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Characterization of the Solution Properties of a 1.7% Sulfonated Polystyrene Ionomer by Fluorescence Probing

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ABSTRACT: Luminescent probing methods were employed to investigate the solution characteristics of a 1.7% sulfonated polystyrene ionomer in a nonpolar solvent. Ion pair/ion pair interactions were shown to give rise to ionic microdomains averaging 6–7 sulfonate groups per aggregate; in dilute solution ion aggregation is only 2–3. The ionic aggregates were shown to maintain constant dimensions over a wide concentration range, indicative of the integrity of the primary aggregates even at high concentrations where the ionomers begin to associate. Inhibition of fluorescence quenching demonstrates that ionic material supported in these systems are effectively screened from the bulk solution phase and is attributed to a mantle of hydrocarbon polymer chain about the ionic regimes. Reactivity of ionic species was manipulated by the addition of a small amount of polar solvent, which acts to disrupt the aggregation and expose the solvated ionic material to reactants in the bulk solution phase.

Introduction

Ionomers can be classified as amphiphilic polymers. In general, ionomers are long-chain hydrocarbon polymers incorporating a small amount of ionizable units within the polymer chain. Typically, they contain less than 10 mol % of ionic units as higher ionic content leads to polyelectrolyte behavior.[1] Ionomers, in contrast to polyelectrolytes, are usually soluble in hydrophobic media and the presence of the ionic groups on the polymer may result in a microheterogeneous solution with ionic, hydrophilic microphases supported in a hydrophobic medium. This study examines the microheterogeneity of solutions of an amphiphilic 1.7% sulfonated polystyrene ionomer in hydrophobic solvents, relying heavily upon photophysical measurements.

Ionomers have become important in a variety of commercial and industrial applications due to the unique and tailored properties that may be imparted to a given polymer system. Some of these applications include thermoplastic elastomers, packaging, films, viscosifiers, permselective membranes, and compatibilizing agents for polymer blending.[2] The novel properties of ionomeric materials are derived from the presence of ionic units in the polymer chains and the morphology that results. The configurations, ion aggregation, and microstructure of such systems, as well as the parameters affecting these, are imperfectly understood. Consequently, ionomers have become the focus of much research, as evidenced by the increasing attention ionomers have received in recent literature.[3-8]

Ionomers, because of their amphiphilic nature, may give rise to microheterogeneous solutions possessing unique chemical environments. Intermolecular and intramolecular associations brought on by the presence of the ionic groups are particularly dependent upon the solvating medium. Manipulation of chain configurations and molecular interactions by chemical and physical means is also potentially possible in ionomer solutions, based on rheological evidence.[9] Thus, the characterization of solution properties of ionomers can prove useful in understanding the relationships between interactions on the molecular scale and the macroscopic properties of polymers.

In bulk partially sulfonated polystyrene ionomers, microphase separation of regions of high ionic content has been demonstrated.[5] In nonionizing solvents, similar aggregation of ionic regimes has been postulated to explain the unusual viscosity–concentration relationships exhibited by these materials.[9,11] Particularly, the viscosity of ionomer solutions is lower than that of the nonionic precursors at low concentrations but is much higher than that of the precursors at moderate and high concentrations. Gelation often occurs in these ionomers at relatively low concentrations—behavior typical of associating polymers. It has been proposed that strong ion pair/ion pair interactions are responsible for the associative nature of ionomers.[12] At low concentrations, intramolecular interactions predominate resulting in contracted polymer chains; at high concentrations, intermolecular interactions become important and networking may occur. Little is known, however, regarding the size, configurations, and chemical environments apparent in these systems.

The aim of the work reported here is to investigate the aggregation phenomena responsible for the novel properties of ionomers in solution. Photophysical and photochemical methods were employed to probe the microheterogeneous nature of a partially sulfonated polystyrene ionomer in nonionizing solvents. Fluorescence probing techniques were particularly suited for studying the mobility, accessibility, chain conformations, morphologies, and size of ion aggregates under a variety of conditions. Manipulations of this system through chemical and physical means can elucidate a molecular basis for the unusual characteristics of ionomer solutions.

Experimental Solution

Instrumentation. Steady-state fluorescence measurements were predominantly made on an SLM/Aminco SPF-500C spectrofluorimeter. This instrument utilizes a xenon arc lamp operating at 250 W as an excitation source; a Nozone coating limits the useful range to 300–900 nm. A Hamamatsu R928P photomultiplier tube (PMT) is included as detector. A 1200 grooves/mm ruled diffraction grating is used for the excitation monochromator, and a 1200 grooves/mm holographic grating is used for the emission monochromator. Wavelength resolution is 0.2-nm accuracy and minimum band-pass is 0.1 nm. Data were transferred to a Zenith PC microcomputer for storage and analysis.

Time-resolved fluorescence measurements were carried out with the configuration described elsewhere.[13,14] The arrangement

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includes a nitrogen laser excitation source, a partial reflector, focusing lenses, a monochromator, a PMT, a digitizing transient capture device, a monitor, and a microcomputer for storage. Data are generally stored as single pulses but may be averaged over many pulses to reduce noise in weak signals.

Excitation sources used were PRA Nitromite LN100 and PRA LN1000 nitrogen lasers. The principal wavelength of each is 337.1 nm. Pulses of 70 μJ, 120-ps fwhm, and 2.5 μJ, 0.8-ns fwhm, are provided, respectively. The excitation beam is split by a partially reflecting mirror where the minor portion of the beam is directed to a photodiode which triggers the data acquisition. Emission from the sample is collected and focused on the monochromator slits. A Bausch & Lomb diffraction grating monochromator with 1350 grooves/mm can select wavelengths in the range 350–800 nm. An R928 PMT or a Hamamatsu 86.4 microchannel plate detector was used for the conversion of the emitted light to an electronic signal suitable for the Tektronix 7912AD digitizer. The digitized signal was transferred to a Zenith PC microcomputer for storage and analysis. Response times of 1 ns are obtainable through this arrangement.

Absorption spectra were obtained by using a Perkin-Elmer Model 552 spectrophotometer having both a DZA tungsten lamp and an 055-0505 deuterium light source with automatic crossover at 315 nm. The instrument, a double-beam spectrophotometer, has a ruled diffraction grating monochromator to select wavelengths between 190 and 750 nm with a minimum band-pass of 0.25 nm. Transmitted light is detected with a Hamamatsu 928P PMT. The analog signal can be collected in a Tektronix 4051 computer for storage. Absorption spectra were primarily used for monitoring concentrations of molecular species.

Gas chromatography was conducted on a Perkin-Elmer 8410 gas chromatograph. A 6 ft × 1/8 in. 10% Carbowax column prepared by Ohio Valley Specialty Chemicals was used in this instrument for the separations.

Materials. Distilled and deionized water was used exclusively for the preparation of aqueous solutions. The toluene and cyclohexane used were HPLC grade obtained from Aldrich and were used without further purification. Spectrophotometric grade anhydrous methanol was used as received from Mallinckrodt. Absolute ethanol, USP grade, was obtained from Midwest Grain Products, Co. Additional solvents were reagent grade and used as received.

Partially sulfonated polystyrene (PS-1.7) was generously provided by Dr. R. D. Lundberg, Exxon Chemicals Co. [4-(1-Pyrenyl)butyl]trimethylammonium bromide (PN^+) was used as received from Molecular Probes, Inc. Pyrene was purchased from Aldrich Chemicals and purified by column chromatography prior to use. Tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate ($Ru(bpy)_3^{2+}$) was used as received from Aldrich. Dr. Deh Ying Chu is gratefully acknowledged for providing 4-(1-pyrenyl)butyl alcohol. All other probes were reagent grade or better and were recrystallized prior to use.

The following quenchers were twice vacuum distilled: nitromethane, *N,N*-dibutylaniline (DBA), and nitrobenzene, all obtained from Eastman Chemicals. Purified oxygen from Union Carbide was used. Sodium dinitrobenzoate (SDNB) was neutralized from dinitrobenzoic acid received from Aldrich, with sodium hydroxide. Other quenchers were reagent grade or better and were used as received.

Polymers and Preparations. The sodium salt of a partially sulfonated polystyrene ionomer was prepared at Exxon Research and Engineering Co. and provided by Dr. R. D. Lundberg. These materials were prepared from a commercial polystyrene polymer by sulfonation with acetyl sulfate in a homogeneous 1,2-dichloroethane solution as described elsewhere.[15,16] The ionomer received was 1.7 mol % (on a monomer basis) sulfonated and completely neutralized to the sodium salt. The 1.7% sulfonated polystyrene (PS-1.7) had an average molecular weight of 105 000 and thus an average of 17 sulfonate groups per polymer chain.

Doping of ions onto the ionomers was carried out by two methods. The first method involved exchanging ions between aqueous salt solutions and toluene solutions of PS-1.7 by contacting the two immiscible solutions in an emulsion. Spectrophotometric measurements from both the aqueous and hydrocarbon phases indicated complete exchange of the sodium counterion was possible with $Ru(bpy)_3^{2+}$. The ionomer was then freeze-dried and redissolved in toluene. This method is tedious and time-consuming because, despite the low ionic content of PS-1.7, solvation in toluene is extremely slow and concentrations must be held low; gelation occurs in toluene above about 10 g/L.

Table I
Estimated Solubility of Salts on PS-1.7 in Toluene per Gram of Ionomer

salts	solubility, mM/g	[PS-1.7] range, g/L
$CaCl_2$	0.20	2–20
$CuCl_2$	0.20	2–20
$Ru(bpy)_3Cl_2{\cdot}6H_2O$	>0.052	2–20
KI	>0.10	5.1
NaCl	>0.10	5.0
methylviologen	0.06	2–10
PN^+	0.10	2–20
copper (dodecyl sulfate)$_2$	0.15	2–20
ammonium persulfate	<0.03	4.9
sodium 1,4-dinitrobenzoate	0.07	4.9

The solvation of the PS-1.7 ionomer in toluene is dramatically accelerated by the addition of 5% v/v methanol; the viscosity is also markedly decreased (remaining fluid above 20 g/L) and visual clarity is improved. The methanol can be removed easily through vacuum distillation at 50 °C, as verified by gas chromatography of the final solutions. Thus, methanol was a convenient medium for the doping of ions onto PS-1.7. Salts soluble in methanol were added to solutions of PS-1.7 in 5% v/v methanol in toluene and the methanol was subsequently removed by vacuum distillation. Concentrations during the distillations were monitored by mass measurements. This was the primary method of introducing ionic species to the PS-1.7 solutions for these investigations. $Ru(bpy)_3^{2+}$ probe concentrations were held low (10^{-6}–10^{-5} M) and are specified for each study.

Results and Discussion

Solvation of Ionic Species. The PS-1.7 ionomer is an excellent medium for supporting ionic species in organic solvents. Exchanged to the ionomer, ions were successfully solvated in THF, xylene, toluene, cyclohexane, DMF, and dioxane. The work reported here is primarily concerned with toluene solutions of PS-1.7.

The amount of ionic salt that can be solubilized in toluene by the ionomer depends primarily upon the ionomer concentration but also on the nature of the salt. Estimated solvation limits for several salts in toluene solutions of PS-1.7 are reported in Table I on a per gram ionomer basis. These values are estimated from observations of precipitate formation within 24 h of the removal of methanol; these values are not intended to be analytically accurate but are provided only as a rough guideline. Each of the salts in Table I is virtually insoluble in toluene without the PS-1.7 support. Addition of as little as 5% MeOH to the solutions greatly extends the solvation limits for each salt whereas their solubility in the absence of ionomer remains nominal. It is concluded that the ionic salts are suspended in organic media primarily through electrostatic interaction with the ionomer.

The spatial arrangement of solvated ions in ionomer solutions is critical in attempts to develop a molecular basis for the observed anomalous behavior of ionomer solutions. Fluorescence quenching of an ionic probe, $Ru(bpy)_3^{2+}$, with an ionic quencher, Cu^{2+}, provides insight to this problem. In many ways this is analogous to the high quenching efficiency of Cu^{2+} for many fluorophases in electrolyte solution.[10] Normally, in a homogeneous medium such as a simple aqueous solution, Cu^{2+} is an inefficient quencher of the $Ru(bpy)_3^{2+}$ emission due to the repulsion of like charges. However, very efficient quenching is observed in solutions of the ionomer containing both types of ion in a toluene solvent. Figure 1

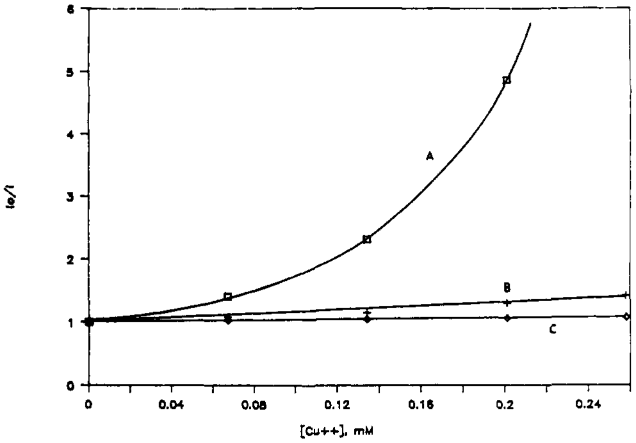

Figure 1. Steady-state quenching of $Ru(bpy)_3^{2+}$ fluorescence by Cu^{2+}: (A) 5.9 g/L PS-1.7 in toluene; (B) 5.9 g/L PS-1.7 in 5% MeOH/95% toluene; (C) 1×10^{-5} M $Ru(bpy)_3^{2+}$ in water.

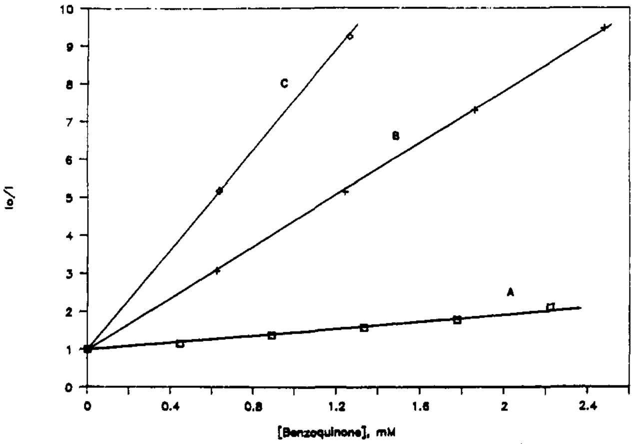

Figure 2. Steady-state quenching of $Ru(bpy)_3^{2+}$ fluorescence by benzoquinone: (A) 4.9 g/L PS-1.7 in toluene; (B) 4.9 g/L PS-1.7 in 5% MeOH/95% toluene; (C) 1×10^{-5} M $Ru(bpy)_3^{2+}$ in methanol.

compares the steady-state quenching in water, PS-1.7 in methanol with 5% MeOH, and PS-1.7 in toluene in the form of a Stern–Volmer plot. Quenching is inefficient in an aqueous medium and in the ionomer systems in toluene with 5% methanol added. The increased quenching in the nonpolar medium leads to the conclusion that the ions solvated in ionomer solutions in toluene are held by the polymer in close proximity to one another, thus enhancing reaction. The results are interpreted as evidence of microdomains and the model is similar to that of sites of high local ionic content within the ionomer solutions, suggested[17] by small-angle X-ray scattering.[18] However, the addition of 5% methanol yields a nonaggregated system, as discussed later.

Probing with $Ru(bpy)_3^{2+}$. The accessibility of materials in the ionic sites can be readily measured by the ability of fluorescent probes located in those sites to interact with fluorescence quenching molecules solvated in the bulk solvent phase. The quenching efficiency of benzoquinone (BQ) is shown in Figure 2 to be dramatically decreased in the ionomer solutions versus homogeneous methanol solutions in the quenching of $Ru(bpy)_3^{2+}$ fluorescence. Quenching rate constants, k_q, defined by Stern–Volmer kinetics are provided in Table II for a variety of neutral quenchers (solvated in the bulk phase) with the ionic probe $Ru(bpy)_3^{2+}$, which is supported in the ionic domains. In toluene, the ionomer solutions exhibit substantially reduced quenching rates compared to those in the nonaggregated systems. The ionic regimes in PS-1.7 solutions in toluene are inhibited from reacting with species in the bulk phase. It is suggested that ionic aggregates that form in a nonpolar solvent such as toluene are apparently encompassed near the core of regions of high polymer density, which is reponsible for the inhibition of interaction between probes in those sites and quenchers in the bulk phase. This picture is consistent with models proposed by Roche et al.[19] for ionic aggregate formation whereby a considerable amount of the hydrophobic polymer backbone is necessarily brought to the area about the ionic sites through the covalently bound sulfonate groups, in a shell/core configuration.

Table II
Quenching Rate Constants for $Ru(bpy)_3^{2+}$ Fluorescence Decays in 5 g/L Solutions of PS-1.7

	k_q	
quencher	in toluene	in 5% MeOH
none	$1.5 \times 10^6\ s^{-1}$	$1.1 \times 10^6\ s^{-1}$
oxygen	$8.2 \times 10^8\ M^{-1}\ s^{-1}$	$2 \times 10^9\ M^{-1}\ s^{-1}$
benzoquinone	$3.8 \times 10^8\ M^{-1}\ s^{-1}$	$5.1 \times 10^9\ M^{-1}\ s^{-1}$
1,4-dinitrobenzene	$3.7 \times 10^8\ M^{-1}\ s^{-1}$	$2.1 \times 10^9\ M^{-1}\ s^{-1}$

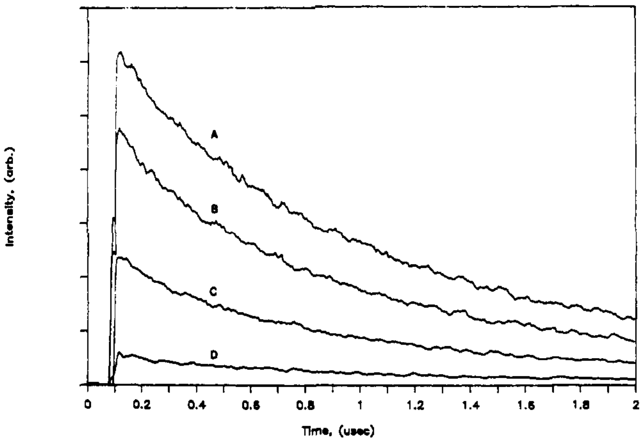

Figure 3. Transient fluorescence decay profiles for $Ru(bpy)_3^{2+}$ on PS-1.7 in toluene; static quenching by Cu^{2+}. 2×10^{-6} M $Ru(bpy)_3^{2+}$; (A) 0.0, (B) 0.065, (C) 0.135, and (D) 0.2 mM Cu^{2+}. Intensities decrease without a change in fluorescence lifetime, indicating a static mechanism for the quenching reaction.

Quenching Studies. Each ionic quencher studied displays only "static" quenching as exemplified by the Cu^{2+} quenching of the $Ru(bpy)_3^{2+}$ emission in Figure 3. The quenching reaction is too rapid to be observed on the time scale of fluorescence. In effect, sites containing Cu^{2+} are quenched instantaneously and do not contribute to the observed fluorescence. Unoccupied sites are free to emit with the usual probe lifetime. Hence, no changes in the $Ru(bpy)_3^{2+}$ lifetimes are observed as Cu^{2+} is added, despite the substantial decreases in the intensity of emission. Consequently, the static quenching indicates normal diffusional motions of quencher and probe are not important in the quenching reaction. This suggests ions are rigidly held in close proximity within the ionic domains.

Probing with PN^+. The probe PN^+ provides complementary information to the $Ru(bpy)_3^{2+}$ studies. Monovalent PN^+ is less likely to perturb the ionomer configurations than the larger doubly charged $Ru(bpy)_3^{2+}$ probe. Also, the emitting pyrene functional group is pendant from the ionic head group by a four-carbon chain. Therefore, it will probe the interface between the ionic domain and the solvent phase due to a preferential orientation. The fluorescence characteristics of PN^+ are nearly identical to those of 1-pyrenylbutyl alcohol (PBOH), allowing the comparison of the various quenching reactions in the solvent with those in the ionomer systems. An additional

Table III
Quenching Rate Constants for PN$^+$ Fluorescence Decays in 5 g/L Solutions of PS-1.7

quencher	k_q in toluene	k_q in 5% MeOH
none	6.4×10^6 s^{-1}	6.1×10^6 s^{-1}
oxygen	9.5×10^9 M^{-1} s^{-1}	2.7×10^{10} M^{-1} s^{-1}
nitromethane	1.0×10^9 M^{-1} s^{-1}	5.2×10^9 M^{-1} s^{-1}
nitrobenzene	3.6×10^9 M^{-1} s^{-1}	1.6×10^{10} M^{-1} s^{-1}
N,N-dimethylaniline	1.2×10^9 M^{-1} s^{-1}	4.9×10^9 M^{-1} s^{-1}
1,4-dinitrobenzene	4.6×10^9 M^{-1} s^{-1}	1.4×10^{10} M^{-1} s^{-1}

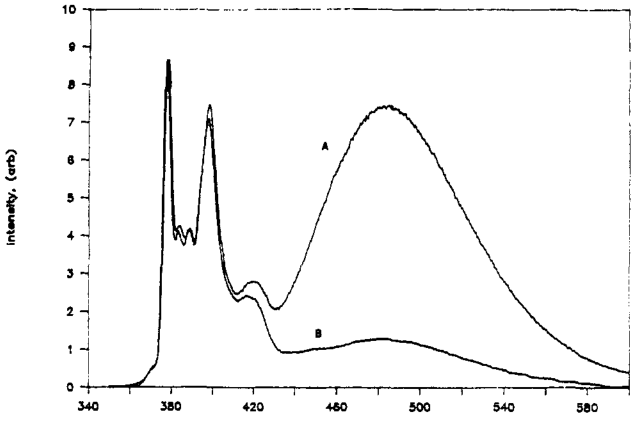

Figure 4. Steady-state emission spectra for PN$^+$ on PS-1.7. 5 g/L PS-1.7 with 3×10^{-4} M PN$^+$. (A) In toluene; (B) in 5% methanol/95% toluene.

advantage of PN$^+$ as a fluorescence probe is its tendency to form excimers under appropriate conditions. Excimer formation depends primarily on the proximity and mobility of the probes and provides a reliable method for monitoring those properties in a given system.

Location and Accessibility of PN$^+$. Experiments using PN$^+$ as a probe of the PS-1.7 ionomer in toluene solutions corroborate the findings of the Ru(bpy)$_3{}^{2+}$ probing studies. PN$^+$ is solvated by the ionomer despite its low solubility in toluene and is expected to be associated with the ionic regimes. Table III presents quenching rate constants for neutral quenchers, confirming that the sites are screened from the bulk solvent phase. Quenching by ionic species is increased in efficiency due to the aggregation and is static in nature. Thus, the arguments presented earlier as a result of probing by Ru(bpy)$_3{}^{2+}$ are supported by the PN$^+$ probing. Particularly, the aggregation of the ionic units on the ionomer, the solvation of ionic species within those aggregates, and the inaccessibility of those sites by the bulk phase are confirmed.

Excimer Formation. Ionic aggregates might be expected to be very rigid due to the relative strength of the ionic interactions that produce them. Excimer emission from PN$^+$ provides an indication of probe mobility and proximity within the ion aggregates, and thus its rigidity may be inferred. The concentration of PN$^+$ at the onset of excimer formation is an order of magnitude lower than that in homogeneous solution (10^{-4} M in PS-1.7/toluene versus 10^{-3} M in methanol). Figure 4A shows the appreciable excimer emission at 3×10^{-4} M PN$^+$ in a 5 g/L PS-1.7 solution in toluene; only monomer emission can be observed in a homogeneous methanol solution at this concentration. The early onset of excimer formation confirms its location in the microdomains.

The excimer emission from PN$^+$ in the ionomer solutions is unusual in that there is no dynamic component to growth of excimer emission, Figure 5A. Typically a grow-in of excimer emission would be expected due to the diffusional processes required for their formation. This grow-in is seen in the non-ion-aggregated system with 5% methanol added, Figure 5B. Excimer formation is also expected to have a dynamic component due to a "clapping" interaction between the pendant pyrene groups. These interactions are absent in the ionomer system. The emitting pyrene group is nonpolar and is pendant on a four-carbon chain from the ionic head group, and it is reasonable that there is also a preferential orientation of the PN$^+$ within the sites: the ionic group attached to the ionic aggregate and the pyrene group radiating outward from the site. The lack of any dynamic component to the excimer formation indicates that the region about the site restricts motion, that a region of high polymer density exists about the ion aggregates.

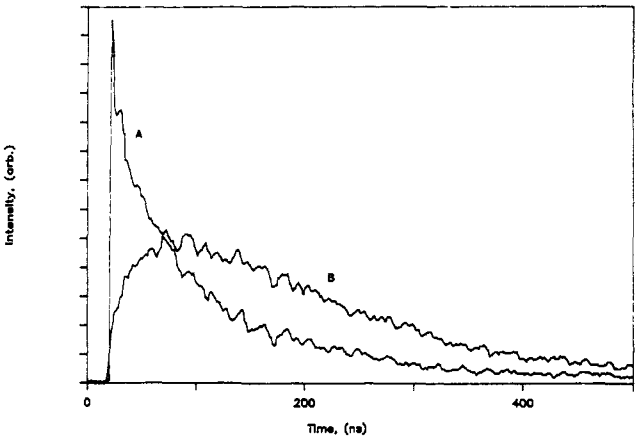

Figure 5. Transient emission from PN$^+$ excimer on PS-1.7. 5 g/L PS-1.7 with 3×10^{-4} M PN$^+$; emission wavelength = 500 nm. (A) In toluene; (B) in 5% methanol/95% toluene.

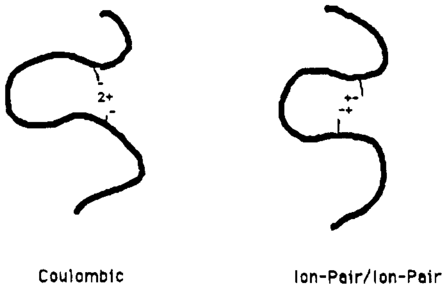

Figure 6. Schematic of Coulombic and ion pair mechanisms for aggregation.

Mechanisms of Aggregation. In nonionizing solvents, it is expected that ion pair/ion pair interactions predominate over simple Coulombic interactions in the ionic aggregation of ionomers.[1] Figure 6 illustrates the distinction between the two mechanisms. Taken for granted that the ion pair/ion pair interactions are responsible for the ion aggregation in ionomer systems, there has been no attempts to prove this point. If it is assumed Coulombic interactions are the dominant mechanism, external negative ions would not associate with the negatively charged PS-1.7 ionomer. However, in Figure 7 it is shown that the iodide ion, I$^-$, is a more efficient quencher for PN$^+$ fluorescence than in a non-ion-aggregated system. Consequently, it is concluded that ionic species solvated in ionomer systems in nonionizing media are solvated as salts; i.e., ion pairs. Thus, ion pair/ion pair interactions are demonstrated to be the primary binding force in ion aggregate formation.

Size of Aggregates. Given that ion pair/ion pair interactions predominate, the attractive forces in ion aggregate formation decrease with increasing ion aggregate

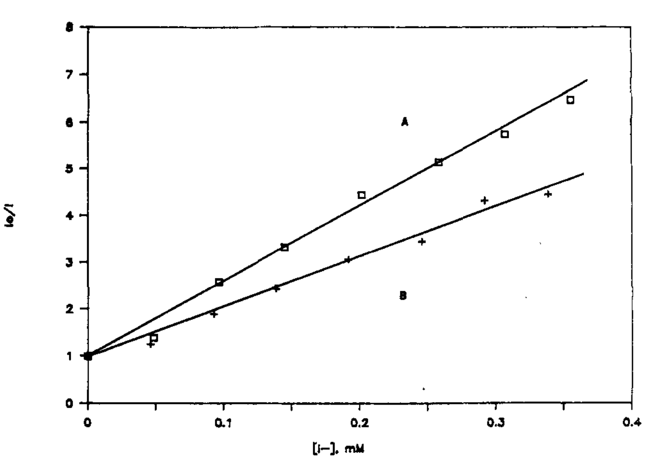

Figure 7. Steady-state quenching of PN^+ fluorescence by I^-: (A) 5.6 g/L PS-1.7 in toluene; (B) 5.6 g/L PS-1.7 in 5% MeOH/95% toluene.

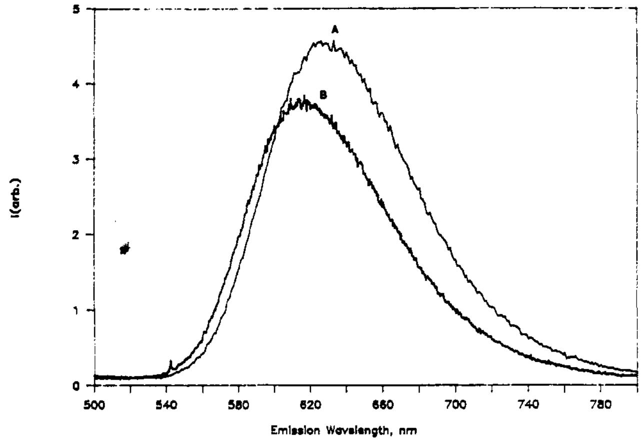

Figure 8. Effects of calcium on the emission spectrum of $Ru(bpy)_3^{2+}$ in toluene solutions of PS-1.7: (A) 5.9 g/L PS-1.7; no Ca^{2+}; λ_{max} = 625 nm; (B) 4.5 g/L PS-1.7; 0.25 mM Ca^{2+}; λ_{max} = 618 nm.

size. In addition, forces that inhibit ion aggregation, steric effects and polymer chain strains, increase with increasing size. Eisenberg[12] calculates a maximum of eight ion pairs in ionomer aggregates formed by the electrostatic interactions of contact ion pairs in low polarity solvents, assuming spherical geometry. These types of ion aggregates have been termed "multiplets". SANS[19] and X-ray analysis[18] have been used to estimate ion aggregate sizes in bulk ionomers. Also, dynamic light scattering has been utilized in solution work for the determination of polymer coil dimensions.[11] A means of determining the size of multiplets under a variety of conditions would be advantageous in understanding the factors affecting the solution properties of ionomers.

Fluorescence techniques have been applied to the determination of ion aggregates sizes in several microheterogeneous systems: e.g., micellar solutions, vesicles, and polymeric systems.[14] Similar methods were applied to the study of ionomer solutions in this work. In a fluorescence probe/quencher system where both probe and quencher associate with the microdomains to the exclusion of the bulk phase, the kinetics observed directly depends upon the distribution of quenchers among available sites. In many other systems,[14] a Poissonian distribution was observed. The Poisson model relies, however, on the ability of the sites to incorporate a large number of quenchers with equal affinity. In very small sites it is conceivable that the ability of a site to accept a quencher is drastically reduced by the prior occupation with another quencher. In this scenario, the quenching would increase more rapidly as a function of quencher concentration than if a Poisson distribution were possible. The fluorescence kinetics for the most extreme case, the exclusion of a second quencher from entering an occupied site, are derived as follows: For the reactions

$$P^* \xrightarrow{k_0} P + h\nu \tag{1}$$

$$P^* + Q \xrightarrow{k_q} P + Q + \text{energy} \tag{2}$$

The time-dependent fluorescence intensity is described by

$$I(t) = I(0)\sum P_i \exp\{-k_i t\} \tag{3}$$

where

$$k_i = k_0 + ik_q \tag{4}$$

The distribution is simplified:

$$P_1 = n_{av} = [Q]/[\text{sites}] \tag{5}$$

$$P_0 = 1 - n_{av} \tag{6}$$

$$P_{i<>1,0} = 0 \tag{7}$$

thus

$$I(t) = I(0)\exp\{-k_q t\}(n_{av}[\exp\{-k_q t\} - 1] + 1) \tag{8}$$

Integrating over all time yields the steady-state expression

$$I/I_0 = 1 - n_{av}k_q/(k_0 + k_q) \tag{9}$$

In the limit where quenching is fast, static quenching, for example, $k_q \ll k_0$ and the following kinetics result:

transient:

$$I(t) = (1 - n_{av})I(0)\exp\{-k_0 t\} \tag{10}$$

steady-state:

$$I/I_0 = 1 - n_{av} \tag{11}$$

Therefore, a linear decrease in the steady-state fluorescence intensities and the transient intensities (at any time, t) would be expected as the quencher concentration is increased. The observed rate of fluorescence decay should be unaffected by quencher concentration with a rate constant characteristic of the probe in the absence of quencher, k_0. The slope of the lines formed from plots of both the steady-state and transient intensities versus quencher concentration equals the negative reciprocal of the concentration of accessible sites, allowing the calculation of an average site size from the ionomer concentration.

As discussed previously, fluorescence from $Ru(bpy)_3^{2+}$ is quenched by Cu^{2+} in PS-1.7 solutions in toluene as both reside exclusively in the aggregated ionic regimes. But, to avoid possible conformational changes in the ionomer as quencher concentration is increased, Ca^{2+} was used to maintain the total $[M^{2+}]$ constant. The calcium, although causing a slight red shift in the $Ru(bpy)_3^{2+}$ emision, was inert with regards to quenching. This red shift from a fluorescence intensity maximum of 625 nm to 618 nm is shown in Figure 8 and is indicative of a more rigidly held probe.[20] When a low concentration of Cu^{2+} is added to the system, maintaining its concentration constant as the $[Ca^{2+}]$ is increased, the intensity of emission goes through a moderate transition as seen in Figure 9. No transition is observed in the absence of Cu^{2+}, demonstrating that while perturbation of the ionomer configuration (toward greater aggregation) is a result of increasing the M^{2+}

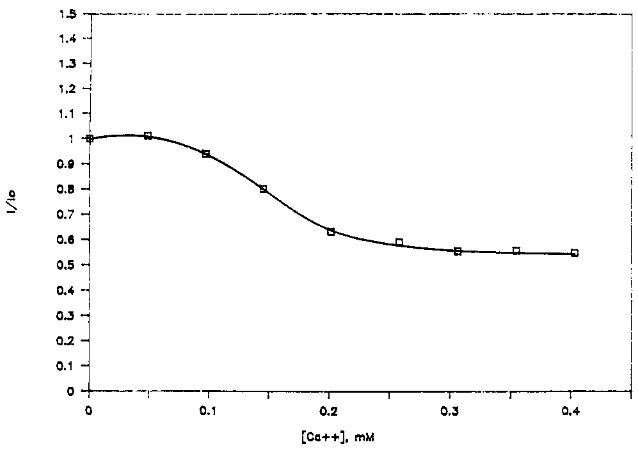

Figure 9. Increased quenching of $Ru(bpy)_3^{2+}$ by Cu^{2+} as total ionic content is increased. 5×10^{-6} M $Ru(bpy)_3^{2+}$ on 5 g/L PS-1.7 with 0.055 mM Cu^{2+}. Increased effectiveness of quenching indicates a transition to a more highly aggregated state, i.e., larger aggregates.

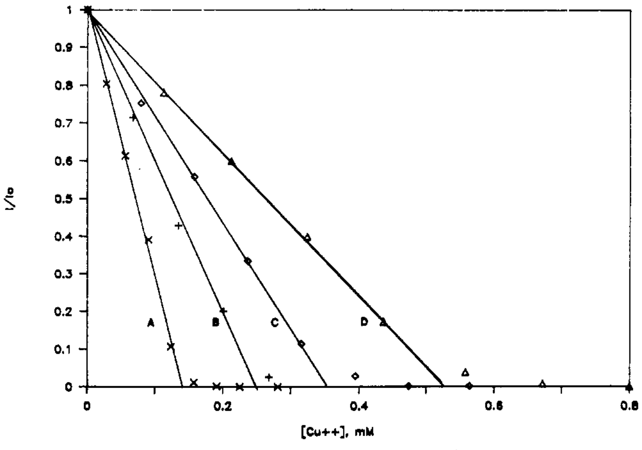

Figure 10. Steady-state quenching by Cu^{2+}. Intensities by integration of emission spectra; λ_{ex} = 425 nm: (A) 4.0 g/L PS-1.7; (B) 5.9 g/L PS-1.7; (C) 10.6 g/L PS-1.7; (D) 20.0 g/L PS-1.7.

concentration, the calcium is inert as a fluorescence quencher. The addition of external ions to the ionomer solutions acts to relax the constraints of the chain strains and steric effects in the aggregation of the sulfonate groups of the ionomer. As the ionic core becomes larger, a larger number of sulfonate groups are permitted to participate in the ion aggregate. These results justify the use of Ca^{2+} to maintain total ionic contents constant throughout a quenching run in the determination of ion aggregate sizes.

Total MCl_2 solubility = 0.07 mM/g of PS-1.7 for the copper quenching runs shown in Figure 10. The degree of quenching increases too rapidly as a function of quencher concentration to be described by Poisson kinetics. The intensities (normalized by I/I_0) decrease linearly with increasing $[Cu^{2+}]$, and the quenching is static in nature (re: Figure 3). Therefore, inhibition of the quencher from sites previously occupied is indicated and the conditions for the use of eqs 10 and 11 to model the system are satisfied.

From the slopes of the lines in Figure 10, site concentrations were calculated by using the model previously developed. An aggregation number, N_{av}, i.e., an average number of pendant sulfonate groups per site, was subsequently calculated from the known degree of sulfonation (1.7%) and the ionomer concentration. These aggregation numbers are presented graphically in Figure 11 for several concentrations of the PS-1.7 ionomer. These values agree with the prediction of small ion aggregates by theory[12] and suggested in light scattering experiments on similar materials.[11,17]

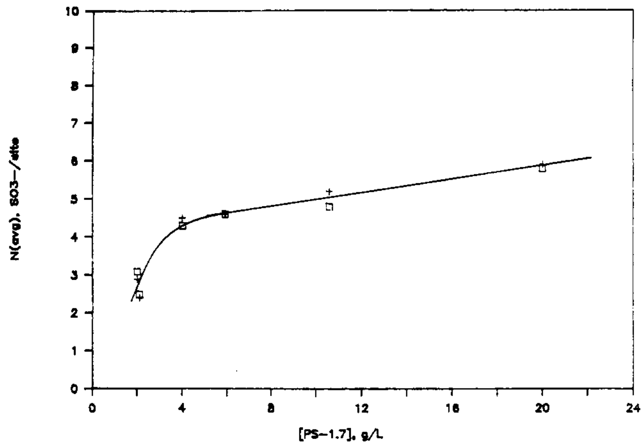

Figure 11. Site size as a function of ionomer concentration: (+) transient data; (□) steady-state data.

The mean site size for the ionomer PS-1.7 in toluene solutions increases only moderately as a function of ionomer concentration, as shown in Figure 11. It is likely, that some maximum value is slowly approached, but the experimental difficulties of working with intractable gels prohibit the extension of the curve to higher ionomer concentrations. At low concentrations, there is a significant decrease in the average size of the multiplets, possibly due to the inability of this ionomer to form stable aggregates at these concentrations.

The above results are, in general, consistent with the model for the solution behavior of sulfonate ionomers in nonionizing solvents proposed by Lantman et al.[21] to describe their light scattering results. They propose that at low concentrations the ionomers exist as individual coils due to the predominance of intramolecular forces. The integrity of these coils is maintained as concentrations are increased, but they begin to associate to form multicoil aggregates, which gives rise to networking and gelation.

Viscosity measurements[9] indicate the transition to the predominance of intermolecular forces occurs at about 9 g/L. The solubility of ionic salts being directly proportional to the concentration of ionomer, even through the transition to high PS-1.7 concentrations, supports the interpretation of these systems by the above model. Also, the relatively constant calculated aggregation numbers indicate the integrity of the sites is maintained through the transition. It may be noted that the disruption of the aggregates at low concentrations indicates that the primary coils may be composed of the association of more than one polymer chain. Elevated temperatures (40 °C versus 22 °C) do not affect the measured aggregation number at 2 g/L PS-1.7, but slightly reduce that measured at 4 g/L (3.6 versus 4.3). Thus, it is concluded that the model might be modified in that intermolecular ionomer associations play an integral role in the formation of the observed aggregates.

Effects of Polar Solvents

Probing by $Ru(bpy)_3^{2+}$. The quenching efficiency of all of the ionic quenchers is dramatically decreased by the addition of 5% v/v methanol to the toluene solutions of the PS-1.7 ionomer. Figure 2 reveals this decrease for the Cu^{2+} quenching, indicating a disruption of the aggregation, which was observed at all ionomer concentrations. The quenching also undergoes a transition from static quenching to a dynamic mechanism, as shown in Figure 12. Thus, although diffusional motions become important in the

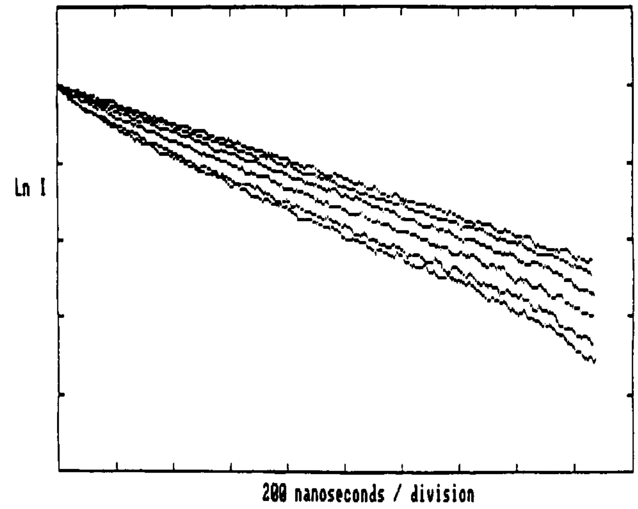

Figure 12. Log plot of transient fluorescence decay profiles for $Ru(bpy)_3^{2+}$ on PS-1.7 in 5% methanol/95% toluene; dynamic quenching by Cu^{2+}. 2×10^{-6} M $Ru(bpy)_3^{2+}$; 0.0, 0.065, 0.135, 0.20, 0.26, and 0.33 mM Cu^{2+}. Lifetimes decrease as quencher concentration increases, but overall quenching efficiency is decreased. This indicates that although mobility is increased on addition of methanol, efficiency is decreased by disruption of aggregation.

Table IV
Quenching Rate Constants for Pyrene Derivative Fluorescence Decays in Various Media by 1,4-Dinitrobenzene

probe	medium	k_q, M^{-1} s^{-1}
PBOH	toluene	2.2×10^{10}
	5% MeOH/95% toluene	1.9×10^{10}
PN^+	6.5 g/L PS-1.7 in toluene	4.6×10^{9}
	6.5 g/L PS-1.7 in 5% MeOH/95% toluene	1.4×10^{10}

quenching mechanism, the ionic material remains roughly associated to the polymer in the presence of 5% methanol. Complete ionization of the system would be unlikely in this solvent, as confirmed by conductivity measurements, which show no change in solution conductivity as the salt concentration in increased. The transition to dynamic quenching is also seen in more polar solvents, such as dioxane and DMF, indicating the increasing solvent dielectric constant disrupts the aggregation by reducing the ion pair/ion pair attractions. It is further concluded that motions of the polymer, both inter- and intramolecular processes, participate in the dynamic quenching mechanism, as opposed to the bulk transport of ions (or salts) through the solvating medium.

The disruption in the aggregation and associations between polymer chains by the addition of methanol is also responsible for the observed decrease in viscosity, which is particularly dramatic at high ionomer concentrations (>10 g/L). This effect is well documented in the literature.[22,23] Although a larger hydrodynamic radius for the individual coils might be expected as aggregation is eliminated, the decrease in the ability of the coils to interact and form intermolecular associations results in the lower viscosity.

Probing by Pyrene Derivatives. The accessibility of the probes by bulk phase quenchers is increased, as summarized in Table III, upon the addition of 5% MeOH. Medium effects on the quenching reactions are ruled out by the data presented in Table IV for various probe/quencher pairs in the different media. In homogeneous solvents, there is no significant change in the quenching of PBOH upon the addition of methanol, but the rate in ionomer systems for PN^+ is substantially increased. Additionally, PN^+ excimer formation is reduced markedly, Figure 6B, and becomes dynamic in nature, Figure 5B. These observations all lead to the conclusion that a more open configuration of PS-1.7 exists upon addition of the polar solvent due to the elimination of the ionic aggregates.

Conclusions

The investigation demonstrates the presence of ionic microdomains is solutions of a 1.7% sulfonated polystyrene ionomer in nonpolar solvents. These aggregates result from ion pair/ion pair interactions between the pendant sulfonate groups; in dilute solution the ion aggregation is thought to be only 2–3. The aggregates are small, consisting of six or seven sulfonate groups on average, and are effectively screened from the bulk phase by the presence of a zone of high polymer density (from the covalently bound polymer backbone) about the sites. A model is forwarded that these sites maintain their integrity as ionomer concentrations are increased but begin to interact to form multicoil associations.

Ionic materials supported within the ionic microdomains can be exposed more effectively to reactants in the bulk phase by the addition of small amounts of polar solvent. The polar solvent acts to reduce the attractive forces that give rise to the aggregation phenomenon, eliciting a breakdown of the aggregates. Thus, the PS-1.7 ionomer configuration can be manipulated between a rigid aggregated state, which enhances reaction between ionic species, and a loose open state, which enhances reactivity with nonionic species in the bulk phase.

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