1334 *Macromolecules* 1988, *21*, 1334-1339

Chemical and Morphological Properties of Solution-Cast Perfluorosulfonate Ionomers

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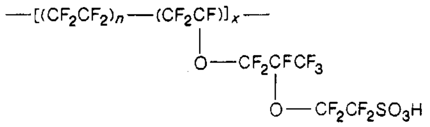
Received July 24, 1987

ABSTRACT: High equivalent weight perfluorosulfonate ionomers (PFSI's) are insoluble in all solvents at temperatures below ca. 200 °C and form pliant, elastic, and cohesive membranes. In contrast, PFSI films cast from ethanol–water solutions (at room temperature) are soluble in a variety of polar organic solvents at ambient temperature. Furthermore, these solution-cast films are brittle and noncohesive. These dissimilarities indicate that the morphologies of the as-received and recast forms of the PFSI are not the same. However, solution-cast PFSI's prepared by using high temperatures and suitable solvents have the desirable physical, mechanical, and chemical characteristics of the as-received polymer. We have conducted a broad-based series of investigations aimed at characterizing the morphologies of the solution-cast forms of a PFSI. We have found that both the high-temperature and low-temperature solution-cast forms contain ionic clusters; in contrast, while the high-temperature form is clearly partially crystalline, no evidence for crystallinity could be found in the low-temperature solution-cast polymer. The results of these and related investigations are presented here.

Introduction

Perfluorosulfonate ionomers (PFSI's, e.g. I and II) are proving to be interesting and useful membrane materials.[1,2]



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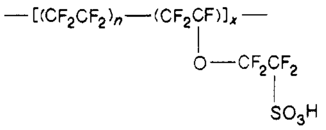

II

PFSI's have been used in a variety of electrochemical processes and devices including chlor-alkali cells,[3] batteries,[4,5] fuel cells,[6] water electrolyzers,[7] and photoelectrochemical systems.[8] PFSI's also have a number of nonelectrochemical applications including uses in chemical separations schemes,[9] organic syntheses,[10] and catalytic systems.[11] The versatility of these polymers stems from their extraordinary thermal, chemical, and mechanical stabilities.

We have previously reported a high temperature/pressure procedure for dissolving PFSI membranes;[12] solutions of Du Pont's Nafion (Nafion is a registered trade mark of the E. I. Du Pont de Nemours & Co.) polymers (I) have since become commercially available (C. G. Processing, Rockdale, MD). Such solutions have recently been used to prepare Nafion-coated electrodes,[13-18] catalysts,[11] and high performance liquid chromatography packing materials.[9,16] It is either tacitly or explicitly assumed that these solution-cast films have the same physical and chemical properties as the as-received polymer.

When the solvent (ethanol–water[12]) is evaporated from a solution of 1100 equivalent weight (EW) Nafion at ambient temperature, a material which is *very different* from as-received Nafion is obtained.[19-21] We call this material "recast" Nafion. Whereas as-received Nafion is pliant and mechanically strong, recast Nafion is brittle and has poor mechanical properties. Furthermore, while as-received Nafion is insoluble in all solvents at temperatures below ca. 200 °C, the recast material is soluble, at room temperature, in a variety of polar organic solvents.[19-21] These are clearly undesirable characteristics, yet the Nafion film-modified surfaces studied in the references cited above[9,11,13-18] were prepared by evaporation at ambient temperatures.

We have recently described a high-temperature, solution-processing procedure which yields solution-cast PFSI films and membranes which are insoluble (at temperatures below ca. 200 °C) and which have the good mechanical and physical properties of the as-received polymer.[19,20] We call this high-quality solution-cast material "solution-processed" PFSI. In a later communication, Gebel et al. described a related thermal processing procedure in which a recast film is annealed at high temperature in air or under vacuum.[21] This annealing procedure apparently converts the recast film to a material that is similar to our solution-processed polymer.

The remarkable differences between the physical and chemical properties indicate that the supermolecular structures of solution-processed and recast Nafion are not the same.[21] We have recently completed a broad-based series of investigations aimed at elucidating the supermolecular structures of the recast and solution-processed versions of 1100 EW Nafion and 1065 EW Dow PFSI (II[2]). A variety of chemical and instrumental methods of analyses were used including analyses of solubilities, wide- and small-angle X-ray scattering and differential scanning calorimetry. We were particularly interested in determining the extent to which ionic cluster phases form in the solution-processed and recast polymers. This issue has not previously been addressed. The results of these investigations are reported here.

Experimental Section

Materials. Nafion 117 (1100 EW, proton form) was obtained from E. I. Du Pont de Nemours & Co. Dow 1065 EW PFSI (proton form) was obtained from the Dow Chemical Co. These polymers were neutralized with 1 M NaOH and dissolved by using the standard procedure.[12] Ethanol, 1-propanol, 1-butanol, dimethyl sulfoxide (DMSO), ethylene glycol (EG), and *N,N'*-dimethylformamide (DMF) were all reagent grade and used as received. High-purity water was obtained by circulating house distilled water through a milli-Q water purification system. All other reagents were of the highest quality commercial grades and were used without further purification.

Investigations of the Effect of Temperature and Solvent on the Properties of Solution-Cast PFSI's. We have conducted a series of investigations aimed at assessing the effects of temperature and solvent on the solubilities and physical properties of solution-cast PFSI films. The following general strategy was used. The original solvent used to dissolve the PFSI (ethanol–water) was first replaced with a second solvent. A quantity of the PFSI solution in this second solvent was then placed in a glass

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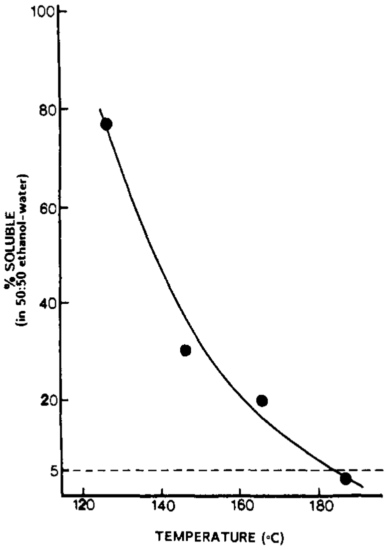

Figure 1. Effect of evaporation temperature on the solubility of solution-cast Na$^+$ form Dow PFSI (solvent = DMSO).

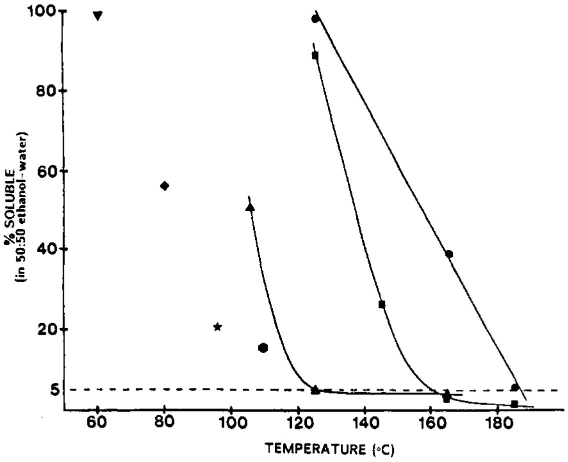

Figure 2. Effect of solvent and evaporation temperature on the solubility of solution-cast Na$^+$ form 1100 EW Nafion. Solvents: ▼, 50:50 ethanol–water; ♦, ethanol; ★, propanol; ●, butanol; ▲, DMF; ■, DMSO; ●, EG.

vial and evaporated to dryness at a desired elevated temperature. An oil bath was used to control the evaporation temperature. The physical and mechanical properties of the resulting solution-cast PFSI film were evaluated qualitatively by noting its mechanical stability and pliancy. The solubility of the solution-cast film was then quantitatively assessed (see below). This process was repeated for a variety of second solvents and evaporation temperatures.

Two different procedures were used to obtain a solution of the PFSI in the second solvent. For the low boiling point second solvents (ethanol and propanol), 10 mL of the ethanol–water solution were first evaporated down to about 2 mL. Ten milliliters of the second solvent was then added, and this solution was evaporated to ca. 2 mL. Ten milliliters of the second solvent was again added, and this evaporation, second solvent-addition process was repeated four times. In this way, a solution in the second solvent, containing only minor amounts of ethanol and water, was obtained. This solution was then evaporated to dryness at the desired temperature to obtain a solution-cast film.

For the high boiling point solvents (butanol, DMF, DMSO, and EG), 3 mL of the second solvent was added to 10 mL of the original ethanol–water solution. The majority of the ethanol and water was then removed by evaporation at 100 °C. The resulting solution was then evaporated to dryness at the desired temperature to obtain the solution-cast film.

The solubilities of the solution-cast PFSI's were assessed by adding 50 mg of a solution-cast film to 10 mL of 50:50 ethanol–water and agitating in an ultrasonic cleaner for 1 h. (Ultrasonication caused the temperature of the ethanol–water to rise to ca. 50 °C.) The ethanol–water solution was then filtered through a Whatman No. 1 filter paper (to remove undissolved solids) and evaporated to dryness. The solid residue obtained was weighed, and the percent of the solution-cast PFSI that had dissolved was calculated as follows:

$$\% \text{ soluble} = \frac{\text{wt. of residue}}{\text{wt. of solution-cast membrane}} \times 100$$

Instrumental Methods. Wide-angle X-ray diffraction (WAXD) data were obtained on a Seifert-Scintag PAD-II automated wide-angle powder diffractometer with Cu Kα filtered radiation. The region scanned was between 15° and 25° (2θ). Small-angle X-ray scattering (SAXS) experiments were performed by using the Oak Ridge National Laboratory 10 meter SAXS system with a two-dimensional detector (Oak Ridge, TN). Prior to SAXS analysis, the as-received and solution-processed PFSI samples were hydrated by boiling in water for 1 h. Because recast Nafion is soluble in warm water,[19] recast samples were hydrated by soaking in room temperature water. The SAXS data were plotted as the invariant amplitude (k^2I) versus k, where $k = (4\pi/\lambda) \sin \theta$, I is the intensity of the scattered X-rays, λ is the X-ray wavelength (1.54 Å), and θ is the scattering angle.[22]

Differential scanning calorimetry (DSC) data were obtained on a Perkin-Elmer DSC-4 with Model 3600 data station. Prior to analysis, the PFSI samples were predried for 3 h at 120 °C in a vacuum oven. The thermograms were obtained over a temperature region from 50 to 300 °C. The scan rate was typically 50 °C/min.

Viscosity Studies. An Ubbelohde viscometer was used to measure the viscosities of the PFSI solutions. The solutions and the viscometer were maintained at 25 °C in a constant temperature water bath. The reduced viscosities of these solutions were calculated as described by Flory[23]

$$\eta_{\text{red}} = (\eta - \eta_0)/\eta_0 C$$

where η_0 is the viscosity of the solvent, η is the viscosity of the polymer solution, and C is the concentration of the polyelectrolyte in grams per deciliter.

Results

Effect of Temperature and Solvent on the Solubility and Mechanical Properties of Solution-Cast PFSI. The solubility of solution-cast PFSI is critically dependent on the temperature of solvent evaporation.[19,20] For example, Figure 1 shows the effect of DMSO evaporation temperature on the solubility of solution-cast Dow PFSI. As the evaporation temperature increases, the solubility of the solution-cast PFSI decreases. Similar results were obtained for solution-cast Nafion PFSI (Figure 2).

The mechanical properties of the solution-cast PFSI are also affected by evaporation temperature.[19,20] Low evaporation temperatures (i.e. below ca. 70 °C) yield mud-cracked films that are very brittle. These films crumbled easily and could not be removed intact from the evaporation vial. High evaporation temperatures (i.e. above ca. 125 °C) produced very pliant and mechanically strong membranes. These membranes could be easily removed intact from the evaporation vial.

It is important to point out, however, that good mechanical properties do not necessarily indicate that the film is insoluble and, just as important, do not mean that the film will maintain mechanical integrity when contacted with solvent. For example, in a recent Du Pont patent,[11] Grot states that the mechanical properties of solution-cast H$^+$-form Nafion can be improved by adding DMSO to the Nafion solution and evaporating to dryness at 125 °C. While the films obtained from this procedure do, indeed, have improved coherency and mechanical strength, we have found that these films are greater than 20% soluble. Furthermore, these films completely disintegrate when ultrasonicated in ethanol–water. Similar results are ob-

Table I
Solvent Parameters

solvent	bp, °C	solubility parameter,[a] Hb
ethanol	78	12.7
1-propanol	97	11.9
1-butanol	118	11.4
N,*N*-dimethylformamide	153	12.1
dimethyl sulfoxide	189	12.9
ethylene glycol	198	16.3

[a] The solubility parameter is the square root of the solvent's energy of vaporization per molar volume.[36] 1 Hb = 1 (cal/cm^3)$^{1/2}$.

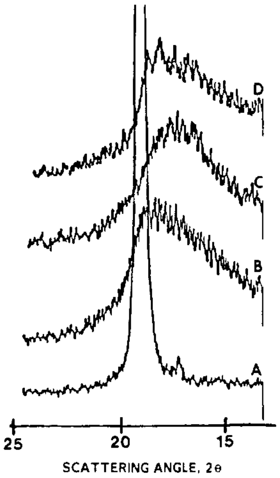

Figure 3. WAXD scans of (A) Teflon, (B) as-received 1100 EW Nafion, (C) recast 1100 EW Nafion, and (D) solution-processed 1100 EW Nafion. All Nafion samples are Na$^+$ form.

tained for both commercial and in-house-prepared Nafion solutions.

We define a high-quality solution-cast film as a film which is insoluble and pliant and which has both dry and wet mechanical strength (i.e., a high-quality film is one whose properties mimic the properties of the as-received PFSI; the terms high-quality and solution-processed are used interchangeably in this paper). We have found that only films that are less than 5% soluble satisfy all of these requirements (below the dashed lines in Figures 1 and 2). Our data suggest that high-quality films can only be prepared at temperatures in excess of ca. 125 °C.

As indicated in Figure 2, a variety of solvents can be used to prepare high-quality, solution-processed PFSI films. It is of interest to note, however, that the temperature required to produce a high-quality film varies with the characteristics of the solvent. The boiling points and solubility parameters for the solvents used here are listed in Table I. In general, the temperature required to produce a high-quality film increased as the solubility parameter of the solvent increased (see Discussion).

Wide- and Small-Angle X-ray Studies. Wide-angle X-ray diffraction and small-angle X-ray scattering experiments were used to provide information about the morphological features of as-received, recast, and solution-processed Nafion. WAXD was used to assay for crystallinity. Typical wide-angle diffractograms are shown in Figure 3. The diffractogram for Teflon is also shown in Figure 3 so that the scattering angle for perfluorocarbon backbone crystallinity can be identified.

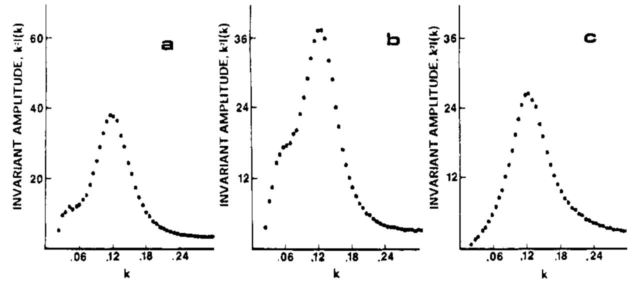

Figure 4. SAXS scans of (a) as-received 1100 EW Nafion, (b) solution-processed 1100 EW Nafion, and (c) recast 1100 EW Nafion. All samples are hydrated Na$^+$ form.

In agreement with Gierke's data,[22] as-received Nafion (curve B) shows a crystalline reflection (ca. 18°, 2θ) superimposed as a shoulder on an amorphous halo (ca. 12–22°, 2θ). Unfortunately, the low level of crystallinity in 1100 EW Nafion[22] and the instrumental noise associated with these WAXD data cause the crystalline shoulder to appear as an extension (or leaning) of the amorphous halo into the crystalline reflection region (Figure 3, curve B).

A typical diffractogram for recast Nafion is shown as curve C in Figure 3. Note that the shoulder has completely disappeared leaving only the Gaussian-shaped amorphous halo. These data indicate that recast Nafion contains much less (if any) crystallinity. Curve D of Figure 3 shows a diffractogram for solution-processed Nafion. Note that the crystalline shoulder at ca. 18°, 2θ, is again observed. Thus, some degree of crystallinity has been reintroduced by the high-temperature solution-processing procedure. It is of interest to note that similar results were obtained from thermally annealed recast films.[21] The high-temperature solution-processing and the high-temperature annealing procedures have the same effect which is to reintroduce crystallinity into the film.

Small-angle X-ray scattering is an ideal technique for the detection and measurement of ionic domains in PFSI's.[24] Figure 4a shows SAXS data from as-received 1100 EW Nafion. In agreement with previous studies, a large scattering peak at $k = 0.12$ (Bragg spacing of ca. 50 Å) is observed. This peak has been attributed to scattering from ionic clusters present in this PFSI.[22,24] Parts b and c, Figure 4, show SAXS data from solution-processed and recast Nafion, respectively. The prominent scattering peaks suggest that ionic clusters are also present in both of these solution-cast forms of the polymer. Furthermore, because the k values are aproximately the same, the Bragg spacing in all three forms of this PFSI are equivalent.

The SAXS data also reveal information about the extent of crystallinity in these polymers. The shoulder at ca. $k = 0.04$ (Bragg spacing = 160 Å) in the as-received polymer has been attributed to scattering from the PFSI crystallites.[24-26] Note that only as-received and solution-processed Nafion produce this shoulder. In agreement with the WAXD studies, recast Nafion shows no evidence for crystallinity.[19-21]

Differential Scanning Calorimetry. Eisenberg and co-workers have used dynamic mechanical analysis (DMA) to study the thermal properties of as-received Na$^+$-form Nafion membrane.[27-29] At temperatures above 100 °C, two distinct thermal relaxations were observed. Eisenberg attributes these relaxations to the glass transition of the matrix (ca. 140 °C) and the glass transition of the ionic clusters (ca. 240 °C).[27] We will refer to the matrix glass transition as $T_{g,m}$ and the ionic domain glass transition as $T_{g,c}$.

A typical DSC thermogram for Na$^+$-form as-received Nafion is shown in Figure 5 (curve A). In agreement with the DMA results, two endotherms, one at ca. 150 °C and one at ca. 260 °C, are observed. The effect of counterion on the high-temperature endotherm is illustrated in Table II. Changing the counterion associated with the fixed ionic sites causes a dramatic shift in the position of this high-temperature endotherm. These data lend further credi-

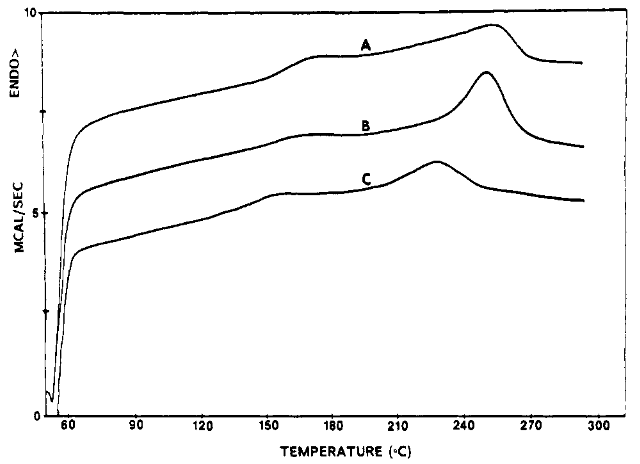

Figure 5. DSC thermograms of (A) as-received 1100 EW Nafion, (B) solution-processed 1100 EW Nafion, and (C) recast 1100 EW Nafion. All samples are Na$^+$ form.

Table II
Effect of Counterion on the Ionic Cluster Glass Transition Temperature, $T_{g,c}$

counterion	$T_{g,c}$, °C	counterion	$T_{g,c}$, °C
Na$^+$	262	Mn^{2+}	296
Cs$^+$	258	Mg^{2+}	308
Zn^{2+}	267		

bility to the assignment of the high-temperature peak to a relaxation (glass transition) of the ionic clusters.[27]

Curves B and C of Figure 5 show thermograms for the solution-processed and recast forms of Nafion, respectively. Both $T_{g,m}$ and $T_{g,c}$ are clearly present in these solution-cast samples. The temperatures of these endotherms in the solution-processed material are essentially identical with the temperatures of the corresponding endotherms in the as-received polymer. In contrast, recast Nafion (curve C) shows a slightly lower $T_{g,m}$ and a 30 °C decrease in $T_{g,c}$ (see Discussion).

Studies of PFSI Solutions. The morphology of a solution-cast ionomer film is critically dependent on the configuration of the polymer chains in the ionomer solution.[30] Therefore, it is essential to understand the characteristics of the PFSI solutions. Light[11] and small-angle neutron[31] scattering studies have shown that PFSI solutions are, in fact, colloidal suspensions. Pineri et al. suggest that the suspended particles resemble regular micelles with the charged sites extending out into the solution and the hydrophobic chain material buried in the interior.[31]

Viscosity studies can also provide information about the configuration of the polymer chains in solution. Curve A of Figure 6 shows a plot of reduced viscosity versus concentration for a Nafion "solution" at 25 °C. Reduced viscosities increase dramatically at low concentrations; this behavior, called the polyelectrolyte effect, is typically observed for free polyelectrolyte chains in solution and results from a globular to extended state transiton in these free chains.[23]

Curve B of Figure 6 shows results of analogous studies conducted on Nafion solutions that had been placed in an ultrasonic cleaner for 1 h. Immediately after sonication, the reduced viscosities at low concentrations are higher than those of the unsonicated solutions. If the sonicated solutions sit undisturbed overnight, the reduced viscosities return to their presonication (lower) values. These data suggest that free polyelectrolyte chains exist in equilibrium with the many chain particles. Furthermore, ultrasonication causes fragmentation of some of the particles, thus increasing the concentration of free chains. This process is reversible, and with time the fragmented particles coalesce.

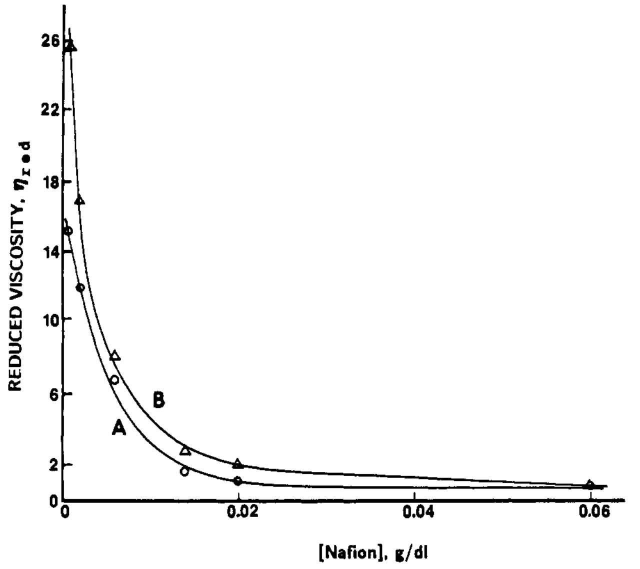

Figure 6. Plots of reduced viscosity vs concentration for 1100 EW Nafion in 50:50 ethanol–water at 25 °C. Curve A is for the unsonicated solutions, and curve B is for the ultrasonicated solutions.

Dicussion

The Effect of Solvent and Temperature on Crystallinity and Film Characteristics. PFSI's can have two important supermolecular features—crystals and ionic aggregates. The SAXS and DSC data show that recast, solution-processed and as-received Nafion all contain ionic clusters (see below for further discussion). In contrast, while as-received and solution-processed Nafion are partially crystalline, no evidence for crystallinity could be detected in the recast films. Thus, recast Nafion's high solubility and inferior mechanical properties can be attributed to a dearth of crystallinity.[20,21] This assessment is in agreement with data obtained from 970 EW Nafion. This polymer contains ionic clusters but is noncrystalline;[22] like the recast Nafion studied here, the 970 EW polymer is soluble at room temperature.[15]

Figures 1 and 2 show that two factors affect the solubility and physical properties of solution-cast PFSI—temperature and solvent. This can be explained through a consideration of the effects of temperature and solvent on polymer chain mobility. If the polymer chains are immobile, crystallization cannot occur and low-quality solution-cast films are obtained. In our solution-processing procedure, the requisite mobility is provided by thermal excitation and by the plasticization effect of the solvent. Gebel et al.'s thermal annealing procedure, which also requires a high boiling point solvent, undoubtedly operates in an analogous fashion.[21]

The extent of thermal energy required to produce a high-quality solution-cast film is highly solvent dependent (Figure 2). Note first that Nafion is only soluble in relatively high solubility parameter solvents (Table I). However, for the solvents which yield high-quality films (DMF, DMSO, EG), the temperature required to yield such a film decreases with solubility parameter. A possible interpretation of these results can be obtained through a consideration of Nafion's solvent swelling characteristics.[32]

Nafion exhibits two distinct solvent swelling envelopes, one with a maximum at about 9.5 Hb and the second with a broad and lower maximum at ca. 17 Hb.[32] The latter swelling envelope has been attributed to solvation of the ionic domains and the former to solvation of the chain material.[32] Figure 2 indicates that solvents which fall in the lower envelope can yield high-quality films at lower temperatures than solvents which fall in the higher envelope. This is in perfect agreement with our premise that solvation, and thus plasticization, of the chain material promotes crystallization. PFSI formed in the presence of such a plasticizing solvent requires less thermal energy to crystallize, and high-quality films are obtained at lower temperatures.

Analysis of the Ionic Clusters. In this section, we first discuss the mechanisms of cluster and crystal formation in recast and solution-processed PFSI. We then describe the physical characteristics of the ionic clusters as deduced from the SAXS and DSC data.

While recast Nafion shows no evidence for crystallinity, it does show a prominent SAXS peak at about the same angle as the solution-processed and as-received polymers. As noted above, this suggests that ionic domains are present in the recast material. An alternative possibility is that the micelle-like particles present in solution[31] remain intact in the solid state[21] and the SAXS peak results from these particles. If this was the case, however, there would be no ionic domain relaxation endotherm in the DSC thermogram.[27] The combination of the SAXS and DSC data provide compelling evidence for the presence of an ionic cluster phase in recast Nafion.

The above discussion raises the following question—if there is insufficient thermal energy during film formation to yield crystallites, how is it that recast Nafion can form ionic clusters? We believe that the answer to this question lies in the relative chain mobilities of the main and side chains. As noted above, in order for crystallization to occur, the main chains must be mobile. Figure 5 shows that the matrix glass transition in recast Nafion occurs at ca. 150 °C. Since the recast films are formed at temperatures well below $T_{g,m}$, the main chains are relatively immobile and reorientation is impossible. Thus, crystallites cannot form in the recast polymer.

Because the side chains are shorter, they will be more mobile than the main chains. Furthermore, note that the charged groups are affixed to the ends of these mobile side chains (I and II). Therefore, it seems possible that some degree (see below) of cluster formation can occur through reorientation of predominantly the side chains. We suggest, then, that the answer to the above question is—because cluster formation is dynamically more facile than crystallization, a cluster phase can from at lower temperatures than can crystallites.

The 30-deg drop in the ionic-domain glass transition temperature, $T_{g,c}$, indicates that the clusters present in the recast Nafion are quite different from the clusters in the solution-processed and as-received polymers (Figure 5). An analogous decrease in $T_{g,c}$ occurs when the number of ionic groups present in the ionomer is decreased (i.e., when the EW is increased).[33] Hence, one explanation for the lower $T_{g,c}$ in recast Nafion is that a smaller fraction of the charged groups present in the polymer are incorporated into the cluster phase (relative to the solution-processed and as-received polymers). The extra-cluster ionic groups are presumably present as multiplets[34] or free ion pairs and thus do not contribute to the electrostatic cluster formation energy. An alternative possibility is that smaller ionic clusters are present in the recast polymer.

The former explanation for the lower $T_{g,c}$ in recast Nafion is perfectly consistent with the mechanism for cluster formation presented above. It is generally believed that some main-chain reorientation is required in order for a complete, equilibrium ionic cluster phase to form.[34] Because main-chain mobility in the recast material is restricted, not all of the charged groups can be incorporated into the recast ionic cluster and $T_{g,c}$ is decreased correspondingly.

Finally it is of interest to note that the Bragg spacings associated with the ionic clusters in the as-received, solution-processed, and recast Nafions are all approximately the same. It is difficult, at this time, to interpret this observation since the water contents of the membranes investigated (see Figure 4) were not the same. Indeed, the recast form of the polymer imbibes much more water than either the as-received or solution-processed polymers. The crystalline regions in polymers act as cross-links and increase the barrier to water induced swelling. Because recast Nafion is noncrystalline, it is not surprising that it imbibes more water than the crystalline forms of the polymer.

Conclusions

These studies have shown that the morphology of the solution-processed Nafion is apparently very similar to that of the as-received Nafion. In contrast, the morphology of the recast Nafion is different from that of the as-received and solution-processed materials. These morphological differences account for the poor mechanical properties and high solubilities of the recast material. It seems likely that other membrane chemical properties should also be affected by the unique morphological features of the recast material. For example, the higher disorder and higher water content in the cluster phase suggest that recast Nafion should be less permselective than the as-received or solution-processed materials. Recent studies by Redepenning and Anson have shown that recast Nafion is, indeed, less permselective.[35]

We are currently conducting a similar series of investigations on a wide range of EW's of the Dow PFSI's (II). These studies should allow us to develop better models for the ionic cluster phase in both solution-processed and recast PFSI's.

Acknowledgment. We thank Dr. J. S. Lin of the Oak Ridge National Laboratory NCSASR for his kind assistance in obtaining the SAXS data and Professor R. Kellman of San Jose State University for valuable consultation. We thank E. R. Alvarez and J. L. Colon for conducting the viscosity studies. Support for this research was provided by the Dow Chemical Co., The Robert A. Welch Foundation and The Office of Naval Research.

Registry No. Nafion 117, 66796-30-3.

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Small-Angle Neutron Scattering from Sulfonate Ionomer Solutions. 1. Associating Polymer Behavior

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Received February 17, 1987

ABSTRACT: Small-angle neutron scattering (SANS) experiments have been carried out on a series of sulfonated polystyrene solutions. At a fixed sulfonation level, polymer concentrations in perdeuterated tetrahydrofuran ranging from 0.5 to 4.0 g dL^{-1} were studied. Even at the lowest concentration, intermolecular association of ionomer coils was observed. By use of a mixed-labeling technique, the radius of gyration of a single chain within these aggregates was determined. The results provide a molecular basis for the understanding of the solution behavior of ionomers in nonionizing solvents.

Introduction

Ionomers such as lightly sulfonated polystyrene are long-chain flexible polymers with a few ionic groups randomly spaced along the backbone. These ionic groups interact strongly with one another. The morphology and properties which result from ionic interactions in solid-state ionomers have been widely studied, as evidenced by an extensive literature.[1-3]

Previous solution viscosity studies[4-7] have revealed several unusual phenomena in dilute and semidilute ionomer solutions. These phenomena are due to the presence of polar ionic groups in the polymer and hence are highly dependent upon solvent polarity. This study focuses on sulfonated polystyrene ionomers dissolved in a relatively nonpolar solvent where available evidence indicates that the salt groups exist as contact ion pairs.

Ionomers dissolved in these nonionizing solvents exhibit a marked reduction in solution viscosity as the dilute concentration regime is approached. This has previously been interpreted as due to coil collapse. As polymer concentration is increased, the solution viscosity increases dramatically and gelation eventually occurs due to extensive intercoil associations. At an intermediate concentration, the ionomer solution viscosity is the same as that of an equivalent solution of unmodified polymer. This has previously been understood as a delicate balance between inter- and intrachain associations.

The provision of a molecular basis for the observed viscometric phenomena is clearly of interest. To this end, small-angle neutron scattering measurements (SANS) have been performed on a model system. Specifically, sodium salts of lightly sulfonated polystyrene (SPS) with a narrow molecular weight distribution have been studied in tetrahydrofuran (THF). This nonionizing solvent ($\epsilon = 7.6$) was used in its perdeuterated form to provide sufficient contrast for the neutron scattering experiment and to reduce incoherent background scattering. When we consider the ionomer chains in solution, it is reasonable to assume that aggregation occurs due to the strong tendency of the chains to associate. Due to these strong interactions, a conven-