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Morphology of dry and swollen perfluorosulfonate ionomer by fluorine-19 MAS, NMR and xenon-129 NMR

G. Meresi, Y. Wang, A. Bandis, P.T. Inglefield*, A.A. Jones, W.-Y. Wen

Carlson School of Chemistry, Clark University, Worcester, MA 01610, USA

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Abstract

At magic angle spinning speeds above 5 kHz, two major fluorine-19 resonances can be resolved in the acid form of the perfluorosulfonate ionomer Nafion (DuPont trademark). The larger signal at −120 ppm versus $CFCl_3$ is assigned to the backbone CF_2 groups and the second signal at −80 ppm is assigned to the OCF_2 and CF_3 groups in the pendant chain. Spin diffusion experiments between these two resonances are performed on dry Nafion, water swollen Nafion and ethanol swollen Nafion. The analysis assumes a morphology comprised of pendant group domains and backbone CF_2 group domains. In dry Nafion, the thickness of the pendant group domain is found to be 3.8 nm with an overall periodicity of about 10 nm. Upon addition of water, on one hand, the pendant group domain increases to 6.5 nm at a level of 20 wt% water while the overall periodicity hardly changes. On the other hand, both overall periodicity and the pendant group domain increase significantly upon the addition of ethanol. At 20 wt% ethanol, the pendant group domain is 11 nm and the overall periodicity is 19 nm. Thus ethanol appears to induce a larger morphological rearrangement, though it is still the pendant group domain that primarily increases in size with increasing ethanol concentration. Analysis of the static fluorine-19 line shapes indicates that ethanol is a selective plasticizer of the pendant group domain. Xenon-129 NMR is used as an alternative probe of morphologically based sorption environments in Nafion. The xenon-129 spectrum of xenon sorbed into Nafion under a pressure of 12 atm shows two resonances corresponding to two sorption environments. The first resonance closer to the signal from free gas has a shift comparable to that of xenon-129 in amorphous poly(tetrafluoroethylene) and is assigned to that type of environment in Nafion. The second broader and larger intensity peak is assigned to the pendant group domain. The two domain view from xenon-129 NMR is consistent with the assumption of the presence of pendant group and backbone domains used to interpret the fluorine-19 spin diffusion data. Two-dimensional xenon-129 NMR shows the onset of exchange at a mix time of 1 ms at room temperature leading to an estimate of the average effective diffusion constant for xenon in Nafion of 4×10^{-11} cm^2/s.

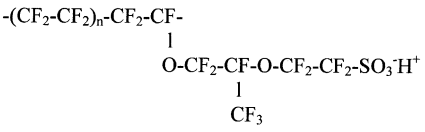
Keywords: Nafion; NMR; Morphology

1. Introduction

Ionomers have a complex morphology that can be studied by a variety of experimental approaches [1] including small angle X-ray scattering, small angle neutron scattering, and transmission electron microscopy. These techniques have been applied to fluorinated ionomers [2] but fluorine-19 NMR presents an interesting opportunity because the large chemical shifts associated with this nucleus [3] allow for the study of morphology based on the chemical structure of the ionomer. The disadvantage of fluorine-19 NMR is the broad line widths observed in the solid state which arise from the dipole–dipole interaction between fluorine-19 nuclei, and from the large chemical shift anisotropy of this nucleus. Recently the technology associated with magic angle spinning has allowed for such rapid spinning that the dipole–dipole interaction and chemical shift anisotropy interaction can be averaged to their isotropic values producing essentially high-resolution solid state fluorine-19 NMR spectra [4].

Under these conditions, chemical shift selection can be used to create magnetization gradients suitable for spin diffusion studies [5]. This technique has been applied to a number of morphological problems in polymer science including ionomer blends [6].

The most common perfluorosulfonate ionomer with the chemical structure



is Nafion (DuPont Trademark) which has many morphological features. A variety of domains have been reported

* Corresponding author. Tel.: +1-508-793-7116; fax: +1-508-793-8861.
E-mail address: chemistry@clarku.edu (P.T. Inglefield).

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including crystalline poly(perfluoroetheylene) domains, amorphous poly(perfluoroethylene) domains, ionic clusters and interfaces [1]. SAXS shows an 'ionic peak' in metal cation neutralized forms of Nafion as well as many other ionomers [1,2]. The presence of this prominent feature has led to numerous morphological models that contain spherical nanometer sized clusters of ions and the associated pendant group as the dominant structural feature. In Nafion, rapid transport of water over macroscopic distances was also observed. To accommodate this observation, channels between ionic clusters were proposed. The clusters and the channels were thought to be composed of the ionic groups or ionizable groups which are on the pendant side chains of this ionomer [7].

This morphological picture can be studied by fluorine-19 NMR since the shift of the fluorines on the side chain with the sulfonate group leads to resonances which are well separated from the resonances of the perfluoroethylene groups in the backbone. Thus the proposed morphological features coincide nicely with the differences arising from fluorine-19 chemical shifts. Also solvents like water are only expected to enter the clusters and channels so these regions should selectively swell which can again be monitored by fluorine-19 NMR. Some reorganization of the morphology has been proposed in Nafion upon swelling [8]; and the study of the morphology in the presence of two solvents, water and ethanol, may indicate changes in morphology associated with different solvents.

The rotational mobility of the pendant groups and the backbone of the perfluorosulfonate ionomer are reflected in the static fluorine-19 line widths. Mobility of the polymer in the presence and absence of penetrants can affect spin diffusion. Mobility of the polymer can influence the translational mobility of penetrants and it can be related to the extent of morphological rearrangement upon addition of penetrants. Solvents may selectively induce mobility in one domain if they are primarily sorbed into that domain.

In an accompanying study, the self-diffusion constant of the same two solvents considered in this morphological study will be measured as a function of concentration and temperature using pulse field gradient NMR [9]. As mentioned, the rapid transport of such solvents in Nafion has played a role in the development of morphological models, and by combining with it a study of domain size by spin diffusion with the measurement of translational diffusion on the same systems should be helpful. The same commercial samples of Nafion are also used in a third study on permeability and solubility to link the traditional measurements of diffusivity and sorption to the NMR results [10].

The last morphological experiment included in this investigation will be xenon-129 NMR. Xenon-129 shielding is sensitive to the sorption environment in a variety of systems including polymers [11–14]. Xenon-129 NMR can help identify the number of domains that participate in the uptake and transport of a penetrant. Xenon gas is not likely to favor domains associated with ions and pendant groups over amorphous fluorocarbon regions so that both these types of domains may be detected. However, xenon is likely to be excluded from the crystalline domain or from other more ordered domains associated with the fluorocarbon backbone units of Nafion. If xenon-129 signals from different sorption environments are observed, two-dimensional exchange experiments can be used to detect the transport of xenon from one domain to the other.

2. Experimental

Nafion-117 in the hydrogen(acid) form (NR 50) was purchased from Aldrich. The equivalent weight per ionic group was 1250 g. The Nafion was cryo-milled to produce a powder suitable for magic angle spinning experiments and vacuum dried for several days at a temperature of 60°C. The Nafion powder was then swollen to different levels with deionized water or absolute ethanol. For the xenon-129 spectra, Nafion was placed in a sealed 10 mm glass tube under a pressure of 12 atm of xenon gas.

All fluorine-19 NMR experiments were performed on a Bruker MSL 300 at a frequency of 288.4 MHz in a 4 mm MAS probe except for the magic angle spinning spectra taken at 35 kHz which were acquired on a Bruker Avance 400 in a 2.5 mm probe. The fluorine-19 spin diffusion measurement were made at a spinning speed of 5 kHz with care taken to prevent spinning side bands from overlapping the center band resonances involved in the magnetization exchange. The fluorine-19 $\pi/2$ pulse width was typically 3.2 μs and a DANTE sequence was used to selectively invert one of the resonances to create a magnetization gradient. In the experiments reported here the OCF_2 and CF_3 resonances of the pendant group at -80 ppm relative to $CFCl_3$ were inverted and spin exchange to the CF_2 of the backbone at -120 ppm then occurred. A series of spectra was acquired as a function of time after the inversion to monitor the return to the spin–spin equilibrium. Typically spin–spin equilibrium was reached in 50 ms which was considerably shorter than the spin–lattice relaxation times which are at an order of a second or longer. Static fluorine-19 spectra were taken in the MAS probe with the bearing pressure turned off to prevent spinning.

Xenon-129 experiments were performed on a Varian Unity 500 at 138.3 MHz. The typical $\pi/2$ pulse width is 21 μs and recycle times of 60 s were employed which are approximately three times the spin–lattice relaxation time. Two-dimensional exchange spectra were acquired to monitor exchange of sorbed xenon gas between different sorption environments [11–14]. The total spectral width was set at 25 kHz with 64 data points in t_2 and in t_1. Spectra were referenced by setting the free gas signal to 0 ppm.

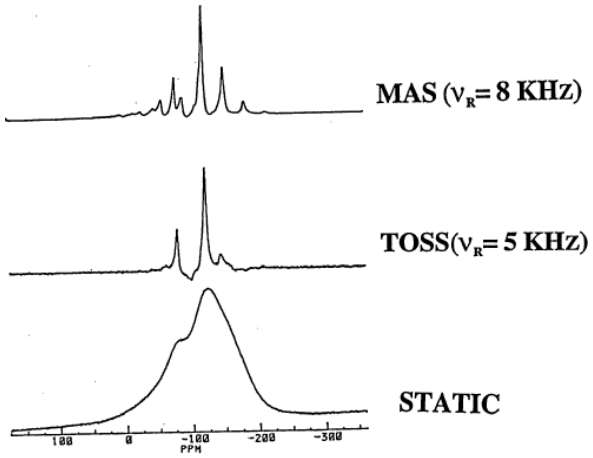

Fig. 1. Fluorine-19 spectrum of dry Nafion, a MAS spectrum taken with a 5 kHz spinning rate with side band suppression using the TOSS sequence and an 8 kHz spinning rate spectrum with side bands present.

3. Results

In Fig. 1, a static fluorine-19 spectrum of dry Nafion is compared with a MAS spectra taken with a 5 kHz spinning rate with side band suppression using the TOSS sequence and an 8 kHz spinning rate spectrum with side bands present. In Fig. 2, a 35 kHz spinning rate spectrum is presented.

In Fig. 3, a static fluorine-19 spectrum is compared with water and ethanol swollen Nafion at several concentrations.

Fig. 4 displays a series of spectra taken at different times after the selective inversion by the Dante pulse which shows the return to spin–spin equilibrium following the creation of a magnetization gradient. Fig. 5 is a standardized spin diffusion plot based on the change in intensity of the type shown in Fig. 4. The form of the plots follows the approach suggested by VanderHart and McFadden [5]. In this example the change of the normalized pendant group magnetization is plotted against the square root of time after the DANTE inversion. The initial linear region is fit to a straight line, which is extrapolated to zero intensity to determine the intercept on the square root of time axis, which is the parameter $t_{sd}^{1/2}$. Table 1 reports values of $t_{sd}^{1/2}$ as a function of water and ethanol concentration.

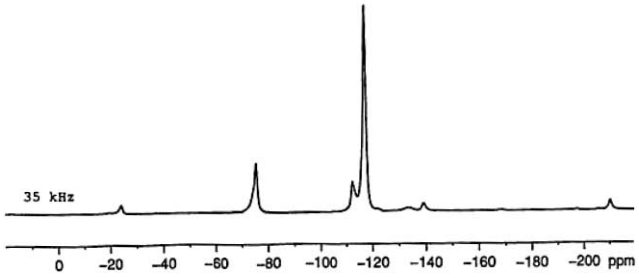

Fig. 2. Fluorine-19 35 kHz spinning rate spectrum of dry Nafion.

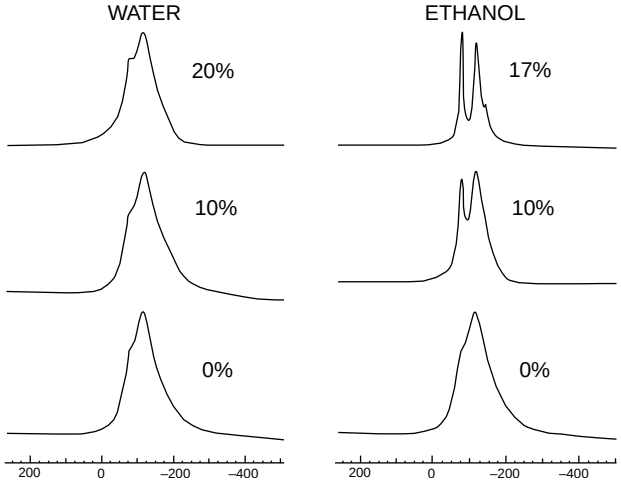

Fig. 3. Static fluorine-19 spectrum of water and ethanol swollen Nafion at several concentrations.

Fig. 6 shows the one-dimensional xenon-129 spectra taken on dry Nafion under a pressure of 12 atm at several different temperatures. Fig. 7 is a two-dimensional xenon-129 spectrum for a sample of Nafion under 12 atm of xenon gas.

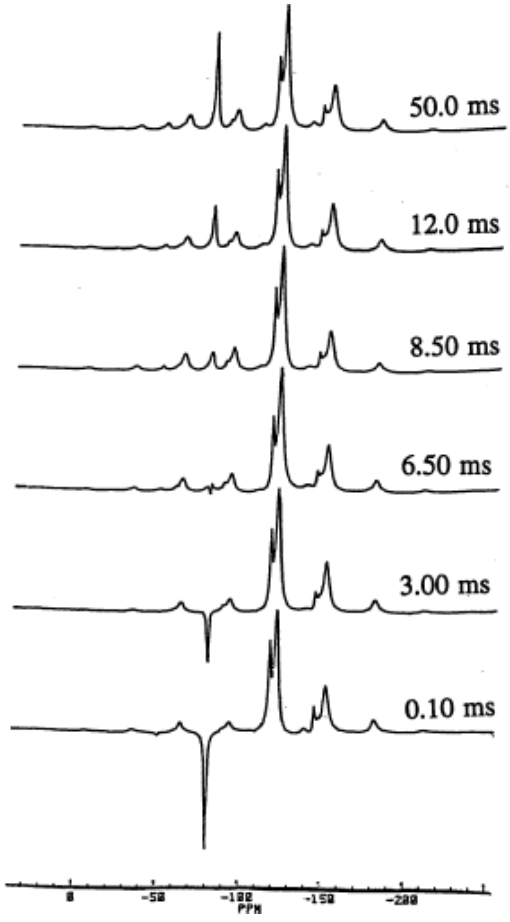

Fig. 4. Fluorine-19 MAS spectra taken at different times after the selective inversion by the Dante pulse for Nafion with 10% ethanol.

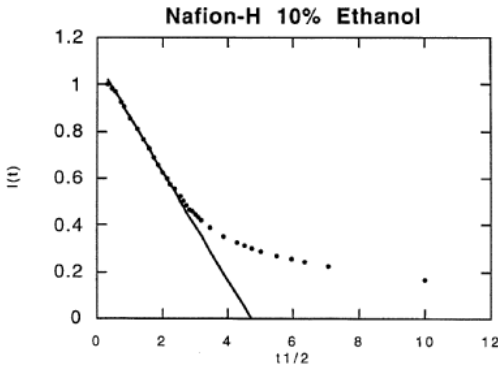

Fig. 5. Spin diffusion plot based on the change in intensity of the type shown in Fig. 4, following the approach suggested by VanderHart and McFadden [5].

4. Interpretation

The fluorine-19 spectrum taken at 35 kHz shown in Fig. 2 has five resolved resonances that can be largely assigned following the earlier structural study of Schick et al. [3]. The small signal at −146 ppm relative to CCl_3F corresponds to the CF groups in the back bone and in the pendant group. The second small resonance at −139 ppm corresponds to the CF_2 adjacent to the sulfonate group. The large resonance at −120 ppm arises from the CF_2 groups in the backbone. The smaller signal at −115 ppm which overlaps the backbone CF_2 resonance corresponds to the backbone CF_2 groups which are adjacent to the backbone CF group to which the pendant group is attached. This last assignment is slightly different from that given earlier and is based on the relative intensity of the signals at −115 and −120 ppm. The last resonance at −80 ppm arises from the CF_2 and CF_3 groups on the side chain.

Following VanderHart and McFadden [5], the repeat length, L, of the morphological structure can be calculated from the parameter $t_{sd}^{1/2}$ derived from plots such as that shown in Fig. 5. In this interpretation, two types of domains are assumed: one is made up of the pendant groups and the other is made up of the backbone CF_2 groups. A one-dimensional interpretation [5] is chosen, though the structure is certainly not simple lamellar, since spin diffusion data provide little information on the dimensionality of the morphology. The equation relating L to $t_{sd}{}^{1/2}$ is

$$L = \frac{[4(t_{sd}^{1/2})(D_A D_B)^{1/2}(\rho^{F_a} f_A + \rho^{F_B} f_B)]}{[f_A f_B \pi^{1/2}(\rho^{F_A} D_A^{1/2} + \rho^{F_B} D_B^{1/2})]} \quad (1)$$

where ρ^{F_A} is the fluorine-19 spin density in domain A, ρ^{F_B} the fluorine-19 spin density in domain B, D_A the spin

Table 1
Domain size determinations from ^{19}F spin diffusion measurements

Penetrant (%)	$t_{sd}^{1/2}$ $(ms)^{1/2}$	f_a	L (nm)	Pendant domain size (nm)
0	2.57	0.33	11.4	3.80
10 (H_2O)	2.73	0.45	10.1	4.59
20 (H_2O)	3.44	0.56	11.8	6.56
10 (EtOH)	4.68	0.48	16.9	8.12
17 (EtOH)	5.60	0.56	19.1	10.7
40 (EtOH)	10.8	0.75	37.7	28.4

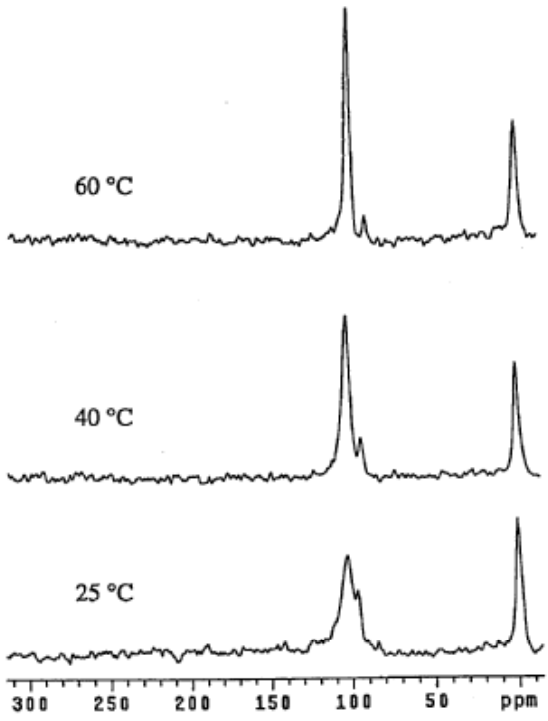

Fig. 6. Xenon-129 spectra taken on dry Nafion under a pressure of 12 atm at different temperatures.

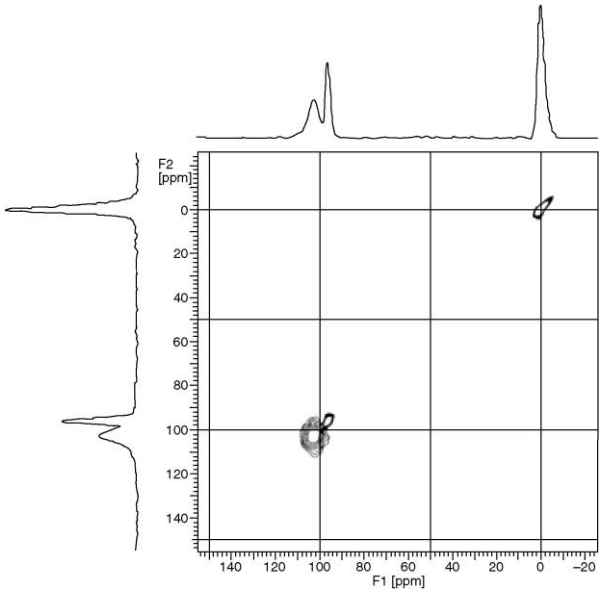

Fig. 7. Two-dimensional xenon-129 spectrum for a sample of Nafion under 12 atm of gas, mix time 1 ms.

Table 2
Line shapes and apparent values of $1/T_2$ from line shape simulations

Ethanol concentration (wt%)	$1/T_2$ (kHz)				
	Resonances				
	−80 ppm	−115 ppm (amorphous)	−120 ppm (crystalline)	−139 ppm	−146 ppm
0	Gaussian	Lorentzian	Gaussian	Gaussian	Gaussian
	82	22	82	82	82
10	Lorentzian	Lorentzian	Gaussian	Lorentzian	Lorentzian
	12	22	82	22	22
17	Lorentzian	Lorentzian	Gaussian	Lorentzian	Lorentzian
	6.2	14	82	14	14

diffusion constant in domain A, D_B the spin diffusion constant in domain B, f_A the volume fraction of domain A and f_B is the volume fraction of domain B. Note that the symbol F refers to fluorine in this equation.

The pendant group domain will be considered as the A domain and the backbone group domain will be considered as the B domain. The domain size is given by the product of f and L. For dry Nafion, the volume fraction corresponds to the weight of the pendant group, 363, divided by the equivalent weight of 1250. For the swollen Nafion, the volume associated with a weight of pendant chain is calculated assuming a density of 2.0 g/cm^3. The same density is used for the backbone domains. Simple additivity of volumes is assumed so that

$$f_a = \frac{(V_{solvent} + V_{pendant})}{(V_{solvent} + V_{pendant} + V_{backbone})} \quad (2)$$

This equation also assumes that all of the water or ethanol is in the pendant group domain. The spin diffusion constant will be assumed as 0.62 nm^2/s which is the value for a rigid organic hydrocarbon [5] given that fluorine interatomic distances are similar in fluorocarbons and hydrocarbons as are the gyromagnetic ratios. Table 1 lists the parameters used to calculate domain sizes as well as the sizes obtained by substituting these values in Eq. (1).

Some investigators [15,16] reduce the spin diffusion constant in semi-solid systems where there is limited molecular motion. The effect of this possibility can be considered with the usual form of the relationship as

$$D_i = \frac{K}{T_{2i}} \quad (3a)$$

where K is a constant and T_{2i} is the spin–spin relaxation time of one of the domains. Recently Mellinger et al. [17] suggested a linear form of this equation

$$D_i = \left(\frac{K}{T_{2i}}\right) + b \quad (3b)$$

where b is a positive intercept. There is little molecular motion in dry Nafion so this system will be used to set the constant K. The systems swollen with water narrow rather little as can be seen in Fig. 3 so lower values of the spin diffusion constant need not be considered for water but the ethanol swollen systems show significant narrowing as can also be seen in Fig. 3. Values of T_{2i} can be estimated by fitting the ethanol swollen spectra in Fig. 3 to a combination of Lorentzian and Gaussian line shapes. For the ethanol-swollen spectra, each resonance is centered at the isotropic shift value determined from high-speed magic angle spinning spectra. The relative fluorine populations of each resonance are known from the structure and are therefore also fixed in the interpretation of the swollen spectra. The swollen spectra are fit and the relevant line width parameters are given in Table 2. The dry spectrum is fit with a series of Gaussians centered at each of the resolved resonance positions obtained from the high speed MAS spectrum except for one Lorentzian positioned at −120 ppm which corresponds to the amorphous backbone units which are somewhat mobile. All the Gaussians for the dry sample were given the same width though the populations of the resonances at −80, −115 and −120 ppm are weighted as a group by the repeat unit structure relative to the resonances at −139 and −146 ppm. The latter two resonances are small and are not resolved at all in the dry spectrum so they are inserted at the known position with the known relative weighting. The Gaussians are only an approximation of the true line shape since the more rigid lines result from both the dipole–dipole interactions and chemical shift anisotropy interactions. Using this line width fitting approach, estimates of T_{2i} are obtained which can be used to determine a level of line narrowing relative to the dry state. Assuming that the dipole–dipole contributions to the line width narrow to about the same extent as the chemical shift anisotropy contributions, the relative level of dipole–dipole reduction pertinent to the spin diffusion problem can be considered.

An examination of the relative T_{2i} estimates in Table 2 for the ethanol-swollen system shows that the resonances associated with the pendant group at −80 ppm narrow by almost an order of magnitude. The backbone CF_2 resonances at −115 and −120 ppm are not resolved in either the dry or

swollen static spectra. They should be fit by a single line width parameter based on the repeat unit structure but actually two different line components are required. The origin of the two is associated with the morphological characteristics of the backbone domains which are partially crystalline. Arbitrarily, the resonance at −115 ppm is fit as a broad Gaussian which does not narrow with the addition of ethanol in the simulations of the two swollen spectra. This line shape component is identified with the crystalline or more ordered regions of the backbone domain. The other component is a narrower Lorentzian positioned at −120 ppm which is identified with the amorphous component of the backbone domains. In the swollen spectra, the intensities of these two backbone components are equal indicating crystallinity or more ordered regions of about 50% of the backbone domain. The amorphous component of the backbone resonance narrows by less than a factor of two in going from dry Nafion to 17% ethanol. These simulations are consistent with the interpretational approach used here which assumes that the ethanol is primarily located in the pendant group domain.

The question remains whether it is helpful to scale the spin diffusion constants according to Eqs. 3(a) or 3(b). First there is rather little narrowing associated with the backbone domain so scaling seems unnecessary for this component. The pendant group resonance at −80 ppm does narrow by a factor of almost 10 but the apparent $1/T_2$ for this resonance is still 6 kHz. According to Mellinger et al. for protons if $1/T_2$ is 1 kHz or larger the spin diffusion constant is reduced by less than a factor of 3. In our case the true fluorine dipolar $1/T_2$ value is going to be appreciably less than the apparent value of 6 kHz but still larger than 1 kHz. Given all the complexities of Nafion, the best course of action would seem to be to use a single value of the spin diffusion constant D associated with a rigid system. The absolute value of the domain size may have a systematic error but comparisons and trends will still be informative. Spin diffusion results and domain sizes are listed in Table 1.

5. Discussion

To interpret the spin diffusion observed when the fluorine-19 pendant group resonance is inverted, the assumption made is that the pendant group constitutes a distinct domain separate from a domain consisting of perfluoroalkane groups associated with the polymer backbone. This assumption is consistent with the general picture of ionomers [1,2] and appears to lead to meaningful results in the case of spin diffusion data on both dry and swollen Nafion. Spin diffusion indicates domains in the dry and swollen systems are in the nanometer range. This is of a larger dimension than that associated with the chemical structure indicating that there is an aggregation of pendant groups. The actual size of several nanometers is comparable to the size of clusters seen by SAXS in salt forms of ionomers [1,2]. As both the interpretation of the spin diffusion data and the SAXS data are model dependent, this general agreement is reassuring. The spin diffusion results tell little regarding the shape or dimensionality of the aggregates [5]. Thus the presence or absence of spherical clusters connected by channels is not demonstrated. However, the NMR results presented here require only two phases to be interpreted. The spin diffusion data does indicate the presence of some interface [5] as the spin diffusion plots as shown in Fig. 5 usually have a curvature at short times before the linear portion of the magnetization equilibration is reached in the plots of magnetization change versus the square root of time. The actual values of L and the pendant group domain size might be in error as only a single value of D is employed and a simple one-dimensional interpretation is used. However the trend of the relative size of the domains with the addition of solvent is felt to be valid as is the fact that the repeat length L is larger for ethanol relative to water in comparably swollen samples. These aspects of the morphological description are important and provide an alternative view of the morphology from SAXS and SANS data which also suffer from similar model dependent interpretational choices.

The one-dimensional xenon-129 line shape consists of two overlapping resonances.. The sharper peak at 96 ppm coincides with that seen for xenon-129 in poly(perfluoroethylene) and is assigned to an amorphous poly(perfluoroethylene) environment [18]. The second more intense resonance at 103 ppm is assigned to domains containing the pendant group including the sulfonate functionality and hydrogen ion. This domain is more heterogeneous as indicated by the breadth of the line, which is consistent with a domain containing the pendant group, since this group is comprises several different chemical groups. While two domains are described as containing either pendant groups or backbone groups, there is undoubtedly some mixing. The level of mixing is not known but the xenon-129 signals overlap indicating that the environmental influence on the xenon shielding has no sharp boundary. On the other hand there are definitely two distinguishable environments affecting the xenon-129 shielding.

In the two-dimensional spectrum shown in Fig. 7, off diagonal intensity represents exchange between different sorption environments by translational diffusion. Most of the off diagonal intensity is centered around each of the two diagonal peaks. The peaks are heterogeneous in nature so this off diagonal intensity represents exchange within the heterogeneous environment of one or the other of the two domains. For the mix time shown of 1 ms, there is a small amount of off diagonal intensity appearing associated with exchange between the two peaks. It manifests itself as a small change in the contour levels at a position corresponding to the intersection of lines drawn from the diagonal maxima of each of the two peaks associated with the two environments. This onset of exchange allows for an estimate of the average effective diffusion constant for xenon, D_{Xe},

in Nafion. Using the following equation

$$D_{Xe} = \frac{b^2}{6t_{mix}} \quad (4)$$

where b is the domain size and t_{mix} is the mix time. If a value of $b = 5$ nm is chosen for dry Nafion, then D_{Xe} is 4×10^{-11} cm^2/s which is two orders of magnitude slower than the value determined for Xe in poly(styrene) [19]. This result should be regarded as an order of magnitude estimate.

Note the projections shown as a part of the two-dimensional spectrum tend to indicate that the amorphous poly(tetrafluorethylene) type of environment contains more xenon than the pendant group environment. This is superficially just reversed from the one-dimensional spectrum. However if one integrates over the area associated with each of the two resonances in the two-dimensional diagram, the intensity associated with the pendant group domain is larger in agreement with the one-dimensional spectrum.

From the NMR data presented, one need only assert that there are two domains with no further structure than the presence of some interface between the domains. The rapid long range transport of water and low molecular weight alcohols, as seen in the accompanying paper, and widely reported, argues that the domain which supports this transport must be continuous [1,2] with rather little tortuosity. The pulse field gradient experiment is sensitive to tortuosity [20,21]; and, though not extensively investigated, no signs of it were observed on the time and length scales studied by us and others [21,22]. The diffusion results then add one further point to the description of the morphology: the pendant group domain must be continuous. The simplest structure consistent with the NMR data and the presence of rapid long-range diffusion of water and alcohols would be a random morphology with the pendant group domain being continuous.

This differs pictorially from the spherical clusters and channels. However Eisenberg [23] in a review concludes that there is no evidence for channels other than the need to explain the rapid transport of water. This author also states that the ionic clusters may actually be a continuous phase without a particular shape. From the point of view of the NMR data, a random continuous phase largely composed of ionomer side chains is all that is required. The second perfluoroalkane phase must be random if the other phase is random but the second phase may or may not be interconnected in the same manner. This could be established by studying the transport of species which are selectively sorbed into this phase.

As Nafion is swollen with either water or ethanol, the value of $t_{sd}^{1/2}$ increases indicating slower spin diffusion which is attributed to growth in the domain associated with the pendant group. The overall periodicity increases with addition of solvent and the size of the pendant group domain increases according to the assumptions and Eq. (1). The size of the domain associated with backbone units increases more slowly. Even at an ethanol concentration of 40% where the pendant group domain is an order of magnitude larger, there is only a fractional increase in the backbone fluorocarbon domain. This is at least consistent with the assumption that these solvents are selectively sorbed into the pendant group domain.

Ethanol induces greater overall periodicity and correspondingly larger pendant group and backbone domains. There may be several inter-related reasons why ethanol has the ability to produce more reorganization of the morphology than water. One is related to the increase in T_2 which is significantly greater for ethanol relative to water as can be seen in Fig. 3. The increased rotational mobility of the backbone units and especially the pendant groups induced by ethanol contributes towards the increased morphological reorganization. Another aspect of the local mobility and morphological reorganization is the difference in the ability of ethanol to plasticize the pendant group domain. The perfluoroether functionalities of the pendant group are apparently more compatible with ethanol than water. This allows for the greater uptake of ethanol over water and the better plasticization of the pendant group. Water is a good solvent for the acidified sulfonate group but not the rest of this ionomer.

Once the reorganization is produced at the lowest concentration studied for either water or ethanol, then only the pendant group domain increases significantly in size as more solvent is added. However, ethanol is sorbed to a greater degree and at a level of 40% there is a truly significant morphological reorganization relative to dry Nafion. This continued change in morphology in the case of ethanol would likely influence an interpretation of translational diffusion of the ethanol.

If the change in mobility as determined by the apparent T_{2i}s is used to lower the spin diffusion constant D according to Eqs. (3a) and (3b), the periodicity and domain size are somewhat reduced. However, the trends remain generally the same.

6. Conclusions

The acidified form of the perfluorosulfonate ionomer Nafion displays a predominantly two-phase morphology based on fluorine-19 spin diffusion measurements. A two-phase morphology is also consistent with the xenon-129 NMR spectrum. One of the domains consists primarily of pendant groups containing the ionomer functionality and the other domain is primarily composed of perfluoroethylene backbone groups. Within the backbone group domain, the study of the static fluorine line shape indicates the presence of more rigid and less rigid groups which may be related to crystalline or more ordered domains and amorphous domains in approximately equal amounts. The size of both the backbone and pendant group domains is in the

nanometer range and a random shape is sufficient to explain the spin diffusion data. The addition of ethanol or water increases the periodicity mainly by increasing the size of the pendant group domain up to a level of 20 wt%. Ethanol causes an increase of local mobility of the pendant groups and to a lesser extent the amorphous backbone groups. Water has less of an effect on local mobility. Ethanol induces the creation of larger domains relative to both the dry form of Nafion and water swollen Nafion. It should be remembered that the pendant group domain is continuous with little tortuosity since there is rapid transport of either water or ethanol.

Acknowledgements

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