^{19}F NMR Spectroscopy of Acid Nafion Membranes and Solutions

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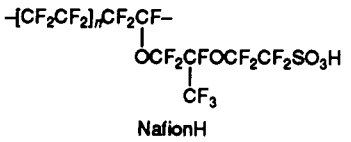
ABSTRACT: We present an ^{19}F NMR study of acid Nafion solutions and corresponding membranes swollen by water, formamide, methanol, and ethanol. The main objective of this study is to assess the mobility of the perfluorinated chains in the solutions and to provide structural details that complement data obtained from small-angle scattering experiments. All spectra consist of sharp peaks superimposed on a broad component. The sharp signals are assigned to fluorine nuclei with different chemical shifts, in the perfluorinated backbone and in the pendant chains; the signals are identified by comparison with the chemical shifts measured for a short-chain perfluorinated surfactant. In ethanol solutions the narrow component is dominant, suggesting a nearly isotropic motion of the polymer molecule (backbone *and* pendant chains), with $\tau_c \leq 10^{-4}$ s. The spectra of the membranes swollen by water, formamide, methanol, and ethanol are intermediate between the spectra of the dry membrane and of the solutions. The spectra of the solutions and of the swollen membranes at ambient temperature, as well as the spectra of the dry membranes and of Teflon as a function of temperature, have been simulated by use of hyper-Lorentzian line shapes, by varying one parameter only, the component line width. An Arrhenius plot of the line width in dry Nafion vs temperature allows determination of the activation energy for the motion. Above 385 K the activation energies are 65.1 kJ/mol for the ionomer and 13.1 kJ/mol for Teflon. The simulations suggest a different approach of modeling complex spectra, as an alternative to superposition of a component moving isotropically in a fluid solution, and static chains behaving as a solid phase.

I. Introduction and Motivation

The ionomers known as Nafion are produced by Du Pont and consist of a perfluorinated polymer backbone and ether side chains terminated with sulfonic groups SO_3^-.[1] The formula for the acid form (NafionH) is



NafionH

For an equivalent weight of 1100, n in the formula above is 6.5, which means that the repeat unit of the backbone has 14 CF_2 groups and 1 CF group. This is the Nafion 117 membrane used in all experiments.

The technological importance of Nafion as a separation membrane in electrochemical processes has prompted extensive studies, by spectroscopic and scattering methods.[2] It is generally accepted that at low solvent content the ionomer separates into polar and nonpolar domains, forming a reverse micelle structure consisting of solvent "pools" where the ionic charges are clustered, surrounded by the polymer backbone.[1] The size of the pools has been determined from small-angle neutron and X-ray scattering (SANS and SAXS, respectively), and is about 40–80 Å, depending on the solvent, the degree of neutralization of the sulfonic groups, and the nature of the counterions. The local structure of the counterions has been deduced in Nafion swollen in various solvents in extended X-ray absorption fine structure (EXAFS),[3,4] infrared,[5] Raman,[6] and Mössbauer spectroscopies,[7] and by electron spin resonance (ESR) studies of the membranes neutralized by paramagnetic cations.[8,9] No model has yet been proposed for membranes with high solvent content.

Recently a procedure for solubilization of the Nafion membrane has been proposed[10,11] and has been followed by studies using electron microscopy and small-angle scattering methods. Details on the structure of the ionomer in solutions are only now beginning to emerge, based on the study of the solutions using SANS and SAXS.[12–14] Structural parameters have been obtained in small-angle scattering studies from an analysis of the peak position as a function of polymer concentration in various solvents. Best agreement with all experimental results has been obtained for the model of parallel rods of radius 18–30 Å, depending on the solvent, arranged in a planar hexagonal array.[15] It has been suggested that the rods consist of a central core of perfluorinated backbone, while the ionic charges are on the outer surface, in contact with the polar solvent.[14] The radius of the rods in a given solvent seems to depend on the length of the pendant chain of the ionomer; recent, still unpublished, results on carboxylated ionomers containing a considerably shorter side chain seem to substantiate this hypothesis.[16]

The study of Nafion solutions by ^{19}F NMR was initiated with the general objective of obtaining information on the mobility of the perfluorinated backbone and of the side chains, as a function of ionomer structure, polarity and structure of the solvent, and nature of the counterions used for partial or full neutralization of the membrane.

^{19}FNMR spectroscopy is expected to be a powerful method for the study of Nafion solutions. The ^{19}F chemical shifts cover a broad range (~1000 ppm) and are dominated by paramagnetic shifts, which depend on the excited electronic states.[17–19] The chemical shifts are sensitive to the solvent, and this is an advantage for the study of Nafion solutions in various solvents and solvent mixtures. In addition, the coupling between nonequivalent geminal ^{19}F nuclei is large, of the order of several hundred hertz. Because of these advantages, ^{19}F NMR has become an important method for the study of the stereochemistry and dynamics of partially fluorinated homopolymers, copolymers, and terpolymers.[20–22]

Solid-state-type NMR studies of Nafion have been reported, and relaxation times (T_1, T_2, and $T_{1\rho}$) have been measured. We will come back to these studies in the Discussion.

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In this report we present initial results and conclusions obtained from ^{19}F NMR studies of NafionH membranes and solutions. To the best of our knowledge, no other NMR studies of Nafion solutions have been published.

II. Experimental Section

The Nafion 117 membrane, as the lithium salt, was solubilized in a 50/50 by volume water/ethanol mixture at 523 K in an autoclave, as previously described.[12-14] A soluble Nafion powder was then obtained by evaporation of the solvent at ~350 K for 1 h. The soluble acid form of Nafion was prepared by stirring the lithium salt with 2 M nitric acid at ambient temperature for 5 h. Solutions of NafionH (20% by weight) in the various solvents were then prepared.

^{19}F chemical shifts were measured with respect to $CFCl_3$, which is the most commonly used standard in ^{19}F NMR spectroscopy. A capillary containing the standard was inserted in all the samples measured. The Bruker CXP90 spectrometer was used, at a frequency of 84.8 MHz for ^{19}F nuclei. For these experiments the Teflon in the probe was replaced by a polysulfone plastic. This spectrometer is appropriate for the study of the Nafion solutions, because it is a high-power instrument and therefore can detect the broad lines from "rigid" nuclei in solids; moreover, its resolution is good enough for the detection of "mobile" nuclei. In polymer solutions the signals are broader than for small molecules because of the slower rate of rotational diffusion of the polymers, and also because the rotation of side chains attached to fixed ends can be anisotropic. Therefore a high-power NMR spectrometer is preferable for the type of studies presented here. Typical spectra were measured with a pulse length of 1 μs, a repetition rate of 2 s, a sweep width of 125 kHz, and 4K data points; the line broadening parameter used in the Fourier transformation was 3 Hz.

The Teflon polymer studied had an index of crystallinity of ~60%, as measured by wide-angle X-ray diffraction.

III. Results

1. ^{19}F Chemical Shifts in NafionH. The short-chain perfluorinated surfactant given below was used to identify the origin of the chemical shifts in the NafionH solutions.[23]

NMR spectra of the surfactant and of NafionH in form-

$$CF_3(OCF_2C(CF_3)F)_2OCF_2COONH_4$$
perfluorinated surfactant

amide and ethanol solutions are presented in Figure 1. The spectrum of the surfactant is typical of a small molecule in the liquid phase, with well-resolved signals corresponding to fluorine nuclei with different chemical shifts. The spectra of the Nafion solutions consist of similar signals and, in addition, a very broad component; the intensity of this broader component is less important in ethanol, compared to formamide.

The chemical shifts, in ppm with respect to $CFCl_3$, and the assignments are also indicated in Figure 1.[23] For the surfactant, the strong peak at -80.9 ppm is most likely due to the *pendant* CF_3 group;[24] signals at -75.9 and -86.0 ppm are assigned to the OCF_2 groups near the carboxylic group and in the repeat unit, respectively. The corresponding signal in the ionomer solution is broader and appears at -80 ppm. The weak signal at about -146 ppm is due to ^{19}F nuclei in the CF groups, as suggested previously.[23] The equally weak signal near -139 ppm in the ionomer solutions is tentatively assigned to the ^{19}F nuclei in the CF_2 group near the sulfonic group, by comparison with a similarly situated CF_2 group near a COOH group, which has a chemical shift of -138 ppm relative to $CFCl_3$.[25,26]

By comparison with the spectrum given in Figure 1a, it is clear that the strong signal near -120 ppm in the NafionH solutions, Figure 1b and 1c, is due to the backbone ^{19}F nuclei; this assignment is supported by the value of the chemical shift,[18] and by the absence of this signal in the perfluorinated surfactant. This is an important conclusion, because it indicates that the mobility of the backbone is similar to that of the pendant chain: The line widths of the signals at -120 ppm are about the same as those from the side-chain nuclei, which are represented by the strong signal near -80 ppm.

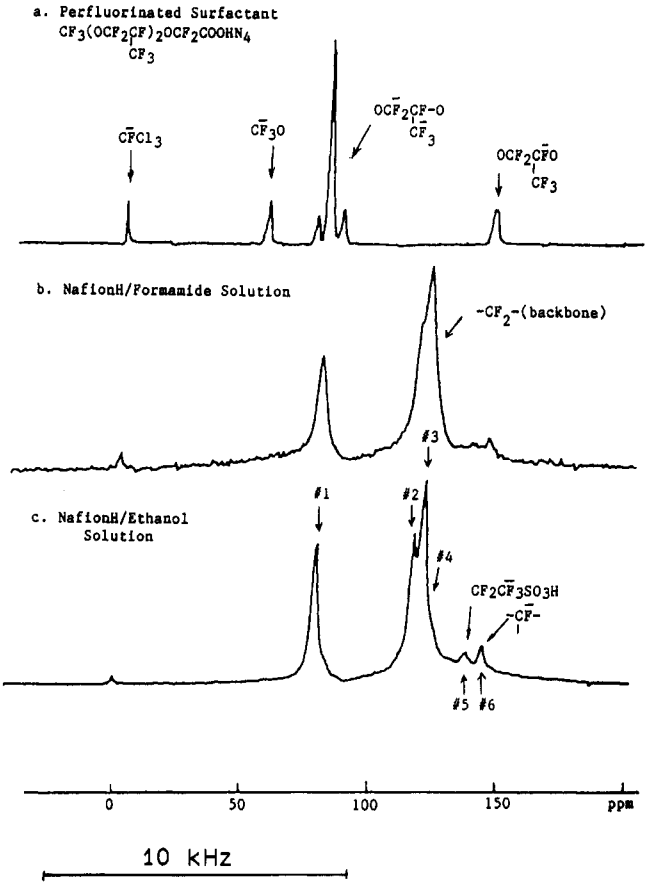

Figure 1. ^{19}F NMR spectra at 298 K and ν = 84.8 MHz of a perfluorinated surfactant (a) and of a NafionH solution in formamide (b) and in ethanol (c). Chemical shifts are indicated with respect to $CFCl_3$ as standard. The assignments are explained in the text. In (c) the six signals considered in the simulations are indicated by arrows.

The structure of the main peak at -120 ppm may be due to different backbone nuclei, because the ^{19}F chemical shifts are sensitive to the details of the chain structure. High-resolution ^{19}F NMR spectra of fluorinated polymers have been analyzed at the level of pentads, within a range of typically 5-10 ppm.[20-22] For a perfluorinated chain $-(CF_2)-$ only one resonance is expected. For a chain containing 1 pendant group for each 14 CF_2 groups, we expect that on the level of pentads only the 6 central CF_2 groups will have the same chemical shift, and 8 CF_2 groups, on both sides of the central 6 CF_2 groups, will have slightly different resonances.

The intensity of the signal at -120 ppm in Figure 1c is 69.4% of the total spectral intensity; this value can be compared with a calculated intensity of 71.8% (based on 28 fluorine nuclei in the backbone out of a total of 39 fluorine nuclei in the repeat unit) and means complete dissolution of the polymer in ethanol. This conclusion is supported by experiments that indicate the same total intensities in NMR spectra of the surfactant and the NafionH solutions at the same concentrations.

The relative intensity of the signal at -80 ppm can provide additional support for the above conclusion. This signal is due to the ^{19}F nuclei near the ether links and to the CF_3 group in the side chain, seven nuclei per repeating unit, or 18.0% of the total intensity. The measured value

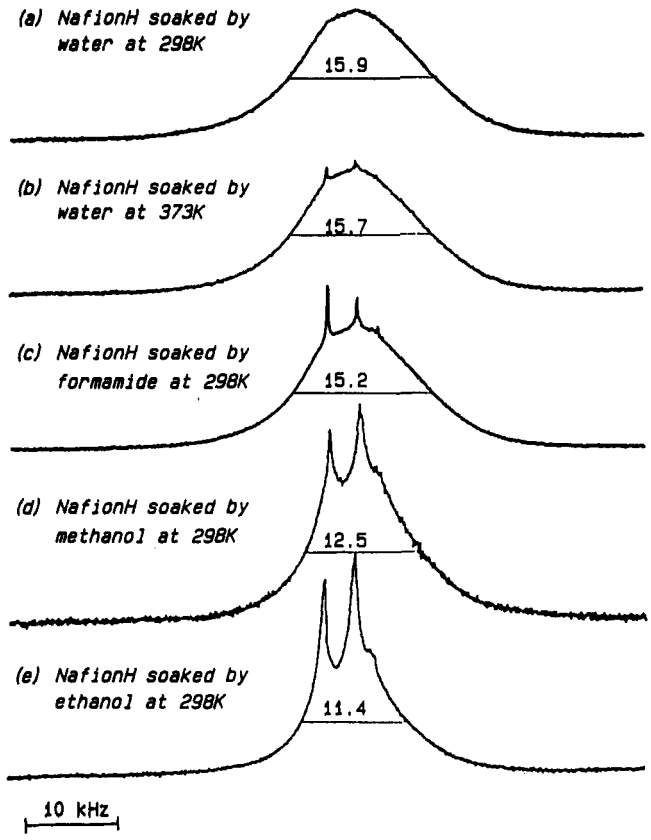

Figure 2. ¹⁹F NMR spectra at 298 K and ν = 84.8 MHz of NafionH membranes soaked by (a) water at 298 K, (b) water at 373 K, (c) formamide at 298 K, (d) methanol at 298 K, and (e) ethanol at 298 K. The width at half-height of the broad component (in kilohertz) is indicated for each spectrum.

is 19.2%. The agreement with the calculated value of 18.0% is satisfactory.

The line widths in NafionH solutions in formamide are broader than in ethanol and there is a hint of a broad component in addition to the resolved signals.

2. Bulk NafionH Membranes. a. Effect of Solvent. Separate ¹⁹F NMR signals from the backbone and pendant nuclei are observed also in Nafion membranes that have been soaked with water (at 298 and 373 K), formamide, methanol, and ethanol, as seen in Figure 2. The narrow signals are similar to those given in Figure 1, but the broad component is more important; an extreme case is the water-swollen membrane, where the narrow lines are barely visible. In each spectrum in Figure 2 the intensity ratio of the two major narrow lines, from backbone and pendant ¹⁹F nuclei, is similar to that detected in the solutions, as seen for instance in Figure 2e. This result suggests that the signals arise from whole chains, and not from portions of chains, and is contrary to what would be expected for the three-phase model of ionomers, which assumes penetration of the pendant chains into the solvent pools in the membranes swollen by polar solvents.[27]

b. Effect of Temperature. ¹⁹F NMR spectra of dry Nafion membranes (dried to constant weight in vacuum[33]) were measured in the temperature range 298–459 K; representative spectra are given in Figure 3. The separate signals from the pendant chain and the backbone gradually appear and their widths decrease with increasing temperature. In parallel, the broad signal becomes less intense; the width of this signal can be estimated by taking the top of the broad component at the position shown in Figure 3 as the maximum intensity of the broad component and measuring the full width at half-maximum intensity. The widths obtained in this way are 27.6 kHz at 298 K, 20.4 kHz at 339 K, 12.4 kHz at 400 K, 9.7 kHz at 415 K, and 9.0 kHz at 445 K. Qualitatively, these values indicate a continuous change in the spectra with temperature, and not a simple superposition of two components with constant widths.

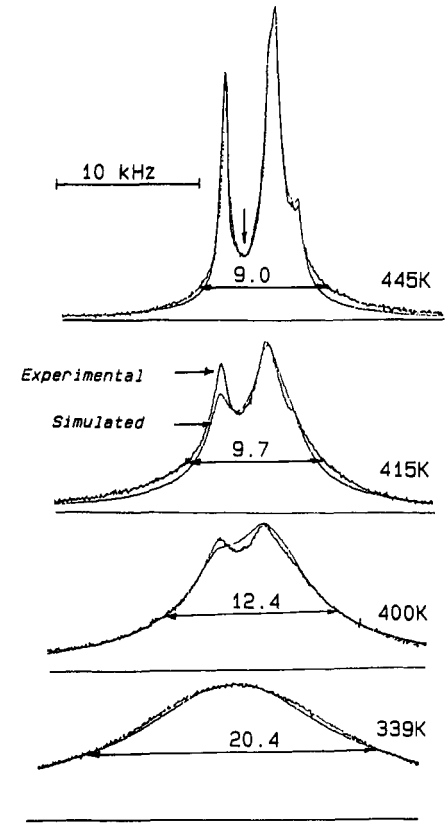

Figure 3. ¹⁹F NMR spectra at ν = 84.8 MHz of dry NafionH as a function of temperature. The simulated spectra are superimposed on the experimental results. The width at half-height of the broad component (in kilohertz) is indicated for each spectrum.

Increasing the solvent content of the membrane has qualitatively the same effect as increasing the temperature (as seen in Figure 3) and is most likely due to increased polymer mobility.

¹⁹F NMR spectra of Teflon as a function of temperature in the range 298–463 K are shown in Figure 4. The narrow signal that develops with increasing temperature corresponds to the position of the signal from the CF_2 groups of the backbone, at a chemical shift of about −120 ppm.

IV. Discussion

Nafion bulk membranes swollen by water have been studied previously by ¹H and ¹⁹F NMR, and the relaxation times T_1, T_2, and $T_{1\rho}$ for both nuclei have been deduced as a function of temperature, in the range 150–430 K.[28-30] No spectra were presented in these papers.

The line width and spin–lattice relaxation times T_1 of water protons in Nafion have been studied as a function of temperature and water content of the membranes and have been correlated with results obtained by other techniques.[31,32] A method for the determination of the water content in Nafion has been developed, based on the intensity of proton signals.[33] This method allows characterization of the samples for different drying conditions.

NMR line widths of polymeric systems have often been interpreted in terms of a superposition of broad and narrow components, as orginally suggested by Wilson and Pake;[34] this approach is sometimes applied to the case of two phases, for instance amorphous and crystalline components.[35]

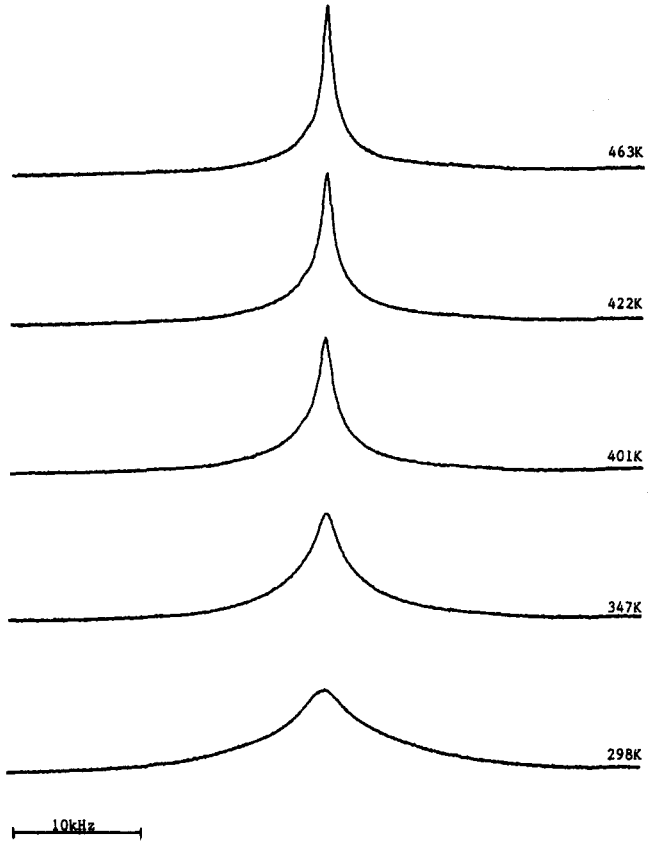

Figure 4. ^{19}F NMR spectra at ν = 84.8 MHz of Teflon as a function of temperature.

Deconvolution of the ^{19}F NMR spectra from Teflon into amorphous and crystalline fractions has been proposed, using a multiple-pulse sequence.[36] This deconvolution is most effective above the glass transition temperature of ~400 K, because the signal from the chemical shift tensor of the amorphous fraction is averaged. In general, however, the deconvolution method is not easy to apply, as amply demonstrated in a recent study of Nylon using ^{13}C and ^{15}N magic-angle spinning.[37]

The problems associated with the deconvolution of the NMR signal into two components are expected to be much more severe in Nafion, compared with pure Teflon, because of the additional presence of the pendant chain and the polar end groups. Some of the results presented here suggest that such a deconvolution is not only very difficult to do, but would be artificial and arbitrary in this system. The most compelling argument *against* deconvolution of the spectra presented in Figures 1–4 into *two* components is the gradual change of the spectra with temperature, and with the various solvents; this is true for the bulk membranes (Figures 2 and 3) and for the solutions (Figure 1).

We attempted to simulate the spectra at all temperatures and in the solvents in the simplest way, by the smallest number of parameters. The simulation procedure started with the spectrum of the Nafion solution in ethanol, which was considered as consisting of six signals, as shown by the arrows in Figure 1c, with half-widths at half-intensity δ_i and the following line shape.

$$F(\nu_i) = (I_i/\delta_i)/(1 + ((\nu_i - \nu_{oi})/\delta_i)^{\alpha}) \quad (1)$$

For α = 2, the line shape in eq 1 is Lorentzian; for $\alpha <$ 2 the wings are more important and the line shape is called hyper-Lorentzian.

The line widths and the relative intensities of the six lines were varied in order to obtain the best visual fit with the experimental spectra. The intensities obtained for the best fit were within ±10% of the intensities calculated on the basis of the assignment deduced from Figure 1. In making this comparison the sum of the signals 2, 3, and 4 was compared with the intensity expected from the backbone nuclei.

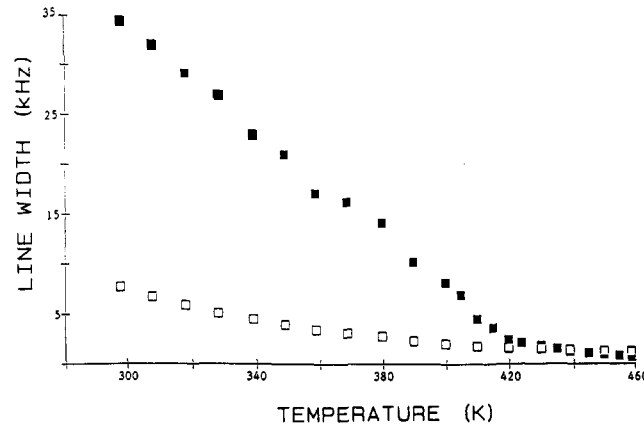

Figure 5. Full width at half-height of signal 3 (in Figure 1) used for spectra simulations, as a function of temperature for dry NafionH (■) and for Teflon (□).

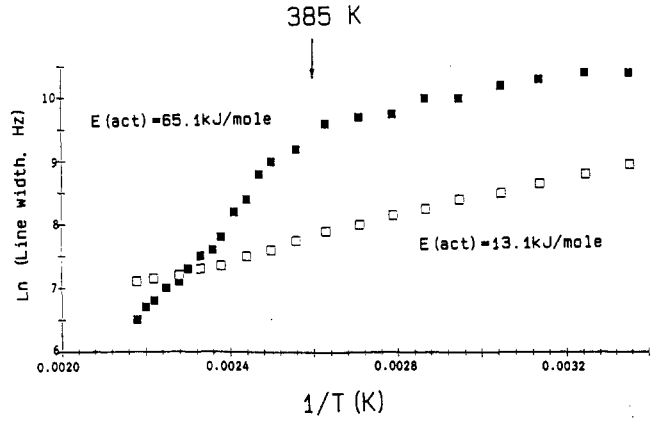

Figure 6. Arrhenius plot of the line widths used for spectra simulations, for dry NafionH (■) and for Teflon (□).

The next step was an attempt to stimulate all other spectra by keeping the same relative intensities and modifying only the line widths, i.e., replacing δ_i with $B\delta_i$. It was however impossible to simulate the experimental spectra with Lorentzian line shapes. After numerous simulations with various line shapes, we opted for a hyper-Lorentzian expression for the line shapes with α = 1.5. Each simulated spectrum was characterized by the constant B.

All spectra were simulated in this way, including those for Teflon (Figure 4). Typical fits are shown in Figure 3, superimposed on the experimental spectra. Considering that all spectra were simulated by varying one parameter, the agreement is considered satisfactory.

The variation of the *full* line width of signal 3 (Figure 1) as a function of temperature for dry NafionH and for Teflon are given in Figure 5; the same data are plotted as an Arrhenius plot in Figure 6. The effect of the pendant chains on the chain mobility is evident in both figures. For NafionH a clear break between two motional regimes is detected around 385 K; this break is similar to that detected in DSC studies of acid Nafion[38] and is not detected in Teflon. For the low-temperature regime the activation energy for the motion is 13.1 kJ/mol in both systems, while it is 65.1 kJ/mol for NafionH above 385 K. The line widths for NafionH increase significantly, compared to Teflon, below 420 K; at the lowest temperature (298 K) the full line widths, $2B\delta_i$, are 34.5 kHz for the ionomer

and 7.7 kHz for Teflon. We suggest that this is due to the motional constraints introduced by the pendant chains.[30]

From water to ethanol, the solvent uptake of Nafion membranes increases and a *gradual* change can be observed in the NMR spectra (Figure 2). The gradual appearance of the sharper peaks as a function of increasing the temperature or addition of solvent can be viewed as an increase in the mobility of the perfluorinated chain as a whole; no evidence for the preferential solvation of the pendant chains compared to the backbone has been detected. The solvent can be regarded qualitatively as having a plasticizing effect on the chain mobility. It appears that ^{19}F NMR spectroscopy is sensitive to the specific solvent effects. We plan to study this effect more quantitatively in the future, in order to understand the process of Nafion dissolution, and the solvent importance in the structure of the polymer as a membrane and in solution.

Solutions of NafionH in ethanol seem to be true solutions, in the sense that the broad component is hard to detect; this component is clearly visible in the other solvents studied (methanol and formamide). In addition, the line width of the signal at −80 ppm (228 Hz) is similar to that of the bandwidths measured for fluorinated polymers, for instance, in poly(fluoromethylene) solutions in acetone.[20]

V. Conclusions

1. In a solution of NafionH in ethanol, all ^{19}F nuclei are represented by motionally averaged signals, suggesting the formation of a true solution.

2. Increase of the temperature, or gradual addition of ethanol at a constant temperature, has the same qualitative effect on the ^{19}F NMR spectra: Appearance of separate signals from nuclei in the backbone and in the pendant chain, and progressive narrowing of the signals from rigid polymer chains.

3. All spectra obtained can be simulated by considering six types of nuclei with different chemical shifts and fixed relative intensities, by assuming hyper-Lorentzian line shapes, and by changing only the scaling factor.

4. The effect of the pendant chain on the ionomer mobility can be obtained by comparing the line widths for Teflon and for NafionH. The motional activation energies above 385 K are 65.1 kJ/mol for the ionomer and 13.1 kJ/mol for Teflon.

5. The solvent can be qualitatively considered as being a plasticizer, and the effect is gradual, from the dry membrane to the true solution in ethanol.

6. Addition of solvent to the dry Nafion membrane has qualitatively the same effect on the ^{19}F NMR spectrum as the increase in temperature.

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References and Notes

(1) *Perfluorinated Ionomer Membranes*; Eisenberg, A., Yeager, H. D., Eds.; ACS Symposium Series 180; American Chemical Society: Washington DC, 1982.
(2) *Structure and Properties of Ionomers*; Pineri, M., Eisenberg, A., Eds.; NATO ASI Series; Reidel: Dordrecht, The Netherlands, 1987.
(3) Pan, H. K.; Meagher, A.; Pineri, M.; Knapp, G. S.; Cooper, S. L. *J. Chem. Phys.* **1985**, *82*, 1529.
(4) Pan, H. K.; Knapp, G. S.; Cooper, S. L. *Colloid Polym. Sci.* **1984**, *262*, 734.
(5) Mattera, V. D., Jr.; Risen, W. M., Jr. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 67.
(6) Neppel, A.; Butler, I. S.; Eisenberg, A. *Macromolecules* **1979**, *12*, 948.
(7) Boyle, N. G.; Coey, J. M. D.; Meagher, A.; McBrierty, V. J.; Nakano, Y.; MacKnight, W. J. *Macromolecules* **1984**, *17*, 1331.
(8) Pineri, M.; Meyer, C.; Levelut, A. M.; Lambert, M. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 115.
(9) Bednarek, J.; Schlick, S. *J. Am. Chem. Soc.* **1990**, *112*, 5019, and references therein.
(10) Grot, W. G.; Chadds, F. U.S. Patent 0066369, 1982.
(11) Martin, C. R.; Rhoades, T. A.; Ferguson, J. A. *Anal. Chem.* **1982**, *54*, 1639.
(12) Aldebert, P.; Dreyfus, B.; Pineri, M. *Macromolecules* **1986**, *19*, 2651.
(13) Gebel, G.; Aldebert, P.; Pineri, M. *Macromolecules* **1987**, *20*, 1425.
(14) Aldebert, P.; Dreyfus, B.; Gebel, G.; Nakamura, N.; Pineri, M.; Volino, F. *J. Phys. Fr.* **1988**, *49*, 2101.
(15) Gebel, G. Ph.D. Thesis, Université Joseph Fourier, 1989.
(16) Loppinet, B.; Gebel, G.; Pineri, M., to be published.
(17) Mooney, E. F. *Introduction to ^{19}F NMR Spectroscopy*; Heyden & Son: London, 1970.
(18) *Progress in NMR Spectroscopy*; Emsley, J. W., Feeney, J., Sutcliffe, L. H., Eds.; Pergamon: Oxford, U.K., 1971; Vol. 7.
(19) Emsley, J. W.; Phillips, L.; Wray, V. *Fluorine Coupling Constants*; Pergamon: Oxford, U.K., 1977.
(20) Cais, R. E. *Macromolecules* **1980**, *13*, 806.
(21) Tonelli, A. E.; Schilling, F. C.; Cais, R. E. *Macromolecules* **1982**, *15*, 849.
(22) Ishigure, K.; Watanake, S.; Tabata, Y.; Oshima, K. *Macromolecules* **1980**, *13*, 806.
(23) Caporiccio, G.; Burzio, F.; Corniselli, G.; Biancardi, V. *J. Colloid Interface Sci.* **1984**, *48*, 202.
(24) Bonesteel, J. K.; Scherer, K. V., Jr.; Seidel, W. C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 131.
(25) Sheppard, W. A.; Muetterties, E. L. *J. Org. Chem.* **1960**, *25*, 180.
(26) Shielding of fluorine nuclei shifts the resonances to higher magnetic fields compared with $CFCl_3$, resulting in negative chemical shifts. In some reports, for example in ref 24, positive chemical shifts are given, by convention. We prefer to keep the negative sign of the ^{19}F chemical shifts, for clarity of presentation.
(27) Yeager, H. L.; Steck, A. *J. Electrochem. Soc.* **1981**, *128*, 1880.
(28) Boyle, N. G.; Coey, J. M. D.; McBrierty, V. J. *Chem. Phys. Lett.* **1982**, *86*, 16.
(29) Boyle, N. G.; McBrierty, V. J.; Douglass, D. C. *Macromolecules* **1983**, *16*, 75.
(30) Boyle, N. G.; McBrierty, V. J.; Eisenberg, A. *Macromolecules* 1983, *16*, 80.
(31) Duplessix, R.; Escoubes, M.; Rodmacq, B.; Volino, F.; Roche, E.; Eisenberg, A.; Pineri, M. In *Water in Polymers*; Rowland, S. P., Eds.; ACS Symposium Series 127; American Chemical Society: Washington, DC, 1980; Chapter 28, p 487.
(32) Pineri, M.; Volino, F.; Escoubes, M. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2009.
(33) Bunce, N. J.; Sondheimer, S. J.; Fyfe, C. A. *Macromolecules* **1986**, *19*, 333.
(34) Wilson, C. W., III; Pake, G. E. *J. Polymer Sci.* **1953**, *10*, 503.
(35) McCall, D. W.; Douglass, D. C.; Falcone, D. R. *J. Phys. Chem.* **1967**, *71*, 998.
(36) Vega, A. J.; English, A. D. *Macromolecules* **1980**, *13*, 1635.
(37) Hatfield, G. R.; Glans, J. H.; Hammond, W. B. *Macromolecules* **1990**, *23*, 1654.
(38) Kyu, T.; Eisenberg, A. in ref 1, Chapter 6, p 79.

Registry No. Nafion 117, 66796-30-3; Nafion H, 63937-00-8.