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Table I
Limiting Characteristic Ratio of the End-to-end Distance, $C = \langle r^2 \rangle_0 / nl^2$ $(n \to \infty)$, Calculated with the *Erroneous* RIS Model[a]

	$\pi - \theta''$				
$\pi - \theta'$	108°	109°	110°	111°	112°
122°	4.51	4.67	4.83	5.00	5.18
124°	4.58	4.74	4.91	5.08	5.27
126°	4.65	4.81	4.98	5.16	5.35
128°	4.71	4.88	5.06	5.24	5.43
130°	4.78	4.95	5.12	5.31	5.50

[a] $\xi = 0.007$; $\{\varphi\} = \{+15°, -15°, +130°, -130°\}$.

Table II
Limiting Characteristic Ratio of the End-to-end Distance, $C = \langle r^2 \rangle_0 / nl^2$ $(n \to \infty)$, Calculated with the *Corrected* RIS Model Proposed Here[a]

	$\pi - \theta''$				
$\pi - \theta'$	108°	109°	110°	111°	112°
122°	6.08	6.29	6.51	6.74	6.98
124°	6.17	6.39	6.61	6.84	7.08
126°	6.25	6.47	6.70	6.94	7.18
128°	6.33	6.55	6.78	7.03	7.28
130°	6.40	6.63	6.87	7.11	7.37

[a] $\xi = 0.007$; $\{\varphi\} = \{+25°, -25°, +120°, -120°\}$.

parameters being kept unchanged, quite unacceptable values for C. Table I shows the results of some such calculations, where the only statistical weight parameter in the model, ξ, was set to 0.007, the value deemed most probable at a temperature of 300 K; other values for ξ in the range $0 < \xi \leq 0.1$ (which spans all possible values[1]) are not significantly different from those given in Table I. If one computes the molecular scattering intensities for X-ray and neutron radiation, with the methods from ref 2, from this erroneous RIS model *without* inadvertently switching the two skeletal bond angles, one obtains scattering patterns significantly different from those observed experimentally.[2,3] Obviously, the RIS model given in ref 1 is in error, and the same mistake has been made, independently, in ref 1 and ref 2 and 3. (The calculations reported in ref 2 and 3 have been repeated by us in order to be certain of this unusual double mistake.)

Closer inspection of all results in ref 1 point, however, to the fact that small changes in the torsional angles associated with the rotational isomeric states, still in accord with the molecular mechanics computations reported in ref 1, are sufficient to bring calculated characteristic ratios to agreement with experiments. Results of computations, identical with those reported in Table I except for the set of torsion angles chosen, are shown in Table II. Hence, we propose here a revision of the four-state RIS model of ref 1:

$$\pi - \theta' = 124°$$

$$\pi - \theta'' = 110°$$

$$\{\varphi\} = \{+25°, -25°, +120°, -120°\}$$

together with the unchanged statistical weight matrices

$$\mathbf{U}' = \begin{bmatrix} 0 & 0 & 1 & \xi \\ 0 & 0 & \xi & 1 \\ 1 & \xi & 0 & 0 \\ \xi & 1 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}'' = \begin{bmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \end{bmatrix}$$

where $\xi = 1.0 \exp(-1500/T)$, with T in units of kelvin. The limiting characteristic ratio at 300 K is then 6.6, in agreement with experiment.

When this new version of the four-state RIS model is used to compute scattering intensities, one obtains curves *indistinguishable* (within the uncertainty inherent to the Monte Carlo simulations) from the ones published by Hayashi, Flory, and Wignall[2,3] and hence in near perfect agreement with experiment.

Registry No. PIB, 9003-27-4.

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Structure and Related Properties of Solution-Cast Perfluorosulfonated Ionomer Films

Methods for obtaining solutions of high equivalent weight Nafion perfluorosulfonated ionomers (PFSI) have been reported during the past few years.[1-3] Dissolution at 250 °C under pressure of the as-received PFSI film in a 50/50 mixture of water and lower aliphatic alcohols such as ethanol is the best procedure for obtaining clear homogeneous colorless solutions.[1,2] It is also of interest to prepare solution-cast films in order to repair pin holes in PFSI chlor-alkali membranes[1,4] or for the coating of modified electrodes.[5] However, the cast film is poor, brittle, and cracked and dissolves readily at room temperature in many polar solvents, especially in water. A first answer to that problem has been given by Grot et al.[1] The procedure consists of adding triethyl phosphate (TEP), dimethyl sulfoxide (Me_2SO), or 2-ethoxyethanol (2EE). The room-temperature evaporation of the mixture then gives rise to a clear uncracked film with good mechanical properties after heating to 120 °C.[1] Quite recently Moore et al.[6] indicated that other polar solvents such as *N*,*N*-dimethylformamide (DMF) and ethylene glycol (EG) can be added to the PFSI solution in order to get good insoluble reconstructed films. Water and alcohol are first removed by evaporation at 80 °C and then the high-boiling solvent is removed by vacuum heating around 20 °C below its boiling point. Grot et al.[1] first suggested that differences observed between reconstructed films, without additive, evaporated at room temperature, and as-received PFSI membranes could arise from the micellar structure of the PFSI solution. In addition Moore et al.[6] assessed morphological differences between films reconstructed at room temperature without additive and as-received membranes as well as films reconstructed at high temperature with additive. In fact, very little is known about reconstructed Nafion membranes and even less about their structure. In this communication, we outline the differences in the properties of membranes reconstructed under various experimental conditions. These differences in

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Table I

Swelling Rates (%) of As-Received and Reconstructed PFSI Membranes in Several Polar Solvents with 2EE (Sample 1) and NMF (Sample 2) as Additional Solvents[a]

	Li$^+$ Nafion 1100						
	as-received membrane			sample 1		sample 2	
swelling solvent	direction 1	direction 2	thickness	length	thickness	length	thickness
water	10	13	13	12.5	13	10	11
ethanol	28	43	51	46	52	42	44
ethanol/water (50/50)	27	42	39	44	44	43	43
NMF	36	51	55	52	55	54	55
2EE	22	35	37	29	36	32	41
TEP	33	44	69	43	67	47	64
Me$_2$SO	26	35	35	35	31	35	42
DMF	33	46	52	51	47	54	50

[a] Direction 1 and 2 refer respectively to parallel and perpendicular laminating directions.

properties will be correlated with the structure analyzed by WAXS (wide-angle X-ray scattering) and SAXS (small-angle X-ray scattering).

The as-received Nafion 117 H$^+$ membranes (E.I. duPont de Nemours, Inc.) or the exchanged membrane (Li$^+$ or Na$^+$) is dissolved following the above-mentioned procedure.[1,2] A solution containing between 5 and 10% (w/w) PFSI in a mixture of water, ethanol, and ether is obtained. Then a polar solvent with a boiling point above 120 °C and more generally above 150 °C is added. The quantity of additional solvent depends upon both its volatility and the thickness desired for the reconstructed film. For instance, less TEP (Θ_B = 215 °C) is needed compared to 2EE (Θ_B = 135 °C) and less solvent for a thick film (a thickness equivalent to that of the as-received film, i.e., 180 μm) rather than for a thin film ($\sim$50 μm). The minimum weight of additional solvent required to obtain uncracked films has to be equal to that of the dried polymer (100% (w/w)). In the present study modified solutions have been prepared with 200% additive. The solution is then allowed to slowly evaporate at low temperature, i.e., between room temperature and 80 °C. A clear, uncracked, but brittle and soluble film is obtained. It immediately dissolves when soaked in ethanol and disintegrates into small pieces that progressively dissolve when in contact with water. This behavior is observed to varying degrees with numerous polar solvents. The reconstructed membrane is heated in air or under vacuum at temperatures higher than 80 °C, 250 °C being the practical upper limit; 200 °C is an optimum temperature to obtain a good film that is resistant to water and polar solvents to the same degree as the as-received film. However, the properties and behavior of the reconstructed film are strongly dependent upon the experimental procedure, i.e., upon the counterions of the PFSI membrane, the presence of additional polar solvents, and the thermal history.

The as-received H$^+$ Nafion membrane is known to be a superacid,[7] an especially active catalyst for numerous organic reactions such as the dehydration of aliphatic alcohols observed during the dissolution process. For example when 2EE, TEP, or propylene carbonate (PC) is added to the solution, the thermal treatment of the reconstructed film above 80 °C gives rise to an almost irreversible blackish color. Soaking in boiling concentrated nitric acid, a procedure that usually restores the original colorless appearance to aged brownish as-received H$^+$ Nafion membranes, is here inefficient. This effect cannot be totally avoided but is significantly reduced when the reconstructed film is either pumped prior to heating or vacuum heated. This observation explains why it is preferable to carry out dissolution on exchanged membranes, although it has been shown that this discoloration has no influence on structural properties. However, large monovalent cations such as K$^+$, divalent cations such as Cu^{2+}, or large alkylammonium cations in solution-cast PFSI cause it to crack into small pieces when dried. It is evident that Li$^+$ and Na$^+$ are much preferred for reconstructing good, clear films. The exchange capacities of the reconstructed membranes are unchanged compared to the as-received membranes. They can be completely reexchanged exactly like the as-received membranes.

As-received membranes and reconstructed PFSI Li$^+$ films have been swollen in various polar solvents. Small rectangular samples (1 cm × 0.7 cm, 180 μm thick) are first dried at 110 °C for at least 24 h. The two planar dimensions along parallel and perpendicular laminating directions are measured to $\pm$10 μm using a vernier eyepiece microscope, and the thickness is measured to $\pm$1 μm with a micrometer. Samples are then soaked in the solvent at room temperature for 24 h until equilibrium is attained. Results are given in Table I. One can observe less swelling of the native membrane along the laminating direction (direction 1) indicated by the manufacturer. Lamination can induce orientation of the polymeric chains, explaining this anisotropy in swelling. This phenomenon disappears in reconstructed membranes except with TEP, which leads to an important unexplained swelling along the thickness of the membranes.

Permselectivity of reconstructed membranes toward Na$^+$ vs. Cl$^-$ has been found to be identical with that of the starting membranes. Large circular reconstructed membranes (120 mm in diameter) have been designed in order to study their behavior in chlor-alkali test cells at 85 °C. Current density through the membranes was 30 A/dm^2 with a 20% (w/w) soda concentration. As-received and reconstructed membranes behave similarly: a 1-week experiment has given no evidence for chemical degradation of the reconstructed membrane and led to the same soda yield.

The WAXS structure of as-received Nafion membranes has been extensively studied.[8,9] The diffraction pattern consists mainly of a large amorphous halo, on which is superimposed a Bragg peak (indexed as the 100 reflexion of the hexagonal structure), the intensity of which is reduced as the equivalent weight of the PFSI decreases. This peak is hardly detectable with the as-received membrane (Figure 1a). One can observe that for the membrane reconstructed at room temperature (Figure 1b) and the membrane heated at high temperature (Figure 1c) the Bragg peak is broad and intimately mixed with the halo in the first case and is sharper and distinct from the halo in the other case. The morphology of PFSI membranes reconstructed at room or high temperature is thus different from that of the as-received membrane. The modification of the diffraction pattern of the reconstructed membrane on heating at different temperatures is shown in Figure

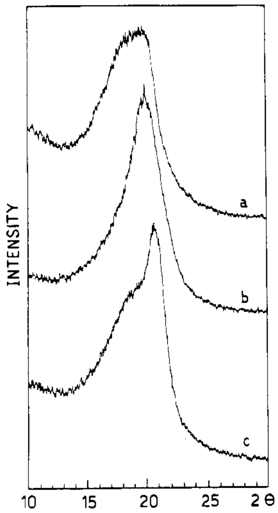

Figure 1. Wide-angle diffraction pattern ($\lambda = 1.789$ Å) of Li^+ Nafion 1100 as-received membrane (a); reconstructed membranes with NMF as additional solvent without annealing (b); and after a 3-h annealing at 200 °C (c).

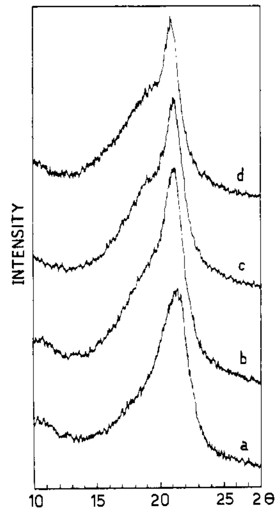

Figure 2. Wide-angle diffraction pattern ($\lambda = 1.789$ Å) of H^+ Nafion 1100 reconstructed membranes from solutions with 2EE heated for 3 h at (a) 80 °C, (b) 150 °C, (c) 200 °C, and (d) 250 °C.

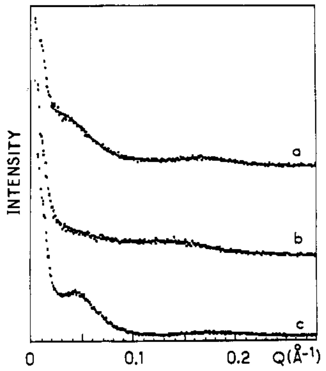

Figure 3. Small-angle X-ray scattering pattern corresponding to the samples of Figure 1 ($Q = 4\pi \sin \theta/\lambda$ with $\lambda = 1.549$ Å).

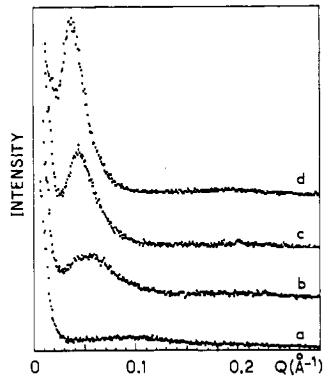

Figure 4. Small-angle X-ray scattering pattern corresponding to the samples of Figure 2 ($\lambda = 1.549$ Å).

2. By comparison of Figure 2a, a membrane reconstructed at low temperature that dissolves in polar solvents, to Figure 2d, an insoluble membrane, one can note that an increase of the annealing temperature results in a sharpening of the Bragg peak. The annealing induces strong modifications of the diffraction pattern during the first hour. Longer heating periods, typically over 3 h, have only very little effect, particularly above 150 °C, but only correspond to shorter periods at higher temperatures. However, especially for solvents of high boiling point that have a very low vapor pressure, such as TEP, time and/or temperature must be appropriately increased for optimization.

Small-angle scattering with both X-ray and neutrons performed on PFSI membranes reveals the existence of two maxima.[9,10] The maximum at very low Q values ($Q \sim 0.05$ Å^{-1} with $Q = 4\pi \sin \theta/\lambda$) arises from the long identity period of lamellar crystallites. This peak is encountered in semicrystalline polymers such as polyethylene[11] or PTFE.[12] The second maximum at higher Q value ($Q \sim 0.15$ Å^{-1}) appears only in charged polymers and is attributed to charge clustering, the so-called "ionomer peak".[9,10] SAXS experiments have been performed with synchrotron radiation (DCI, Lure, Orsay, France) on the same samples scanned by WAXS. The first maximum is just a pronounced shoulder on the SAXS pattern of the as-received membrane (Figure 3a). This maximum disappears in the membrane reconstructed at the room temperature (Figure 3b) but reappears as a well-defined peak after annealing (Figure 3c). In the three samples the second maximum is very weak because of the lack of electronic contrast between poorly solvated ionic clusters and the perfluorocarbon matrix. Studies on this second maximum are now in progress. The SAXS pattern in Figure 3 thus confirms the structural differences between the three samples. In addition, Figure 4 reveals a particularly strong effect of annealing on the reconstructed membranes. It is clear that crystalline order develops with temperature, better defined as the peak sharpens, with a longer repetition distance as the peak shifts toward smaller Q values.

From the combination of information from WAXS and SAXS experiments, a tentative structural description of reconstructed membranes can be proposed. Before thermal treatment reconstructed PFSI membranes exhibit large fractions of either poorly crystallized material or material with small-size crystallites, or both, together with amorphous fractions. Almost no long-range order exists between these lamellar crystallites, which are randomly distributed over the amorphous phase. As the sample is annealed, several phenomena simultaneously occur: the size of the lamellar crystallites increases, their internal order probably improves, and a long-range order develops. Such reorganization is favored by both the annealing temperature and the presence of residual additional solvent that probably acts as a plasticizer. This high-temperature evolution thus leads to a reconstructed membrane that exhibits at room temperature a more well-defined crystallinity inside larger crystallites with a long-range order characterized by a repetition distance of the order of 200 Å, a distance that compares well with polyethylene.[11] Changes in solubility and mechanical properties are undoubtly related to this structural modification. The membrane reconstructed at room temperature may be considered to be "a compact nearly dried solution", meaning that only small rearrangements and small reentanglements can occur, not enough to prevent room-temperature dissolution in numerous polar solvents. On the other hand, annealing in the presence of residual additional solvent leads to large structural modifications with entanglements and cross-links preventing dissolution. Although they exhibit similar macroscopic behavior, for instance their insolubility in polar solvents, there are marked structural differences between the as-received Nafion membrane and the membrane reconstructed at high temperature.

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

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Nuclear Magnetic Resonance of Xenon Absorbed in Solid Polymers: A Probe of the Amorphous State

The characterization of amorphous regions within solid polymers is important to the understanding of polymer structure and properties. However, there are but a few physical techniques that can be applied to amorphous structure on a microscopic scale. Here we report a technique that uses a small probe molecule contained within the amorphous solid.

The xenon atom is well suited for use as a probe of liquids and noncrystalline solids. It is a small, nonpolar atom, and it is chemically inert under ordinary conditions.

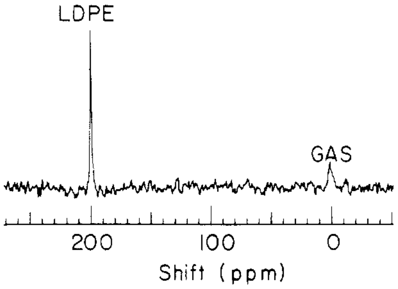

Figure 1. ^{129}Xe spectrum at 24.79 MHz from 8 atm of xenon gas in contact with granulated low-density polyethylene.

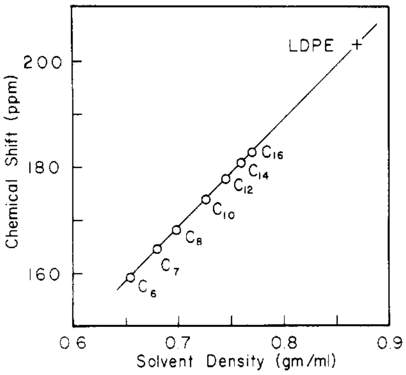

Figure 2. Chemical shifts of ^{129}Xe dissolved in liquid *n*-alkanes compared with the shift in low-density polyethylene. The shift reference is xenon gas extrapolated to zero pressure.

It causes minimal disruption of the structure being probed. It has been shown that the xenon NMR spectrum is unusually sensitive to the nature of its immediate environment.[1] Xenon NMR has been used as a probe of simple liquids,[2-4] zeolite surfaces,[5] clathrates,[6] mordenites,[7] and proteins.[8] The NMR spectrum of ^{129}Xe absorbed in poly(vinyl chloride) has been observed.[9] Here we report its use as a probe of amorphous and semicrystalline polymers.

Linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) were obtained from the laboratory of R. S. Stein. They are characterized as follows: LDPE, $M_w = 286000$, $M_w/M_n = 16$, density of 0.920 gm/cm^3; LLDPE, $M_w = 114000$, $M_w/M_n = 4.5$, density of 0.918 gm/cm^3. Secondary standard poly(ethyl methacrylate) was obtained from Polysciences, Inc. It is characterized by $M_w = 340000$ and $M_w/M_n = 2.7$. The NMR samples were prepared by placing 1 or 2 g of the granulated polymer in a 10-mm NMR tube that had a wall thickness of 1 mm. The tube was attached to a vacuum line, and the sample was thoroughly evacuated. Liquid nitrogen was used to condense in sufficient xenon to produce a gas pressure of ca. 8 atm in the tube at room temperature, and the tube was sealed off under running vacuum.

NMR spectra were obtained on two instruments, a JEOL FX-90Q located at Mount Holyoke College and a Varian XL-300 at the University of Massachusetts NMR Center. Center-band frequencies for the nuclide ^{129}Xe were 24.79 and 82.974 MHz, respectively. Despite the high xenon concentration, acquisition times of 1 h or more are required, because the lines are broad and the relaxation times are long. The higher field of the XL-300 gave no great advantage in this regard, since the lines are broader and the relaxation times longer at the high field.

The ^{129}Xe spectrum of xenon in LDPE is shown in Figure 1. The signal labeled "gas" arises from gaseous xenon which fills the spaces between the polymer granules. This peak has essentially the same chemical shift as pure

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