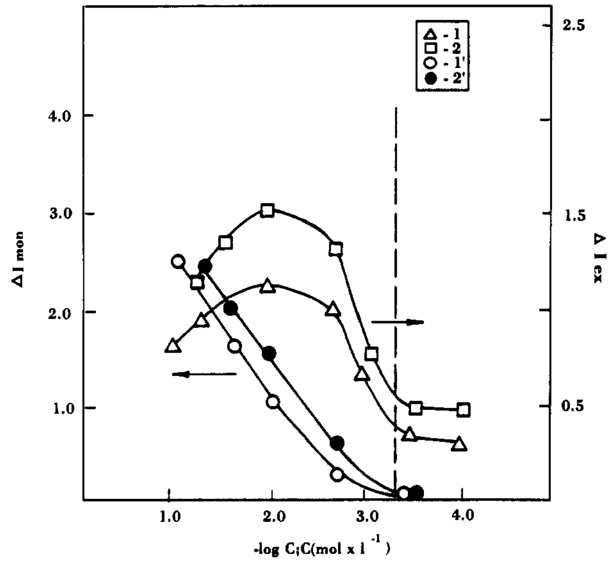

Figure 5. Excimer and monomer fluorescence intensities of the mixtures (SP)Zn (m = 1.80%)-THF-(PTS)Na (1 and 1′) and (SP)Zn (m = 4.16%)-THF-(PTS)Na in H_2O (2 and 2′) as a function of ionomer concentration. λ_{ex} = 360 nm; λ_{em} = 500 nm (excimer); λ_{em} = 409 nm (monomer).

SPS-(PTS)Na mixtures at low concentrations is very weak, and it disappears completely at higher SPS concentrations, while the monomer fluorescence increases strongly and completely dominates at the high concentrations, as seen in Figure 4. Interesting trends occur in the (SP)Zn ionomer, as shown in Figures 5 and 6. Excimer fluorescence is still quite noticeable as in the case with the (SP)Na ionomers, but appreciable differences from (SP)Na excimer fluorescence behavior exist. The strong increase of (SP)Zn excimer fluorescence with increasing ionomer concentration occurs at much lower concentrations than is the case with (SP)Na or SPS. A further increase of (SP)Zn concentration leads to a decrease of excimer fluorescence, while monomer fluorescence increases progressively. Excimer and monomer fluorescence both increase with an increase in (SP)Zn salt group content.

One has to point out that an increase of the salt group content in the ionomer chains leads to an increase of both excimer and monomer fluorescence for (SP)Zn ionomer and for the (SP)Na ionomer, at least in the dilute regime, Figure 6.

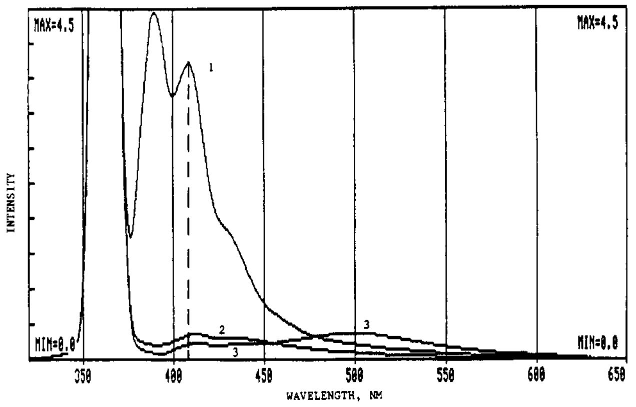

Figure 6. Fluorescence spectra: (SP)Zn (m = 1.80%)-THF-(PTS)Na (1); (SP)Zn (m = 1.80%)-THF (2); PS-THF-(PTS)Na (3). $C \sim 5 \times 10^{-2}$ M. λ_{ex} = 360 nm.

Before passing to a detailed discussion of the experimental fluorescence data, one has to define more clearly the nature of excimer and monomer fluorescence phenomena from the ionomer solution in connection with the specific structural organization of the ionomer coils in nonpolar solvents. The appearance of the excimer fluorescence from ionomer solutions in THF can be considered to result from solubilization and concentration of the (PTS)Na molecules inside a spatially restricted polar medium composed of aggregates of ionomer salt groups. The monomer fluorescence may be simply the result of (PTS)Na solvation by a few isolated ionomer salt groups, which are not involved in aggregate structures and are randomly distributed within the ionomer coils. Such an interpretation of the fluorescence means that the excimer fluorescence is connected with the formation of large aggregates, while the monomer fluorescence does not necessarily indicate salt group association, or if such association takes place, the number of salt groups involved in the associates are too small to solubilize more than one (PTS)Na molecule per aggregate. As we mentioned above, we used 1 vol % (PTS)Na-water solution to get it mixed with the THF solution of the ionomer. This amount of water is not large enough to change appreciably the aggregation behavior of the ionomer in THF.[2] An increase of the water content in water-THF mixtures can lead to the suppression of association and even to classical polyelectrolyte behavior of the ionomer solution when the water:THF volume ratio is about 6%:95%, as was demonstrated earlier by viscosity measurements of water-THF mixtures of (SP)Na ionomers.[2] The viscosity data correlate with the excimer-monomer fluorescence data, Figure 7. The increase of water content in water-THF mixtures for the same (SP)Na ionomer leads to a gradual decrease of the excimer fluorescence and a concurrent increase of the monomer fluorescence, Figure 7. Finally, when the water content reaches about 5% by volume, the excimer fluorescence is completely suppressed and monomer fluorescence dominates. Also, if we compare these data with the excimer-monomer fluorescence from the polar solvent, DMF, where (SP)Na ionomer shows typical polyelectrolyte behavior by viscosity data and thus no aggregation of salt groups,[2] only monomer fluorescence is observed, as shown in Figure 8.

Now we can go back to the analysis of the fluorescence data. Excimer fluorescence data for (SP)Na, SPS, and (SP)Zn are collected in Figure 9. One can point out some general trends. In the dilute solution regime (I), there is essentially no concentration dependence of the excimer fluorescence for all the ionomers. Further increases in

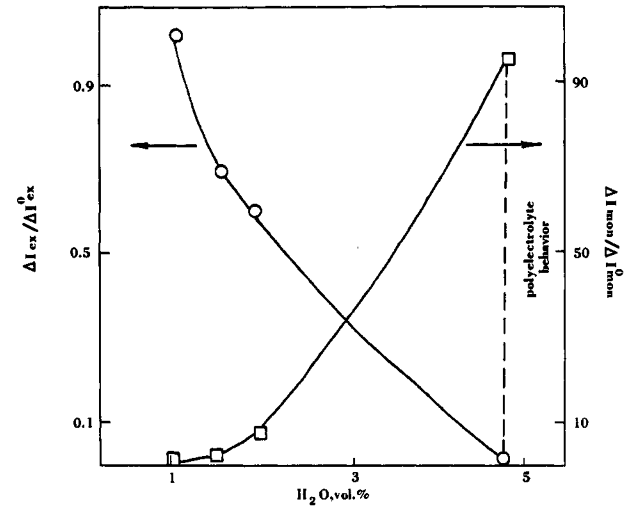

Figure 7. Excimer and monomer relative fluorescence intensities of the mixture (SP)Na (m = 2.8%)-THF-(PTS)Na as a function of the volume percentage of water in the mixture, ΔI_{ex} and ΔI_{mon} are the excimer-monomer fluorescence intensities with 1 vol % water in the mixture. λ_{ex} = 360 nm; λ_{em} = 500 nm (excimer); λ_{em} = 409 nm (monomer).

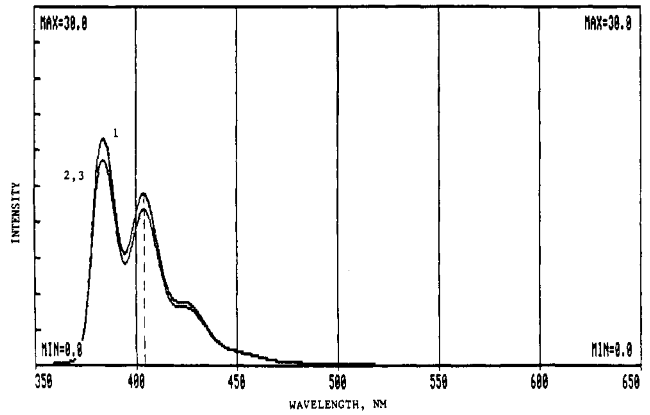

Figure 8. Fluorescence spectra of the solutions (PTS)Na-DMF (1), (PTS)Na-SPNa (m = 2.80%)-DMF (2), and (PTS)Na-PS-DMF (3). $C \sim 1 \times 10^{-4}$ M. λ_{ex} = 378 nm; other conditions are the same as in Figure 2.

concentration are accompanied by a sharp increase in fluorescence for (SP)Zn and (SP)Na ionomers and a very small increase for the SPS ionomer. The dilute regime behavior may be attributed to the same type of salt group association for all ionomers, e.g., to intra-chain aggregation. Further increases of ionomer concentration lead to inter-chain interactions between the salt groups and, finally, to the domination of such inter-chain aggregates.[14] If one accepts this postulate, one would expect a change in the fluorescence intensity of ionomer solutions upon further increases of ionomer concentration. As one can see from Figure 4, this does not occur in SPS; e.g., the association of the acid groups is too weak to produce a strong increase in excimer fluorescence. Such weak association behavior in SPS is also indicated by the viscosity data,[2] which were obtained earlier for the ionomer in the acid form. The increase of the excimer fluorescence intensity shown in Figure 9 for all ionomer solutions other than SPS can be understood if we assume that the number of salt groups involved in the aggregates increases while the ionomer coils interact and penetrate into each other. This can lead to the appearance of new associations as well as to an increase in the dimensions of the aggregates that occur as a result of intra-chain associations. The inter-chain association process results in solubilization of additional amounts of the (PTS)Na molecules inside the polar domains. Meanwhile one could suggest another explanation if one assumes the appearance of (PTS)Na dynamic associates of more than two molecules in such complexes and that the specific fluorescence intensity increases with an increase in the number of molecules in the complex. In order to distinguish between the two different situations, we have measured the excimer fluorescence intensity from a (PTS)Na solution in THF-H_2O mixtures under the same conditions but without ionomer, as a function of probe concentration, and the results are shown in Figure 10. One can see that the dependence of excimer fluorescence on the label concentration is linear. Thus, the specific fluorescence intensity from (PTS)Na multimolecule complexes is the same regardless of the number of molecules in the complex.

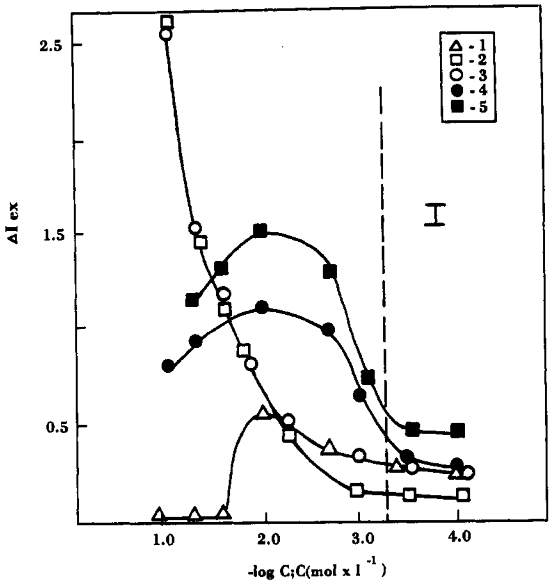

Figure 9. Excimer fluorescence intensities of the mixtures SPS (m = 4.47%)-THF-(PTS)Na (1), SPNa (m = 1.35%)-THF-(PTS)Na (2), (SP)Na (m = 2.80%)-THF-(PTS)Na (3), (SP)Zn (m = 1.8%)-THF-(PTS)Na (4), and (SP)Zn (m = 4.16%)-THF-(PTS)Na (5) as a function of ionomer concentration. λ_{ex} = 360 nm; λ_{em} = 500 (excimer); λ_{em} = 409 nm (monomer).

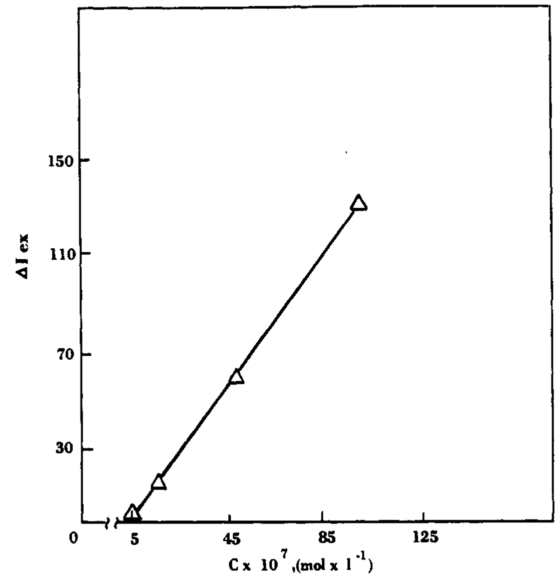

Figure 10. Excimer fluorescence intensity of the (PTS)Na-THF mixture as a function of (PTS)Na concentration. λ_{ex} = 360 nm; λ_{em} = 500 nm.

In the dilute solution regime area (I), Figure 9, the intra-chain association tendency decreases in the order (SP)Zn > (SP)Na ≫ SPS. This order corresponds to the nature of the counterion: the divalent Zn salt has a stronger tendency for intra-chain association in dilute solution than the monovalent Na, and the excimer fluorescence is stronger. The same trends were obtained in light-scattering experiments with the same type of ionomers.[6] It was found that the second virial coefficient decreases for ionomer solutions in THF in the order PS $\geq$ SPS $>$ (SP)Na $>$ (SP)Zn.

The marked increase of excimer fluorescence occurs above a certain critical concentration, C^*, which signifies the concentration when inter-chain ionomer associations become important. The C^* concentration value is much less for (SP)Zn than for (SP)Na or SPS, as shown in Figure 8. These data confirm the important role of the counterion: divalent Zn^{2+} counterions undergo intermolecular associations much more readily than the monovalent counterion, Na^+, or the hydrogen-bonding acid form. The results are in good agreement with the viscosity experiments,[11,14] which have shown that the strong increase in the reduced viscosity in (SP)Zn solutions, which characterizes the onset of inter-chain association, takes place at much smaller concentrations than for (SP)Na.[11,14] It is also important to point out that the increase of excimer fluorescence in (SP)Na and SPS occurs in the concentration region where inter-chain interactions start to dominate by viscosity data,[14] and this region coincides approximately with the overlap concentration for unmodified polystyrene in THF.[14]

There is a substantial difference in the excimer–monomer fluorescence behavior for (SP)Na, (SP)Zn, and SPS ionomers in the semidilute concentration regime. Excimer fluorescence of (SP)Na solutions dominates at all concentrations, while monomer fluorescence is very weak and appears only in the semidilute regime. A strong increase of excimer SPNa fluorescence in the semidilute regime, which can be correlated, as mentioned above, with the increase of the number of salt groups involved in aggregates, is in agreement with the neutron scattering data from the same (SP)Na ionomer in THF.[9,11] As already mentioned in the Introduction, it was shown that, in the semidilute regime, the dimensions of the (SP)Na individual ionomer coils are independent of ionomer concentration while the degree of aggregation increases rapidly.[9,11] These data in combination with the fluorescence results can be considered to indicate the presence of the same type of ionic associates in both the dilute and semidilute solution regimes. In comparison with (SP)Na, (SP)Zn and SPS ionomer solutions exhibit a strong monomer fluorescence that increases while the excimer fluorescence decreases in the semidilute regime, as seen in Figures 4 and 5. This may be the result of structural reorganization of the ionic associates, which can lead to their break up and the appearance of isolated salt groups. The nature of this process is not clear at present, and additional experimental data, such as X-ray scattering from ionomer solutions, are necessary to supplement these results. One of the possible reasons for such a dissociation process with increasing (SP)Zn concentration could be connected with the presence of small amounts of polar impurities in the samples as well as moisture,[15] which are not easy to remove. It is necessary to mention that application of a fluorescent molecular probe technique in this particular case also has some restrictions. For example, fluorescent experiments under the same conditions, but in a less polar solvent than THF, such as xylene, are impossible because of the immiscibility of (PTS)Na–water solution with the xylene solution of the ionomer.

The hydration tendencies of the cations may also be important in determining the fluorescence response. Since Na^+ cation has a much greater tendency to be hydrated under these conditions than ether Zn^{2+} or the acid form, it might be that the local concentration of water and thus of (PTS)Na is much greater in the vicinity of the sodium salt groups than of either the acid or zinc forms. However, Figure 7 shows that the excimer fluorescence decreases strongly with increasing water concentration while the monomer fluorescence increases. This is contrary to the results obtained from the sodium ionomers.

The fluorescence approach is unique in its ability to cover a wide range of ionomer concentrations, from 10^{-1} to 10^{-4} M. It seems to offer the possibility to distinguish between intra- and inter-chain interactions. The results can extend the available information on the salt group association behavior as a function of the nature of the counterion and other characteristic parameters.

Conclusions

The analysis of salt group association behavior was carried out in THF over a wide range of concentrations of sulfonated polystyrene ionomers with hydrogen, sodium, and zinc counterions by fluorescence molecular probe techniques. It was shown that the type of counterion present has a very important influence on the degree and nature of salt group association. The divalent Zn^{2+} counterion associates intramolecularly to a greater extent than the monovalent Na^+ counterion, which in turn associates much more strongly than the acid form.

The excimer and monomer fluorescence data from ionomer solutions provide important information about the structure and structural reorganization of the salt group aggregates as a function of the counterion nature, salt group content, and concentration of ionomer. The fluorescence data are in good agreement with previously obtained information concerning sulfonated polystyrene ionomer behavior in THF by viscosity measurements, light, and neutron scattering. Future progress in this area can be achieved by using a combination of the fluorescent approach and other techniques such as X-ray scattering and neutron scattering.

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