Structural Analysis of a Perfluorosulfonate Ionomer in Solution by ^{19}F and ^{13}C NMR

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ABSTRACT: We demonstrate ^{19}F and ^{13}C NMR assignments and study of the structure in solution of Nafion, a perfluorosulfonate ionomer. Using $^{19}F-^{13}C$ HSQC, $^{19}F-^{13}C$ CIGAR-HMBC, and $^{19}F-^{19}F$ COSY to the model compounds of Nafion, we determine ^{19}F and ^{13}C assignments of model compounds. The combination of the three 2D NMR experiments represents an entirely new approach to analysis of perfluorinated organic compounds. On the basis of the assignments of the model compounds and also based on ^{19}F coupled and ^{19}F complete decoupled ^{13}C NMR for Nafion, ^{19}F and ^{13}C NMR assignments are determined for Nafion. In this study the two ^{13}C signals (OCF_2) in the side chain separate more clearly relative to previously reported results. We also carried out MALDI-MS for Nafion, supporting the results found in NMR. From the result of NMR, it is suggested that the aggregates of Nafion in solution exist, and the structure of the aggregates is estimated.

1. Introduction

The most important development subjects relating to polymer electrolyte fuel cells (PEFC) consist of cost reductions, extending the life of the cells, and improving reliability. As at this point the need for stability in the polymer electrolyte membrane is also significant, the development of a polymer electrolyte membrane offering higher performance, low cost, and long service life is being advanced. The ion exchange membrane of a perfluorosulfonate ionomer is generally used as a polymer membrane that satisfies these requirements. Nafion, Flemion, and Aciplex, with varying grades of ion exchange capacity and film thickness, are among the available marketed products. The catalytic layer in PEFC has a large effect on performance; this catalytic layer is often impregnated with a perfluorosulfonate ionomer solution. In this way, the perfluorosulfonate ionomer fulfills an important role in PEFC. It is therefore necessary to examine the composition and degradation of the perfluorosulfonate ionomer in the research and development of PEFC. In this process, NMR has proven to be one of the most useful analytical tools. The first step in this process entails clarification of the assignment of ^{19}F and ^{13}C NMR in the undegraded article.

To date, three reports have been issued on NMR assignments of perfluorosulfonate ionomers.[1−3] In the report of ref 1, ^{19}F NMR assignment was carried out for Nafion in solution. However, some of the assignments described in that report were corrected by subsequent reports. In refs 2 and 3, ^{19}F and ^{13}C NMR assignments were carried out using the *J*-modulated ^{13}C CP/MAS technique[2] and solid-state 2D NMR experiments.[3] However, in these reports the separation of two ^{13}C signals (OCF_2) in the side chain is not sufficient to be clearly visible. When the degradation of Nafion is examined using these methods, it may not be possible to clarify the initial point from which degradation progressed.

In this context, we carry out ^{19}F and ^{13}C NMR assignments and structural analysis for Nafion, a perfluorosulfonate ionomer in solution. By solution NMR, we can obtain spectra at satisfactory resolution, permitting detailed examination of the chemical structure. After the membranes of perfluorosulfonate ionomers of differing chemical structures and degraded are dissolved[4,5] using the method described here, structural analysis of the membranes can be carried out. As a side note, it has been reported that perfluorosulfonate ionomers aggregate in solution.[5−8] In the meantime, according to solution ^{19}F NMR, it was reported that the Nafion solution was true solution and that the aggregates were not found.[1] Using solution ^{19}F NMR of high magnetic field, we examine the existence of the aggregates more in detail.

For the structural analysis of perfluorinated organic compounds by ^{19}F and ^{13}C NMR, to date, $^{19}F-^{13}C$ heteronuclear multiple-quantum coherence (HMQC) and $^{19}F-^{13}C$ (heteronuclear multiple bond correlation) (HMBC) have been applied.[9−12] However, using the above-mentioned 2D NMR method, assignment of Nafion is impossible due to its chemical structure. We therefore propose new methods to address this issue, referred to as $^{19}F-^{13}C$ heteronuclear single quantum coherence (HSQC[13,14]) and $^{19}F-^{13}C$ constant time inverse-detected gradient accordion rescaled long-range heteronuclear multiple bond correlation (CIGAR-HMBC[15]). In experiments using these methods, it is anticipated that correlations for a wider range of $^2J_{FC}$ with higher resolution for the ^{13}C axis will be obtained, relative to conventional experiments. Moreover, in addition to use of $^{19}F-^{19}F$ correlated spectroscopy (COSY),[12,16] we have found that structural analysis for a greater number of perfluorinated organic compounds than previously thought possible is attainable. However, we are hardly able to obtain correlation peaks in 2D NMR of Nafion. We therefore carry out 2D NMR on some model compounds, and the ^{19}F and ^{13}C assignments of these model compounds are determined.

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On the basis of the NMR assignments of the model compounds and on ^{19}F coupled and ^{19}F decoupled ^{13}C NMR of Nafion, we determine ^{19}F and ^{13}C NMR assignments of Nafion in solution. We also examine the chemical structure of Nafion using MALDI-MS. Here we discuss the structural analysis of Nafion in solution.

2. Experiments

2.1. Materials. Two model compounds, perfluoro(2,5,8-trimethyl-3,6,9-trioxadodecanoyl) fluoride (PFTTF) and perfluoro(2-ethoxyethane)sulfonic acid (PFESA), were purchased from Daikin Fine Chemical Laboratory, Ltd., and from Lancaster Synthesis Inc., respectively. No solvents were added to the PFTTF and PFESA for the NMR experiments. Nafion 5% solution in lower alcohols and water was purchased from Aldrich. The nominal EW (equivalent weight) value is 1100. The solution was used as it is for ^{19}F NMR experiments. For ^{13}C NMR experiments, the solution condensed to approximately 1/4 the volume of the original solution and then diluted with an equal volume of methanol-d_4.

2.2. NMR. NMR spectra were collected using a Varian UNITY INOVA 600 and a Varian UNITY Plus 500 at 25 °C. C_6F_6 was used as an external reference ($\delta_{^{19}F} = -163$ ppm) for ^{19}F chemical shifts. For ^{13}C chemical shifts, TMS was used as an external reference ($\delta_{^{13}C} = 0.00$ ppm).

For the complete fluorine decoupled ^{13}C NMR experiments, WURST[17−19] was employed, and for selective fluorine decoupled ^{13}C NMR experiments, continuous wave was employed.

For PFTTF, HSQC, and the CIGAR-HMBC spectra were obtained at 474 MHz using a 1.0 s relaxation delay, a 13.5 μs ^{19}F $\pi/2$ pulse, a 8.5 μs^{13}C $\pi/2$ pulse, an acquisition time of 0.128 s (with ^{13}C GARP decoupling), and coupling constants $^1J_{CF} =$ 285 Hz for HSQC and $^1J_{CF} = 250-310$ Hz and $^2J_{CF} = 30-50$ Hz for CIGAR-HMBC, spectral windows of 12 000 Hz for $F1$ and $F2$ axis, 2048 points on $F2$ and 256 points on $F1$ axis, 16 or 128 transients for each t_1 increment. The $F2$ axis of 12 000 Hz was regions of approximately −149 to −127 ppm and −96 to −74 ppm, and HSQC and CIGAR-HMBC were carried out in the two regions, respectively.

The COSY spectrum for PFTTF was collected at 564 MHz using spectral windows of 50 000 Hz, 8192 points on the $F2$ and 256 points on the $F1$ axis, a 3.0 s relaxation delay, and a 5.8 μs ^{19}F $\pi/2$ pulse. For each t_1 increment four transients were produced. All 2D NMR were of the gradient-selected type.

The conditions of the HSQC, CIGAR-HMBC, and COSY experiments for PFESA were approximately the same as those for PFTTF.

All data were processed using Varian's VNMR software. The HSQC data were processed with a Gaussian weighting function and zero filled to 4-fold in the $F1$ dimension. The CIGAR-HMBC and COSY data were processed with a sinebell weighting function and zero filled to 4-fold in the number of points collected on the $F1$ axis.

2.3. MALDI-MS. A sample solution was prepared by diluting the commercial Nafion solution in 2,2,2-trifluoroethanol (20 mg/mL). Matrix solution was prepared by dissolving the 7-amino-4-methylcoumarin in 2,2,2-trifluoroethanol (10 mg/mL). The two solutions were mixed in a 1:1 ratio by volume. 2 μL of the mixed solution was dropped onto the sample plate and air-dried. MALDI-MS measurements were performed with a Bruker BIFLEX III time-of-flight mass spectrometer. The instrument operates with a nitrogen laser providing 3 ns pulses at 337 nm. Negative ions were detected in the reflectron mode.

3. Results

3.1. Model Compounds. As model compounds, perfluoro(2,5,8-trimethyl-3,6,9-trioxadodecanoyl) fluoride (PFTTF) and perfluoro(2-ethoxyethane)sulfonic acid (PFESA) were used, the chemical structures of which are shown in Table 1. Each compound contains $-OCF_2-CF(CF_3)O-$ or $-OCF_2CF_2SO_3H$ as a part of its chemical structure. Since each substructure corresponds partially to the structure of the Nafion side chain, therefore, PFTTF and PFESA may be deemed suitable as model compounds.

Table 1. Chemical Structure of Model Compounds (PFTTF, PFESA) and Nafion

PFTTF	Perfluoro(2,5,8-trimethyl-3,6,9-trioxadodecanoyl)fluoride
PFESA	Perfluoro(2-ethoxyethane)sulfonic acid
Nafion	Nafion for the acid form

3.1.1. Assignments of PFTTF. In the chemical structure shown in Table 1, the suffixes a to j are attached to each CF_n. For example, "Fa" and "Ca" represent the fluorine and the carbon with "a" attached,

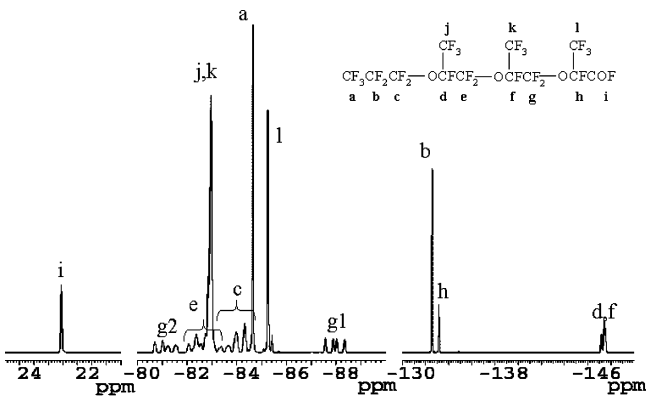


Figure 1. ^{19}F NMR spectrum of PFTTF.

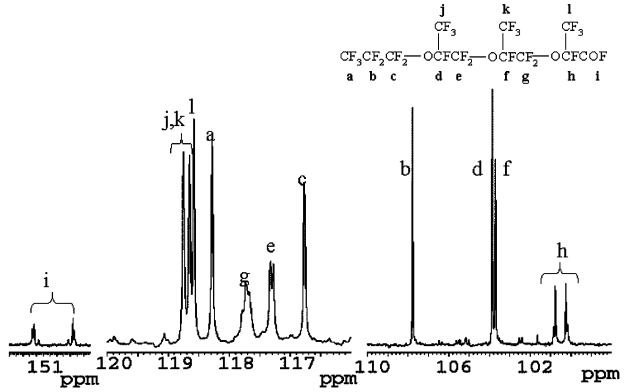


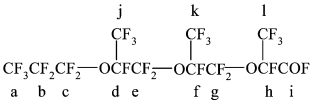
Figure 2. ^{19}F complete decoupled ^{13}C NMR spectrum of PFTTF.

Scheme 1

Table 2. ^{13}C, ^{19}F NMR Assignment and $^{1}J_{CF}$, $^{2}J_{CF}$ of PFTTF

	^{19}F chemical shifts (ppm)	^{13}C chemical shifts (ppm)	$^{1}J_{CF}$(Hz)	$^{2}J_{CF}$(Hz)	multiplicity of ^{13}C peaks
a	-84.7	118.3	284	33	q, t
b	-132.6	107.8	271	40	t, s
c	-85 ~ -83	116.8	289	31	t, t
d	-147.7 ~ -147.1	103.9	269	37	d, s
e	-84 ~ -82	117.3	287	29	t, d
f	-147.7 ~ -147.3	103.7	270	36	d, s
g	-88.0, -81.2	117.7	289	26	t, d
h	-133.2	100.5	262	41	d, q, d
i	23.1	149.7	372	37	d, d
j ,k	-83.0	118.65,118.75	287	31	q, d
l	-85.3	118.6	285	29	q, d

q : quartet
t : triplet
s : sextet
d : doublet



respectively. The ^{19}F NMR spectrum and ^{19}F decoupled ^{13}C NMR spectrum of PFTTF are shown in Figure 1 and Figure 2, respectively. The complete assignments are summarized in Table 2. The reasons for each assignment are described as follows.

The ^{13}C peaks of 149.7 and 100.5 ppm, which are not completely ^{19}F decoupled in Figure 2, are assigned to Ci and Ch, respectively. Fi is assigned to 23.1 ppm on the basis of the chemical shift value.[20] Since the chemical shift of Fi differs significantly from that of other fluorines, Fi is not completely decoupled in Figure 2.

The chemical structure of PFTTF is then divided into four perfluorocarbon substructures, as shown in Scheme 1, and these perfluorocarbons are assigned by HSQC and CIGAR-HMBC of PFTTF (Figure 3 and Figure 4). In HSQC and CIGAR-HMBC spectra, correlation peaks via $^{1}J_{FC}$ and $^{2}J_{FC}$, respectively, are yielded. As a result, the ^{19}F and ^{13}C assignments are determined for four substructures. To connect these four substructures, we apply ^{19}F−^{19}F COSY. ^{19}F−^{19}F COSY yields correlations between fluorine peaks via $^{2}J_{FF}$, $^{3}J_{FF}$, $^{4}J_{FF}$, and $^{5}J_{FF}$.[12,16] In Figure 5 for COSY, the correlations caused by $^{4}J_{FF}$ are identified (Fc−Fd, Fe−Ff, and Fg−Fh). The methods of identification are as follows. The correlations via $^{2}J_{FF}$ are identified by HSQC, and the correlations via $^{3}J_{FF}$ are identified by HSQC and CIGAR-HMBC. The remaining correlations in COSY are identified via $^{4}J_{FF}$. No correlations via $^{5}J_{FF}$ are observed. The ^{19}F and ^{13}C NMR assignments of PFTTF are thus completed. The assignments of the ^{13}C peaks are supported by the multiplicity of carbon peaks in the ^{19}F coupled^{13}C NMR spectrum.

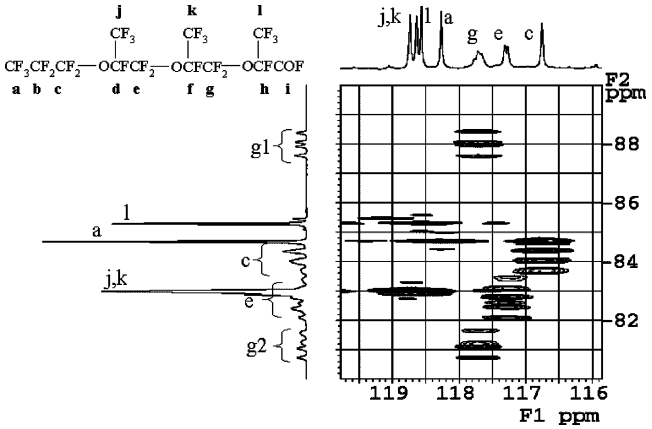


Figure 3. (a) ^{19}F−^{13}C HSQC spectrum of PFTTF. (b) ^{19}F−^{13}C HSQC spectrum of PFTTF.

3.1.2. Assignments of PFESA. In the chemical structure shown in Table 1, the suffixes a to d are attached to each CF_n. Figure 6 shows the ^{19}F and ^{13}C NMR spectra of PFESA. Applying the same method used with PFTTF, we determine complete assignments. The assignments are summarized in Table 3.

3.2. Structure Analysis of Nafion. In Table 1, the suffixes a to g are attached to each CF_n in the chemical structure, with the numbers of the repeating unit represent as x and y.

3.2.1. Assignment of ^{13}C NMR. ^{19}F coupled and ^{19}F complete decoupled ^{13}C NMR spectra are shown in Figure 7. Each ^{13}C peak is assigned using the following

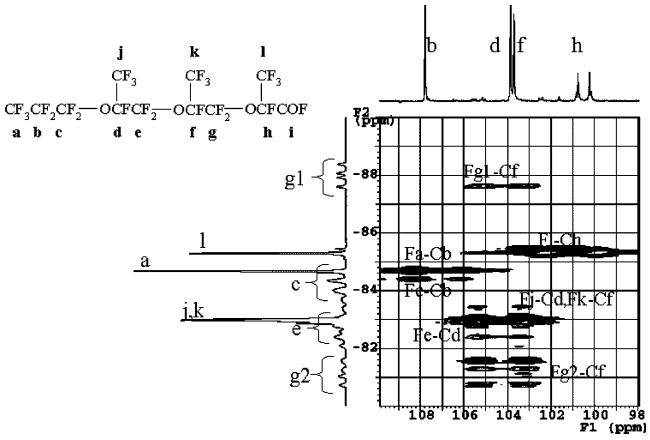


Figure 4. ^{19}F−^{13}C CIGAR-HMBC spectrum of PFTTF.

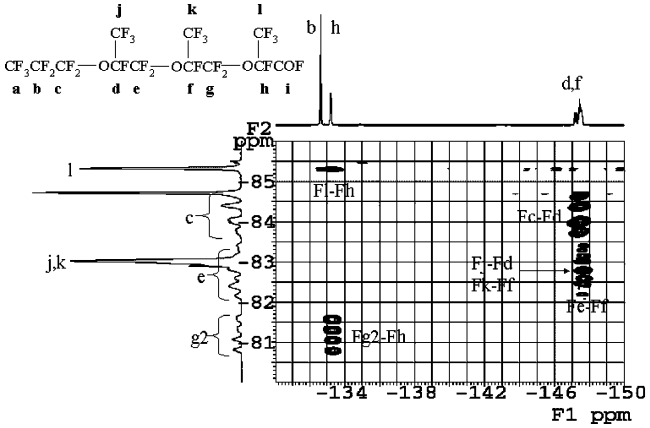


Figure 5. ^{19}F−^{19}F COSY spectrum of PFTTF.

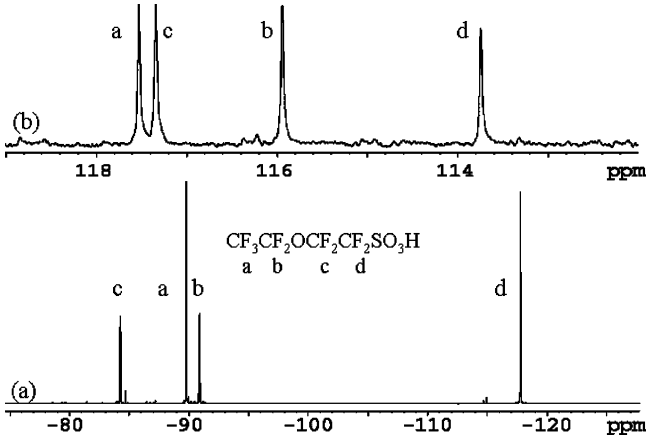


Figure 6. (a) ^{19}F NMR spectrum of PFESA. (b) ^{13}C NMR spectrum of PFESA.

Table 3. ^{13}C, ^{19}F NMR Assignment and $^1J_{CF}$, $^2J_{CF}$ of PFESA

	^{19}F chemical shifts (ppm)	^{13}C chemical shifts (ppm)	$^1J_{CF}$(Hz)	$^2J_{CF}$(Hz)	multiplicity of ^{13}C peaks
a	-89.7	117.5	283	42	q, t
b	-90.9	116.0	286	46	t, q
c	-84.2	117.4	288	30	t, t
d	-117.7	113.8	298	36	t, t

q : quartet
t : triplet
$CF_3CF_2OCF_2CF_2SO_3H$
a b c d

two methods. The first method is based on the chemical shift of the model compounds. We assign the $-OCF_2-CF(CF_3)O-$ component in the side chain of Nafion on the basis of the assignments of PFTTF. For the $-OCF_2-CF_2-SO_3H$ component, assignment is made with reference to the assignments of PFESA. The second method is based on spin couplings between ^{19}F and ^{13}C. In the ^{19}F coupled ^{13}C spectrum, ^{13}C peaks give rise to resolved lines mainly by one-bond and two-bond $^{19}F-^{13}C$ couplings. Because the number of resolved lines depends on the number of ^{19}F atoms that are coupled with the ^{13}C atoms, we can assign ^{13}C peaks. $^1J_{FC}$ is normally near 200−400 Hz, and $^2J_{FC}$ is near 20−50 Hz.

The 104.0 and 113.5 ppm carbon resonances are identified as Cd and Cg, with reference to the chemical shifts of the model compounds. The assignments of Cd and Cg are supported by the ^{19}F coupled ^{13}C spectrum.

From the ^{13}C chemical shifts of the model compounds, Cc, Ce, and Cf are assigned to 118.0, 119.0, or 119.4 ppm. We identify Ce, Cf, and Cc on the basis of the multiplicity of the ^{19}F coupled ^{13}C spectrum. This is because the ^{13}C chemical shifts of the model compounds are closely situated, and it is thus dangerous to assign the three carbons only on the basis of the chemical shifts of the model compounds. Ce is assigned to 119.4 ppm because the peak of 119.4 ppm presents a doublet of quartets. Cf is then assigned to 119.0 ppm, since the peak of 119.0 ppm presents a triplet of triplets. The remaining Cc can be assign to 118.0 ppm. Cc shows a triplet at $^1J_{CF}$, and it overlaps with the Ce peak of the quartet at $^1J_{CF}$ in Figure 7b. There is no contradiction to the assignment of Cc.

Moreover, Ca of the CF_2 in the main chain is assigned to 112.5 ppm. The Ca chemical shift and the multiplicity are also appropriate. Cb, which is CF in the main chain, was assigned to 109.2 ppm and presents a doublet at $^1J_{CF}$ in ^{19}F coupled ^{13}C NMR. All ^{13}C assignments and spin coupling constants are listed in Table 4.

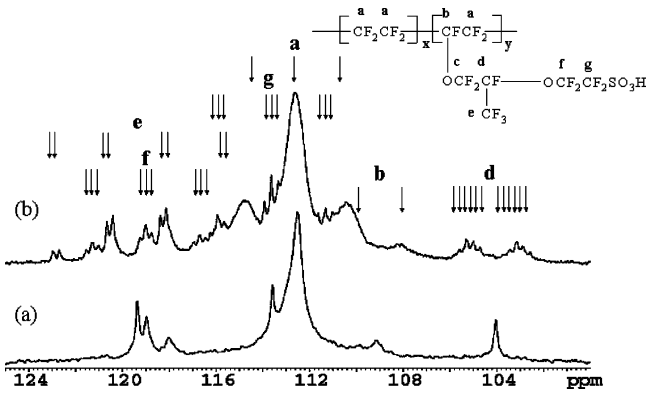


Figure 7. ^{13}C NMR spectrum of Nafion: (a) ^{19}F complete decoupled; (b) ^{19}F coupled.

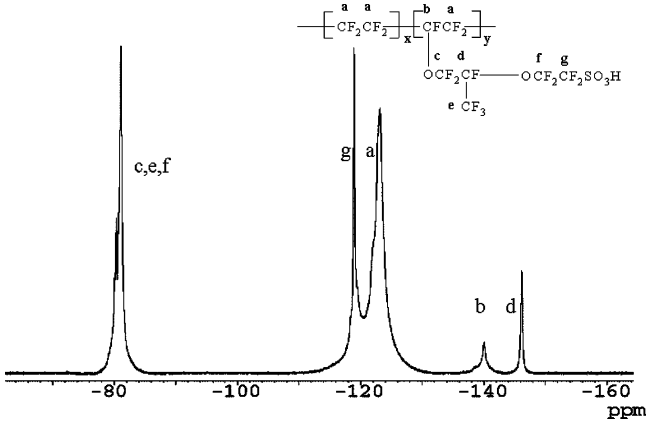


Figure 8. ^{19}F NMR spectrum of Nafion.

3.2.2. Assignment of ^{19}F NMR. The ^{19}F NMR spectrum of Nafion is given in Figure 8. We assign Fc, Fd, Fe, Ff, and Fg peaks in the side chain of Nafion with reference to the chemical shifts of the model compounds (Tables 2 and 3). The remaining peaks are assigned to CF (Fb) and CF_2 (Fa) in the main chain. The larger peak of −123.2 ppm is assigned to CF_2 (Fa), and the smaller one of −140.1 ppm is assigned to CF (Fb). ^{19}F assignments of Nafion are listed in Table 5. This table includes the ^{19}F chemical shifts of the model compounds. All ^{19}F assignments are confirmed by ^{19}F single frequency decoupled ^{13}C NMR experiments. The line shape of the skirt of the Fg peak is not symmetrical. From the chemical shift, both neighbors CF_2 of the Fb may be obtained here; both overlap the Fg peak.

The integrated values of ^{19}F NMR peaks are shown in Table 6.

3.2.3 MALDI-MS. The MALDI-MS spectrum of Nafion is shown in Figure 9. The main peaks are obtained in the *m/z* range between 1302 and 3078. It is assumed that the low molecular weight component is the result of selective ionization, since the molecular weight of Nafion in solution should be much higher. This type of phenomenon is frequently seen in MALDI-MS of polymers with wide molecular weight distribution. The main peaks are observed every 444 Da, which corresponds to $C_7HF_{13}O_5S$. Consequently, it is estimated that the principal structure in the side chain was $-O-CF_2CF(CF_3)-O-CF_2CF_2-SO_3H$. This substructure agrees with that estimated by NMR.

4. Discussion

We perform ^{19}F and ^{13}C NMR assignments of the model compounds of a perfluorosulfonate ionomer using

Table 4. ^{13}C NMR Assignment of Nafion

	Nafion						Model
	CF, CF_2 or CF_3[*1]	previous work (ppm)[*2]	this work (ppm)	multiplicity	$^1J_{CF}$, $^2J_{CF}$ (Hz)	line width (Hz)	compounds (ppm)
a	CF_2	111.3 to 111.8	112.5	t	290[*3]	97	-
b	CF	108.1	109.2	d	265[*3]	92	-
c	CF_2	116.7	118.0	t-d	-[*4]	75	118.0 or 118.4[*5]
d	CF	102.9	104.0	d-s	267, 37	27	104.4 or 104.5[*5]
e	CF_3	117.9	119.4	q-d	287, 32	30	119.3 or 119.4[*5]
f	CF_2	117.0	119.0	t-t	291, 34	51	117.4[*6]
g	CF_2	112.2	113.5	t-t	290, 37	22	113.8[*6]

*1 by ref 2

*2 by ref 3

*3 $^1J_{CF}$ is clear, but $^2J_{CF}$ is not clear.

*4 $^1J_{CF}$ and $^2J_{CF}$ are not clear.

*5 chemical shift of PFTTF

*6 chemical shift of PFESA

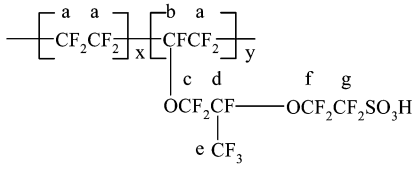


Table 5. ^{19}F NMR Assignment of Nafion

	Nafion				Model compounds (ppm)
	previous work (ppm)[*1]	previous work (ppm)[*2]	this work (ppm)	line width (Hz)	
a	-120	-122.1 to -118.2	-123.2	780	-
b	-	-138.4	-140.1	317	-
c	-80	-80.1	-80.3, -80.1	-[*3]	-84 to -82[*4]
d	-146	-143.8	-146.1	153	-147.7 to -147.1[*4]
e	-80	-80.4	-80.3, -80.1	-[*3]	-83.0[*4]
f	-80	-79.9	-80.3, -80.1	-[*3]	-84.2[*5]
g	-139	-117.1	-118.9	134	-117.7[*5]

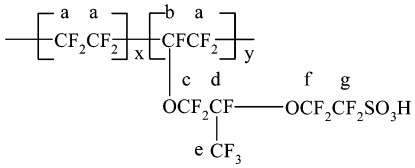
*1 by ref 1

*2 by ref 3

*3 line width is not clear

*4 chemical shift of PFTTF

*5 chemical shift of PFESA



HSQC, CIGAR-HMBC, and COSY. This represents a new approach to the structural analysis of perfluorinated organic compounds. This approach is applicable to structural analysis of a much greater number of perfluorinated organic compounds than previously thought possible.

^{19}F and ^{13}C NMR assignments for Nafion in previous reports[1,3] are also listed in Tables 5 and 4. Our ^{19}F and ^{13}C assignments agree with ref 2 and ref 3, thus confirming these assignments. In our ^{13}C NMR, the two OCF_2 (Cc, Cf) in the side chain are observed to be more clearly resolved. This is because line widths using solution NMR are little smaller than those using solid-state NMR. The respective line widths for Cc and Cf are 0.4 and 0.6 ppm by solution NMR and 0.5 and 1.1 ppm by solid-state NMR.[3]

Table 6 shows the integrated values ^{19}F peaks by solution NMR and by solid-state NMR[3] for Nafion of EW 1100. Here, we assume that the integrated value of the Fd peak is 1.00. The total integrated value of Fc, Fe, and Ff peaks by solution NMR agrees with that by solid-state NMR. That is to say, in the side chain, integrated value by solution NMR agrees with that by solid-state NMR. On the other hand, the integrated value of Fa by solution NMR is smaller than that by solid-state NMR. The integrated value of Fa alone is not obtained in practice by solution NMR because Fa and Fg have not separated. However, as Fg is small, its effect can be disregarded. As this result, in solution NMR, it is proven that over 20% of CF_2 in the main chain is not detected in comparison with solid-state NMR. These phenomena suggest the presence of aggregates in Nafion solution and are explained as follows. Some of the main chains gather inside the aggregates, reducing their mobility, so we are not able to detect them by solution NMR. The side chain is present on the surface of the aggregates, with mobility approximately equivalent to that of the solution state. Moreover, using the line widths of ^{19}F solution NMR, we can also estimate the state of the aggregates. The line width of Fg is the smallest among those in the side chain, and the mobility near the sulfonate group is especially high in the side chain. Specifically, this suggests that the aggregates are pointing their sulfonate groups outward. So far, some reports indicated the presence of aggregates in the Nafion solution, through the use of dynamic light scattering,[6]

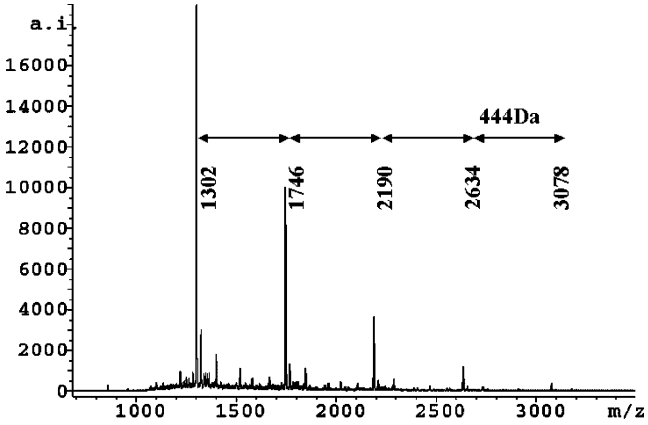
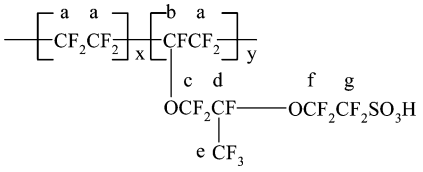


Figure 9. MALDI-MS of Nafion.

Table 6. Integrated Values of ^{19}F NMR of Nafion

^{19}F peak	Fc, Fe, Ff	Fa, Fg	Fb	Fd
Solution NMR: A	6.94	19.70	0.88	1.00
Solid-state NMR: B[*1]	7.00	25.90	0.90	1.00
A/B	0.99	0.76	0.98	1.00

*1 by ref 3



neutron scattering, and X-ray scattering.[7,8] The state of the aggregates suggested here agrees with that in ref 7. In another issue,[1] it was reported that Nafion solution in ethanol was a true solution and that aggregates were undetectable using solution NMR. This contradicts our results. For the Nafion solution at least used here is considered to contain the aggregates, for the following three reasons. (1) In ref 1, there are some errors in the assignments. (2) The magnetic field of the NMR instrument used in ref 1 is low, and the peak separation and signal-to-noise ratio are insufficient. Therefore, this does not seem to indicate an accurate integrated value. (3) The solvent composition of the Nafion solution used in this report does not agree with that in ref 1. The state of the aggregates also changes depending on the solvent compositions[6] and other conditions. The higher-order structures and the physical characteristics of the polymer in catalysis layer in PEFC are greatly influenced by the states of the aggregates in the polymer solution used as the raw material. For these reasons, the evaluation of aggregates provides interesting results.

At first we carried out 2D NMR experiments on Nafion in solution, but we had difficulty obtaining correlation peaks, for the following reasons. The line widths of the ^{19}F peaks in the main chain are very broad, at 300−800 Hz. On the other hand, those of the model compounds are less than 80 Hz. It is well-known that T_2 (transverse relaxation time) generally decreases with increasing line width. This indicates that the T_2 of Nafion is considerably shorter than that of normal perfluorinated organic compounds. It is concluded that magnetization is attenuated for the pulse train of 2D NMR and that the correlation signals cannot be obtained.

It is known that the chemical structures of the perfluorosulfonate ionomers differ by manufacturing company and by type. To elucidate the degradation mechanism and development of a polymer with high durability, it is necessary to examine the chemical structures in detail. Using the assignment method we have presented, it becomes possible to clarify slight differences in chemical structure and the position at which degradation occurs. However, the attention is needed, because the integrated value of CF_2 in the main chain by solution NMR is smaller than practice. Therefore, it is considered that solution NMR is suitable for examining the detailed structure of the side chain of perfluorosulfonate ionomers. To examine the main chain and the whole structure of perfluorosulfonate ionomers, solid-state NMR is appropriate. Moreover, using solution NMR, since information on aggregates in polymer solution is also suggested, significant contributions to research and development of PEFC become possible.

5. Conclusion

1. We apply $^{19}F-^{13}C$ HSQC, $^{19}F-^{13}C$ CIGAR-HMBC, and $^{19}F-^{19}F$ COSY to model compounds of a perfluorosulfonate ionomer, and we determine all ^{19}F and ^{13}C assignments. This represents a new approach to the structural analysis of perfluorinated organic compounds.

2. On the basis of the ^{19}F and ^{13}C assignments of the model compounds and based on the analysis of spin couplings between ^{19}F and ^{13}C of a perfluorosulfonate ionomer, we clearly determine all ^{19}F and ^{13}C assignments of the perfluorosulfonate ionomer. Our assignments agree with those in ref 3, thus confirming the reported assignments of ^{19}F and ^{13}C NMR. In our ^{13}C NMR of the perfluorosulfonate ionomer in solution, two OCF_2 in the side chain are observed as more clearly separated.

3. We clarify the structure of a perfluorosulfonate ionomer in solution by NMR. Results of MALDI-MS support those of NMR.

4. On the basis of the NMR assignments and the integrated values, the presence of aggregates in a perfluorosulfonate ionomer solution is suggested. It is estimated that the aggregates are pointing their sulfonate groups outward and that some of the main chains gather inside the aggregates.

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Supporting Information Available: HSQC, CIGAR-HMBC, and COSY of PFESA; ^{19}F selective decoupled ^{13}C NMR of Nafion. This material is available free of charge via the Internet at http://pubs.acs.org.

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