

Studies on Solution Cast Perfluorocarbonsulfonic Acid Ionomers

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SYNOPSIS

The thermal properties of perfluorocarbonsulfonic acid ionomer films cast from solution and their temperature-dependent far infrared spectra have been investigated. In addition to the endotherms and spectral changes associated with the loss of solvent as the films were heated, a significant exotherm has been observed and assigned to the relaxation associated with rearrangements resulting in partially crystallized phases in insoluble thermally treated membranes. © 1993 John Wiley & Sons, Inc.

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INTRODUCTION

Ionomers are polymers that are functionalized with ionic groups (usually anionic sites) attached along the polymeric backbones, typically at a level of 10 mol % or less.¹⁻⁴ They exhibit a wide range of interesting and useful physical and chemical properties as a consequence of the morphologies they assume.⁵⁻⁷ Perfluorocarbonsulfonic acid (PFSA) ionomers are particularly important because they form membranes which are very stable and have excellent ion-exchange characteristics.⁸ Indeed, they are used widely as membranes in brine electrolysis (chlor-alkali) cells.⁹

The need to repair pinholes or tears in such membranes or to coat metal or semiconducting electrodes¹⁰ led to successful efforts¹¹⁻¹⁴ to obtain solutions of high equivalent weight (EW > 1000) PFSA. It became evident quickly that the structure of the films cast from these solutions was quite different from that of the starting, commercially available, Nafion® material.¹⁵⁻²⁰ If not treated thermally, solution cast films are poor in texture, brittle, and quite soluble in polar solvents.

A large body of evidence has accumulated indicating that when ionomers are in the form of solids they are microphase-separated to some degree.^{21,22}

This is thought to occur by separation of hydrophobic regions of the covalent backbone from hydrophilic regions containing largely ionic groups. The degree to which this microphase separation happens must vary from ionomer to ionomer and lead to differences in the average size and separation of the ionic aggregates, and the sizes and degrees of crystallinity of the hydrophobic regions. The central notion is that this type of bulk material-morphology results from thermodynamic factors, even though various degrees of its attainment can be realized kinetically. Attaining this morphology relative to the alternative one of uniform spatial distribution of ionic segments is an ordering process. Since this is costly entropically, the central idea can be restated as being that attaining this morphology is favored enthalpically. If this is the case and the effect is large enough, it should be possible to observe an exotherm when ionomers which have not reached the pseudoequilibrium form are treated thermally enough to allow them to rearrange to reach that form.

There are two general ways, at least, to obtain the material away from its pseudoequilibrium morphology. One is to heat an ionomer and quench it fast, or impose some other distorting force to put the material in the unstable form for a period which is shorter than its natural relaxation period. The other method is to obtain the solid ionomer in some special form that it attains in solution, at an inter-

face, or, in principle, in the vapor phase. Either of these methods should lead to a material which then can rearrange exothermically to give the pseudo-equilibrium morphology.

It has been shown¹⁵⁻¹⁷ that a solution form of H⁺-PFSA organizes into rod-like micellar structures and that they persist when the solvent is evaporated to form films. These solution cast films differ in major ways from the typical solid H⁺-PFSA. For one thing, the ionic regions in solid H⁺-PFSA are thought to resemble an inverted micellar structure. For another, the organization of the PTFE-like regions appears to be quite special in the dried films. Clearly there should be a considerable enthalpic difference, ΔH , between the solution-derived films and those obtained in the typical form. This ΔH should be observable. Moreover, extensive changes should be observable in the far infrared spectra due to hydrogen-bonding,²³ polymer ordering and solvation-related effects. Thermal and spectral changes accompanying the thermal treatment of solution-cast H⁺-PFSA films are reported.

EXPERIMENTAL

Dissolution of 117 Nafion (E. I. du Pont de Nemours, Inc.) acidic membrane was achieved by ion-exchanging it to its Li⁺ salt form and then using the procedure of Grot and Chadds¹¹ and Martin et al.¹² Small pieces of membrane were swollen in a 50/50 water-ethanol mixture and heated for 1 h at 250°C under pressure. The homogeneous solution obtained was then concentrated by slow evaporation at ca. 80°C. After evaporation of the solvent, the viscous solution became a gel which cracked and formed solid transparent particles when dried. Grinding at room temperature in an agate mortar yielded a white powder which was insoluble in water at room temperature. The acid form of the ionomer was made by stirring it in 2 M HNO₃ for 2 h, filtering through a medium glass frit and drying at a temperature of less than 80°C for several hours. Material made in this manner is soluble in absolute ethanol.

Solutions at 20 wt % concentration were prepared by placing 0.50 g H⁺-Nafion powder in a 25 mL vial and adding 2.0 g absolute ethanol. After adding a small Teflon-coated stirring bar such a vial was capped and its contents were stirred until all of the solid dissolved to give a clear solution.

Two 80-120 μm thick films were prepared from a solution prepared this way. Each was made by pouring solution into a cylindrical section of 45 mm (inside diameter) glass tubing held in place perpen-

dicularly on a glass plate by paraffin wax around the outside of the junction. Upon standing overnight at room temperature, the solvent evaporated and left clear circular films on the glass plate. They needed to be removed carefully because the films are brittle and adhere quite strongly to the glass. One way to remove them involved placing a drop of deionized water just at the edge of the film for a few seconds to swell the edge. Then with the aid of a razor knife the edge of the film may be lifted from the glass. Swelling with minute amounts of water, removing the excess water with absorbant paper, and gentle lifting of the film gives a clear circular film of appropriate thickness (80-120 μm) for far infrared spectral studies. Occasionally during the room temperature evaporation of the solvent the film curls slightly and partially lifts itself off the glass plate. In such cases an unswollen piece is obtained. No differences were detected between these two sample types.

Variable temperature far infrared spectra were taken on an IBM 98 Brucker 113-v Fourier transform infrared (FTIR) spectrometer using a specially constructed variable temperature cell. Power was provided to the cell and its temperature was monitored with a thermocouple via electrical connections through the spectrometer casing, so that the sample remained under vacuum during the experiment. The films dried by heating in vacuum up to 245°C for extended periods acquired a slight brownish coloration similar to aged as-received H⁺ Nafion membranes. Gebel et al.¹⁶ have reported that films which have been oven dried, in air above 100°C are completely black and opaque.

Measurements by DSC and TGA were made using a du Pont 910 DSC and 951 thermal analyzers, calibrated with appropriate standards. The DSC measurements were made on samples in Al pans having a pinhole in the lid at 5°C/min. All Nafion films cast from solution were air-dried and, thus, are referred to as NF(AD). Portions of these same films were equilibrated in ethanol vapor or water vapor by placing them over the liquid in a dessicator chamber for five days at ambient temperature. Films treated in this manner are referred to as NF(AD-EE) and NF(AD-WE) correspondingly.

RESULTS

The thermal behavior of the Nafion films, prepared from solution and treated as described above, was measured by DSC in the 35-240°C region. The upper scan limit was set to 240°C to make it possible to

carry out successive measurements on the samples without the chemical decomposition that occurs above 300°C.

The first and second scans of a typical NF(AD) sample are shown in Figure 1. The first scan (A) shows an endotherm at ca. 75°C and at least one endotherm in the 105–160°C region, which appears to correspond to an endothermic maximum near 120°C. Remarkably, the curve rises to have a slightly higher (more exothermic) value of heat flow (W/g) at 170–190°C than it does at 35°C. Since the film loses some of its mass (0.8%) over the 35–150°C range, due to evaporation of solvent, the value of this variable actually is a bit higher than recorded. The TGA scan on a typical NF(AD) film shows this loss of ca. 0.8% of mass over the 30–150°C range, no change of mass in the 160–190°C range, and loss of ca. 0.4% in the 200–250°C range.

The second DSC scan (B) on this NF(AD) material has two significant characteristics. The main one is that it is more endothermic at all temperatures than the first scan, except near the ca. 75°C endotherm of scan (A). The 75°C endotherm is gone. The other is that there is a broad, weak endothermic deviation from the monotonically increasing (endothermically) curve in the 80–170°C range. This replaces the exothermic deviation observed in the 150–200°C region on the first scan (A).

Taken together, these observations show that air-dried cast Nafion films (NF(AD)) exhibit a large, broad exotherm at temperatures above 150°C. In order to investigate this further, the DSC behavior of air-dried films equilibrated in ethanol vapor NF(AD-EE) or in water vapor NF(AD-WE) were investigated. DSC scans of such films and of another air-dried sample NF(AD) are shown in Figure 2.

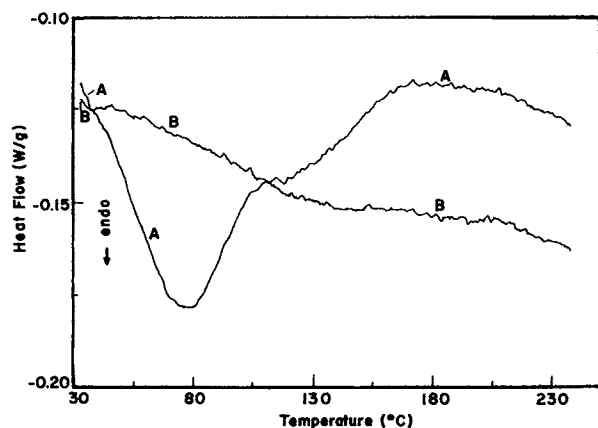


Figure 1. First (A) and second (B) DSC scans of a typical air-dried H^+ -PFSA sample, NF(AD).

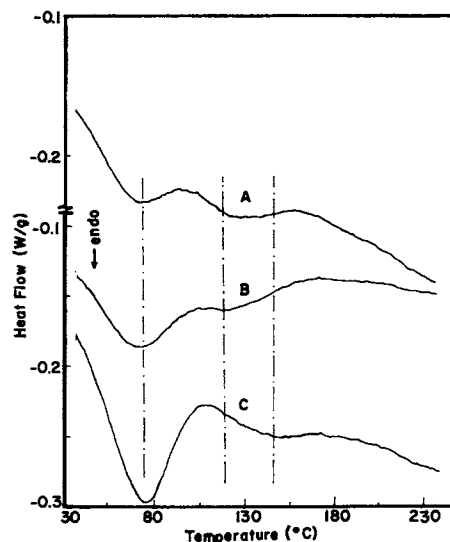


Figure 2. DSC curves of three H^+ -PFSA samples. (A) Film allowed to equilibrate over water vapor in a closed vessel at room temperature for five days, NF(AD-WE). (B) Film air dried at ambient temperature, NF(AD). (C) Film allowed to equilibrate over ethanol vapor in a closed vessel at room temperature for 5 days, NF(AD-EE).

The result for the NF(AD) sample (Fig. 2B) is essentially the same as that shown in Figure 1, of course, but the scans of the ethanol equilibrated NF(AD-EE) (Fig. 2C) and water equilibrated NF(AD-WE) (Fig. 2A), proved to be quite helpful in interpreting the data.

As marked on Figure 2, we identify three endotherms associated with Nafion films in these forms. The endotherm at ca. 75°C is strongest in the ethanol-equilibrated films NF(AD-EE) and we assign it to the heat required to evaporate ethanol. Similarly, the endotherm at ca. 120°C is exhibited by NF(AD-WE) and NF(AD), but practically not at all by the ethanol-equilibrated NF(AD-EE), so it is assigned to the evaporation of water.

The DSC curves are very interesting above 140°C, at which temperature the ethanol-equilibrated film (NF(AD-EE)), curve 2C, has an endothermic slope while curves 2B (NF(AD)) and 2A (NF(AD-WE)) have slopes of the opposite sign. The shape of curve 2C makes it clear that there is an endothermic event centered near 145°C. This helps to interpret all of the curves since each material contains at least some ethanol. Thus, we conclude that the endotherms in the 105–160°C region for NF(AD), as well as for NF(AD-WE), actually are due to two types of events: the evaporation of water (centered near 118°C), and, to a lesser extent than seen for NF(AD-EE), weak endothermic event centered

near 145°C. The TGA runs on NF(AD-EE) and NF(AD-WE) showed mass losses of ca. 1% in the 30–150°C range and 0.5% in the 200–250°C range, analogous to those observed from NF(AD) samples. With 0.1% sensitivity for ca. 1×10^{-2} g samples, differences were not resolved.

Thus, the DSC curves for NF(AD) films are assigned as follows. There is a loss of ethanol near 75°C, loss of water near 118°C, a weak endotherm near 145°C, a broad exotherm within 150 to 210°C range (160–190°C), the gradual background effect of the temperature dependence of the heat capacity, and the effect of mass loss (in the 1% range for the samples studied) on the mass-weighted heat flow.

The far infrared spectra of an NF(AD) film, studied as the film was heated in the evacuated chamber of the spectrometer, are shown in Figure 3. There are several noteworthy features. First, the absorbance due to a band at 240 cm^{-1} decreased as the sample was heated from 25 to 100°C while other spectral features were little changed. This decrease is due to loss of hydrogen-bonding solvent and to the consequent loss of absorption due to localized A-H-B type H-bonding vibrations.²³ At temperatures above 100°C, the far infrared spectra in this region exhibit a general increase in absorption centered at 300 cm^{-1} due to vibrations of a very broad distribution of H-bonding interactions of the desolvated sulfonate groups, and they show the disappearance of the band at 420 cm^{-1} . We assign this 420- cm^{-1} band to the coupled $\delta(\text{C-O-C})$ and $r(\text{CF}_2)$ vibrations of the fluorocarbon-ether side chains of Nafion. As shown by studies of the temperature dependent infrared spectra of polyoxymethylene,^{24–31} the disappearance with rise in temperature can be

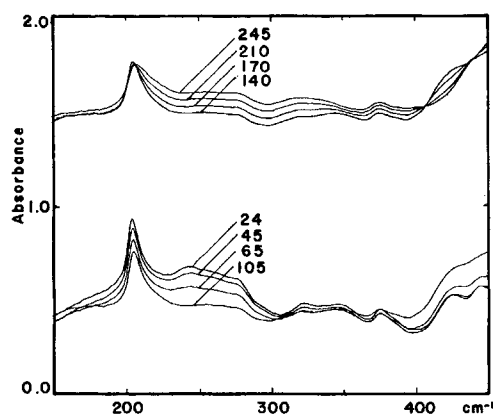


Figure 3. Variable temperature FTIR spectra of a typical air-dried film, NF(AD). Each curve is labeled with the temperature (°C) at which the spectrum was taken. The upper set of spectra have been offset by one absorbance unit for clarity.

taken as due to loss of local order imposed at the ether oxygen. In the present case, the loss of ethanol from the side chain region, where it can H-bond to the ether oxygens, can cause this loss of highly local order. Note that it occurs in the temperature range (albeit in vacuum) in which the DSC curve shows the 145°C endotherm for NF(AD-EE).

DISCUSSION

The DSC curves for the solution cast films exhibit endotherms for loss of ethanol, near its boiling point, and for loss of water of hydration. More interestingly, perhaps, they show that some heat is required to cause an endothermic event at ca. 145°C which is seen more clearly in ethanol equilibrated samples. However, the most significant new feature is the broad exotherm between about 160 and 190°C.

Based on the work of Aldebert et al.,^{15–17} Moore and Martin,^{8–20} and others, a model for the solution cast films has been developed. It is that charged, rod-like micellar structures are present in water/ethanol solutions, that a film formed upon evaporation of the solvent “may be considered to be a compact nearly dried solution,”¹⁶ and that the cohesion of the film is due largely to increased ionic interactions between the acid groups as the solvent leaves. The film material that is left after evaporation and drying in air contains some water and some ethanol.

To this picture we can add the notion that solvents can swell both the ionic (in this case acidic) and side chain regions, as discussed, for example, by Yeo,³² Pineri and co-workers,^{15–17} Moore and Martin,^{18–20} and other authors. We also reconsider the introductory discussion wherein it was pointed out that relaxation to a more highly ordered, lower enthalpy state is exothermic, but that thermal activation is required to provide sufficient mobility for the chain segments to allow this to occur in a reasonable time period.

Considering our results in this light leads us to suggest the following. As an NF(AD) film is heated it first loses ethanol, which is loosely held in acidic/ionic intermicellar regions, near 75°C. When its temperature reaches the 100–130°C region it loses H₂O from these acidic/ionic regions. As the temperature reaches 145°C the heat is sufficient to cause loss of the ethanol that is strongly associated with the side chains. Among its modes of association is H-bonding to ether oxygens, as evidenced by the loss of the 420 cm^{-1} infrared spectral band. This is endothermic and causes a major effect on the DSC curve of the ethanol-equilibrated film but only a mi-

nor effect on the DSC curves of NF(AD) films, which contain less ethanol.

As the temperature exceeds 150°C, the fluorocarbon backbone and side chains become sufficiently activated thermally to rearrange. Given that the SAXS results^{16,19,20} show that about 200 Å crystallites form upon annealing and given that only backbone ordering can be of this extent, the exotherm is assigned as being due largely to the heat released upon this crystal development and growth. The exotherm is apparent only if heat is not required to cause desolvation of ethanol associated with the side chains, as it is in the NF(AD-EE) cases. In the NF(AD) and NF(AD-WE) cases, the films have lost enough solvent (in both the ionic and hydrophobic subphases) by the time the temperature at which the chains become mobile is reached that the exotherm is more clearly observable.

It is interesting to note that the morphological changes accompanying this coalescence and annealing process include a changing role for the ionic groups. In a rod-shaped micellar structure they are on the exterior of the hydrophobic phase, but after annealing they apparently are in ionic domains in the interior of a hydrophobic matrix in a inverse micellar structure. This change in role requires the interpenetration or alternatively, the flowing together of hydrophobic segments to form more stable structures, including some crystallites.

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REFERENCES AND NOTES

- L. Holliday (Ed.), *Classification and General Properties of Ionic Polymers* Halsted Press, Barking, England, 1975.
- A. Eisenberg and M. King (eds.), *Ion-Containing Polymers*, vol. 2, Academic Press, New York, 1977.
- A. Eisenberg (ed.), *Ions in Polymers*, American Chemical Society, Washington, DC, 1980.
- M. Pineri and A. Eisenberg (eds.), *Structure and Properties of Ionomers*, Reidel Publishing Co., Dordrecht, The Netherlands, 1987.
- E. J. Roche, M. Pineri, R. Cuplessix, and A. M. Levelet, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1 (1981).
- T. D. Gierke, G. E. Munn, and F. C. Wilson, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 1687 (1981).
- E. I. du Pont de Nemours, Inc., *Nafion Perfluorinated Membranes* (product literature), Feb. 1, 1984.
- A. Eisenberg and H. L. Yeager (eds.), *Perfluorinated Ionomer Membranes*, (eds.), ACS Symposium Series 180, American Chemical Society, Washington, DC, 1982.
- W. G. Grot, G. E. Munn, and P. N. Wamsley, paper 154 presented at the Electrochemical Society Meeting, Houston, TX, May 7-11, 1972.
- I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, **102**, 6641 (1980).
- W. G. Grot and F. Chadds, European Patent 0 066 369 (1982).
- C. R. Martin, T. A. Rhodes, and J. A. Fergusson, *Anal. Chem.*, **54**, 1639 (1982).
- M. Covitch, *J. Am. Chem. Soc.*, Philadelphia, PA (Aug. 1984).
- H. W. McCain and L. L. Benezra, European Patent 0 079 218, 1983.
- P. Aldebert, B. Dreyfus, and M. Pineri, *Macromolecules*, **19**, 2651 (1986).
- G. Gebel, P. Aldebert, and M. Pineri, *Macromolecules*, **20**, 1425 (1987).
- P. Aldebert, B. Dreyfus, G. Gebel, N. Nakamura, M. Pineri, and F. Volino, *J. Phys. France*, **49**, 2101 (1988).
- R. B. Moore, III and C. R. Martin, *Anal. Chem.*, **58**, 2570 (1986).
- R. B. Moore, III and C. R. Martin, *Macromolecules*, **21**, 1334 (1988).
- R. B. Moore, III and C. R. Martin, *Macromolecules*, **22**, 3594 (1989).
- E. Hirasawa, Y. Yamamoto, K. Tadano, and W. Yano, *J. Appl. Polym. Sci.*, **42**, 351 (1991), and references 1, 2, 16-22 therein.
- A. Eisenberg, B. Hird, and R. B. Moore, *Macromolecules*, **23**, 4098 (1990).
- G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman and Co., San Francisco, 1960, Chap. 3.
- A. Novak and E. Whalley, *Trans. Faraday Soc.*, **55**, 1484 (1959).
- H. Tadokoro, *J. Chem. Phys.*, **33**, 1558 (1960).
- H. Tadokoro, A. Kobayashi, Y. Kawaguchi, S. Sobajima, S. Murahashi, and Y. Matsui, *J. Chem. Phys.*, **35**, 369 (1961).
- H. Tadokoro, M. Kobayashi, S. Murahashi, A. Mitsuishi, and H. Yoshinaga, *Bull. Chem. Soc. Japan*, **35**, 1429 (1962).
- H. Tadokoro, M. Kobayashi, Y. Wawaguchi, A. Kobayashi, and S. Murahashi, *J. Chem. Phys.*, **38**, 703 (1963).
- T. Yoshihara, H. Tadokoro, and S. Murahashi, *J. Chem. Phys.*, **41**, 2902 (1964).
- K. Majer and O. Hainova, *Kolloid Z., Z. F. Polymer*, **201**(1), 23 (1965).
- H. Tadokoro, *Macromol. Rev.*, **1**, 119 (1966).
- R. S. Yeo, *Polymer*, **21**, 432 (1980).

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