Fluorescent Molecular Probe Technique for Assessing the Interaction between Sulfonated Polystyrene and Poly(ethyl acrylate-*co*-4-vinylpyridine) Ionomers in Tetrahydrofuran

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ABSTRACT: The interaction between sulfonated polystyrene (SPS) and poly(ethyl acrylate-*co*-4-vinylpyridine) (EtAc4VP) ionomers was investigated over a wide range of concentrations in the nonpolar solvent, tetrahydrofuran (THF), using a fluorescent molecular probe technique. The acid-base interaction between the sulfonate groups of SPS and the pyridine groups of EtAcVP and the miscibility of these ionomers are evident for pyridine contents of 7.8 and 4.5 mol % in EtAc4VP and are not detectable for EtAc4VP with 1.7 mol % pyridine groups. Concentration-dependent excimer fluorescence from SPS and EtAc4VP mixtures indicates the occurrence of polar interactions as a result of proton transfer from the styrenesulfonic acid to the pyridine. These interactions are clearly evident at high concentrations and are controlled by the high molecular weight EtAc4VP component.

Introduction

The approach to polymer-polymer miscibility through the introduction of specific interaction sites in normally immiscible polymers has been a subject of interest for a long time. One example of this approach is the introduction of small amounts of acidic or basic groups, usually less than 10 mol %, into the polymer chains. The effect of ionic interactions on interpolymer miscibility has been studied in a number of different ionomer systems and was reviewed by Eisenberg and co-workers.[1] An especially effective way to enhance miscibility is by an acid-base reaction between two ionomers. As was demonstrated for the sulfonated polystyrene/ethyl acrylate-4-vinylpyridine copolymer system, (SPS/EtAcVP), the acid-base interactions between them leads to a single, composition-dependent glass transition temperature observed by dynamic mechanical measurements for acid and base group contents of greater than 4 mol %.[2] The reason for the enhanced miscibility of this particular ionomer system is the existence of strong Coulombic interactions between oppositely charged ions, which occurs as a result of hydrogen transfer between sulfonic acid and pyridine groups.[2,3] The presence of these Coulombic interactions was confirmed for analogous ionomer mixtures by IR spectroscopy measurements.[4]

As shown in ref 5 for the example of poly(ethyl acrylate-*co*-*N*-methyl-4-vinylpyridinium iodide) and SPS mixtures, where one of the components is in the acid form but the other is in the salt form, miscibility can also be achieved by the elimination of microcounterions from the polymer chains. Complete elimination was observed for 5 mol % ions in the ionomers.

All these results were obtained for ionomers in the solid state. At present, there is only one paper devoted to an ionomer complexation study in nonpolar solvents.[6] The interaction and miscibility between zinc and sodium-neutralized sulfonated ethylene propylene terpolymers (EPDM), with styrene-4-vinylpyridine copolymer (PSVP), were studied by viscometric techniques. Strong complexation behavior, which results in aggregation and gelation of the solutions as concentration is increased in THF, was observed for the ZnEPDM-PSVP mixture. This effect was attributed to >N:Zn donor-acceptor interactions between the ionomer groups. The most pronounced association was observed at the stoichiometric ratio of the interacting polar groups. It is important to note that gelation as a result of interaction between the ionomers took place at a concentration less than one-half that at which gelation occurs for pure Zn(EPDM) ionomer in THF. The absolute value of this concentration is strongly dependent on the molar ratio of the ionomers in the mixture. No appreciable interaction and aggregation was observed for the Na(EPDM)-PSVP ionomer mixture.

The interaction and miscibility between SPS and EtAcVP were examined in THF by a fluorescence molecular probe technique in the present paper.

Experimental Section

Materials. The samples of EtAc4VP, as well as homopolymer (EtAc), were synthesized by free-radical emulsion copolymerization. The experimental procedure is as follows. Distilled water (240 mL), sodium lauryl sulfate (6.4 g), potassium persulfate (0.4 g), ethyl acrylate (no. 1, 100 g; no. 2, 98 g; no. 3, 95 g; no. 4, 90 g), 4-vinylpyridine (no. 2, 2.1 g; no. 3, 5.3 g; no. 4, 10.5 g) were mixed in a four-neck flask at 50 °C in an argon gas atmosphere. The reaction mixture was kept under the same conditions for 24 h. All polymers were isolated by precipitation into pentene, filtered, and dried at 70 °C for 48 h. Conversion was about 80-90% percent. The compositions of the polymers by elemental analysis are given in Table I. The molecular weights for EtAc as determined by GPC were M_w = 1160 000 and M_n = 400 000.

The sample of SPS was synthesized from anionically polymerized polystyrene, $\bar{M}_w$ = 115 000 and $\bar{M}_w/\bar{M}_n$ = 1.05, as described in ref 7. The SPS with n = 4.47% sulfur group content was used in these studies. 1,3,6,8-Pyrenetetrasulfonic acid tetrasodium salt ((PTS)Na) was used as the probe in the fluorescence measurements. This was obtained from Eastman Kodak Co. Tetrahydrofuran was used in all experiments as the solvent for the polymers and twice distilled water as the 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. (PTS)Na solution (0.02 mL in H_2O) was mixed with ionomer prediluted solutions of EtAc4VP and SPS (2 mL of ionomer mixture in THF) in a cell suitable for the fluorescence measurements. The polymer solution concen-

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Table I

sample	designation	mol % pyridine groups
1	EtAc	~0
2	EtAc4VP	1.7
3		4.5
4		7.8

tration range was $3.2 \times 10^{-5} < C \leq 1 \times 10^{-1}$ mol L^{-1}. EtAc4VP and SPS ionomers were mixed in stoichiometric ratios of the acid–base groups in all experiments. The probe concentration was kept constant at 5.4×10^{-7} mol L^{-1}.

Measurements. Fluorescence spectra measurements from the polymer solutions were carried out at 378-nm excitation wavelength on a Perkin-Elmer MPF-66 spectrofluorometer at room temperature. Excimer and 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 the fluorescence intensities from the ionomer EtAc4VP/SPS solutions were defined as

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

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

where ionomer mixture means the EtAc4VP/SPS solution in THF.

Turbidimetric measurements from EtAc4VP/SPS solutions in THF were carried out on a Beckman DU-7 spectrophotometer at λ = 500 nm and room temperature.

Results and Discussion

As was already demonstrated in a previous paper,[9] the fluorescence molecular probe technique is a quite efficient tool for testing intra- and inter-chain association behavior of polystyrene sulfonated ionomers with different counterions in the nonpolar solvent, THF. The fluorescence approach is based on the appearance of excimer/monomer fluorescence from ionomer or mixed ionomer solutions predissolved in THF during the addition of a small amount of water solution of the (PTS)Na molecular probe. The excimer fluorescence from the ionomer–(PTS)Na mixture is the result of solubilization and localization of the (PTS)Na probe in the polar groups of the ionomers. Excimer fluorescence indicates an association between the ionomer salt groups, while the excimer/monomer ratio of the fluorescence intensities can be considered to be indicative of the dimensions of the ionic aggregates and their structure. The appearance of concentration-dependent excimer fluorescence from the ionomer solutions leads to the possibility to distinguish between intra- and inter-chain association as discussed in a previous paper.[9] In the present investigation, the fluorescence technique was used to detect interactions between the chemically different SPS and EtAc4VP ionomers in THF. As was found earlier by viscosity measurements, SPS does not show any strong intra- or inter-chain associations between its acid groups over a wide range of concentrations in THF and with different contents of the acid groups in the polymer.[8,9] The same conclusions were reached for EtAc4VP from viscosity measurements.[6] The absence of any appreciable association for such ionomers in THF is a consequence of the low polarity of the free acid and base groups. However, if these two ionomers are mixed in THF, hydrogen-transfer interactions between sulfonic acid and pyridine groups are expected, and this should lead to polymer–polymer association and complexation. The hydrogen-transfer interaction between SPS and EtAc4VP ionomers can lead to the appearance of quite polar, even Coulombic bonds.[2,3] If such an interaction occurs, one can expect excimer and/or monomer fluorescence from SPS–EtAc4VP ionomer solutions in THF, in mixtures with a water solution of (PTS)Na molecules.

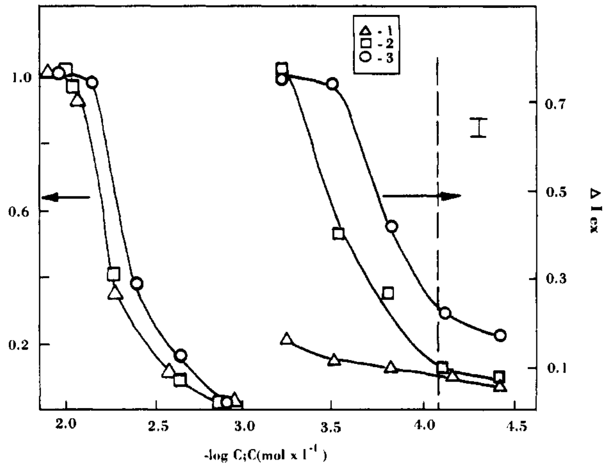

Figure 1. Excimer fluorescence intensities and relative turbidity values of the mixtures SPS (m = 4.47%)/EtAc4VP (m = 1.7%) in THF–(PTS)Na in H_2O (1), SPS (m = 4.47%)/EtAc4VP (m = 4.5%) in THF–(PTS)Na in H_2O (2), and SPS (m = 4.47%)/EtAc4VP (m = 7.8%) in THF–(PTS)Na in H_2O (3). λ_{ex} = 378 nm; λ_{em} = 500 nm; $\lambda_{em}(\tau/\tau_0)$ = 500 nm. The relative turbidity is the ratio of the turbidity to that at 1.0 g dL^{-1}.

Excimer fluorescence intensity values and the relative turbidity of the SPS–EtAc4VP mixtures in THF with different contents of 4VP groups are shown as a function of ionomer concentration in Figure 1. All experiments were carried out for stoichiometric ratios of acid–base groups. One can see that excimer fluorescence is very weak in the dilute solution regime (I) for all SPS–EtAc4VP mixtures. Concentration increases beyond this lead to an appreciable increase of excimer fluorescence for EtAc4VP–SPS mixtures with m = 4.5 and 7.8% base group content, while there is no change for EtAc4VP with m = 1.7%.

Excimer fluorescence data from individual EtAc4VP and SPS ionomer solutions are presented in Figure 2. Comparing the data in Figures 1 and 2 shows that excimer fluorescence from individual ionomers is much weaker than that from ionomer mixtures. Thus, the appearance of strong excimer fluorescence, Figure 1, is the result of localization of (PTS)Na molecules within polar associates that arise due to a hydrogen-transfer interaction between the acid and base groups in SPS–EtAc4VP mixtures. In addition, the presence of weak excimer fluorescence in EtAc4VP–SPS mixtures in dilute solution (I), Figure 1, can be attributed partially to the excimer fluorescence from individual EtAc4VP and SPS ionomer coils, which appears due to weak intra-chain associations of such ionomers.

Increases in ionomer concentration above 3×10^{-1} g dL^{-1} lead to phase separation, which is shown by the rapid increase in turbidity in Figure 1. Phase separation results from the presence of higher aggregates involving many individual chains stabilized by acid–base interactions. It is interesting to point out that the increase in the excimer fluorescence from EtAc4VP–SPS mixtures is accompanied by an increase in monomer fluorescence in the same concentration regime as shown in Figures 3 and 4. Monomer fluorescence from EtAc4VP–SPS mixtures may be a result of (PTS)Na molecules solvated by a few isolated acid or base units that are not involved in aggregates or, if they are, the aggregates are too small to solubilize more

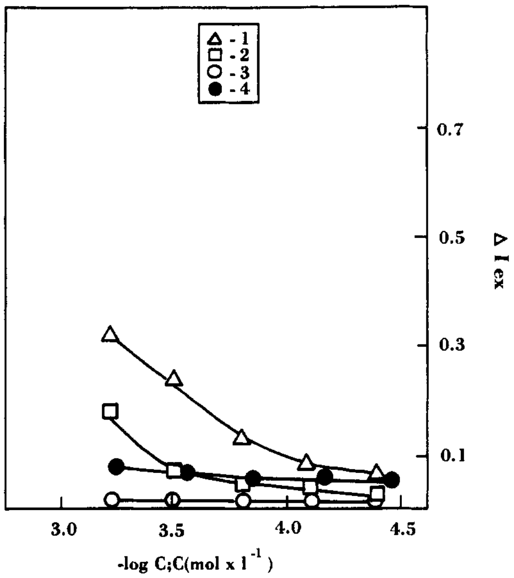

Figure 2. Excimer fluorescence intensities of ionomer solutions EtAc4VP (m = 7.8%) in THF-(PTS)Na in H_2O (1), EtAc4VP (m = 4.5%) in THF-(PTS)Na in H_2O (2), EtAc4VP (m = 1.7%) in THF-(PTS)Na in H_2O (3), and SPS (m = 4.47%) in THF-(PTS)Na in H_2O (4). λ_{ex} = 378 nm; λ_{em} = 500 nm.

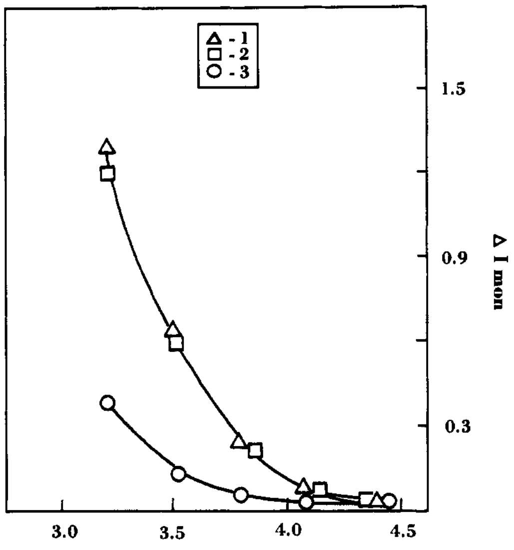

Figure 3. Monomer fluorescence intensities of the mixtures SPS (m = 4.47%)/EtAc4VP (m = 7.8%) in THF-(PTS)Na in H_2O (1), SPS (m = 4.47%)/EtAc4VP (m = 4.5%) in THF-(PTS)Na in H_2O (2), and SPS (m = 4.47%)/EtAc4VP (m = 1.7%) in THF-(PTS)Na in H_2O (3). λ_{ex} = 378 nm; λ_{em} = 409 nm.

than one (PTS)Na molecule, on average, and are randomly distributed within the ionomer coils. The presence of excimer and monomer fluorescence at the same time is an indication of the presence of acid-base ionic aggregates having a wide distribution of sizes.

Conclusions

The appearance of inter-chain associations involving ionic bonds was detected by the excimer fluorescence from EtAc4VP-SPS mixtures with m = 4.5 or 7.8% 4VP base group content and m = 4.47% acid group content at the stoichiometric acid-base ratio. No appreciable excimer fluorescence and inter-chain association was found for the EtAc4VP-SPS mixture with m = 1.7% 4VP base group content. These results correlate with solid-state miscibility data for the same ionomers obtained earlier.[3,4] The presence of excimer and monomer fluorescence in EtAc4VP-SPS mixtures in THF solution provides a basis for postulating the existence of wide size distributions of polar aggregates formed from acid-base interactions. The fluorescent molecular probe approach can be useful for the analysis of interaction and miscibility in nonpolar solvents between other chemically different ionomers, for example, the ionomers where one of the components is a donor of electrons, while the other one is the acceptor.[6]

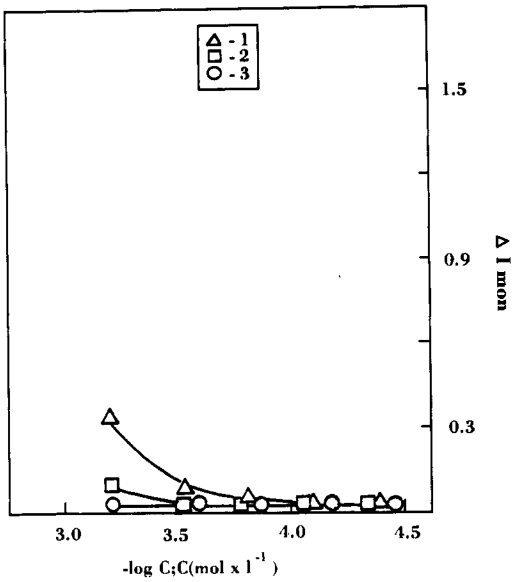

Figure 4. Monomer fluorescence intensities of ionomer solutions EtAc4VP (m = 7.8%) in THF-(PTS)Na in H_2O (1), EtAc4VP (m = 4.5%) in THF-(PTS)Na in H_2O (2), and EtAc4VP (m = 1.7%) or SPS (m = 4.47%) in THF-(PTS)Na in H_2O (3). λ_{ex} = 378 nm; λ_{em} = 409 nm.

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Registry No. EtAc4VP (copolymer), 28963-65-7; (PTS)Na, 59572-10-0.