FTIR Equivalent Weight Determination of Perfluorosulfonate Polymers

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ABSTRACT: Fourier transform infrared (FTIR) and attenuated total reflectance (ATR) spectroscopy studies of the sulfonyl fluoride, potassium salt, and sulfonic acid forms of long and short side chain perfluorosulfonate polymers revealed bands indicative of the sidegroup and backbone compositions, endgroups on the main chain, water content, monomer concentration, and degree of salt hydrolysis. The equivalent weight (EW) of the polymer was obtained by titration and NMR measurements which were then calibrated to either the C—F/C—O—C absorbance band ratio for thin (<1.1 mil) films or to a C—F/SO_2F absorbance band ratio for thick films (5 to 25 mils). An FTIR measurement of the film thickness based on the C—F group concentration was found to be both a function of the actual thickness and the EW; a method for compensating for this EW dependence is described. Esterification and fluorination of the polymers yielded FTIR measurements of the endgroup compositions on the polymer backbone which were shown to consist of —COF, —COOH, —CO_2CH_3, and —CF=CF_2 groups. Thermogravimetric Analysis Infrared (TGA-IR) spectroscopy of the acid form polymers indicates that degradation begins by the decomposition of the —SO_3H group at 320°C followed by bulk deterioration above 400°C. The FTIR techniques detailed herein have been developed for accurate, reproducible, and rapid compositional measurements of Nafion[®] and other perfluorosulfonate polymers. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 165–183, 2011

Key words: FTIR; Nafion[®]; ionomers; equivalent weight; fluoropolymers

INTRODUCTION

The chemical and microstructural properties of Nafion[®] and other perfluorosulfonate polymers control their product and processing characteristics. Throughout the literature, "nominal" equivalent weights are quoted for these polymers since a definitive method for measuring the EW has not been available. The goal of the present investigation was to develop Fourier transform infrared (FTIR) measurement capabilities suitable for fundamental and applied characterization of the polymers.

Nafion[®] (DuPont) is a copolymer of tetrafluoroethylene (TFE) and 2,2,3,3-tetrafluoro-3-[1′,2′,2′-trifluoro-1′-trifluoromethyl-2′-(1″,2″,2″-trifluoro-ethyloxy)ethoxy] sulfonic acid, the polymeric structure of which is

$$\sim CF_2 - CF - (CF_2 - CF_2)_n \sim$$
$$|$$
$$O - CF_2 - CF(CF_3) - O - CF_2 - CF_2 - X$$
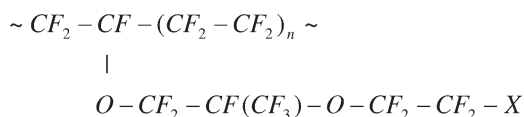
where, $X = SO_2F$ (sulfonylfluoride form), SO_3K (potassium salt form), or SO_3H (sulfonic acid form). The common name for these polymers is Nafion[®] XR which can be alternatively identified as TFE/perfluoro(4-methyl-3,6-dioxa-7-octene-1-sulfonyl fluoride) copolymer.

The polymer composition is expressed in terms of the equivalent weight (EW in g/equiv) defined as the weight in grams of polymer containing one equivalent of acid or, alternatively, the comonomer molecular weight plus $100n$, where n is the number of moles of TFE per mole of comonomer and 100 is the molecular weight of the TFE repeat unit. Thus, the lower the EW, the lower the TFE concentration, and the higher the vinyl ether concentration. The polymer is semicrystalline since the backbone TFE segments tend to crystallize the structure while the sidegroups hinder crystallization. Various ways of computing the concentrations of ion-exchange polymers are summarized in Table I, where MW_{sg} represents the molecular weight of the sidegroup, and Nafion[®] CR is a perfluorocarboxylate polymer.

To examine the chemical properties of these polymers, FTIR spectroscopy was used to study the mid-infrared portion of the spectrum at wavenumbers between 400 and 4000 cm^{-1} to obtain structural information. New analytical and computational methods were developed to determine precise EW values from the FTIR analysis.

Many analytical studies have been performed on Nafion[®] over the years. Dielectric studies[1,2] have

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TABLE I
Composition of Nafion® Polymers

Composition	Form	Nafion® XR	Nafion® CR
MW_{sg} (g/mol)	Unhydrolyzed	446	422
	K^+ Salt	482	446
	Acid	444	408
EW (g/equiv)	Unhydrolyzed	$100n + 446$	$100n + 422$
	K^+ Salt	$100n + 482$	$100n + 446$
	Acid	$100n + 444$	$100n + 408$
Ion Exchange	Unhydrolyzed	$1000/EW$	$1000/EW$
Capacity	K^+ Salt	$1000/EW$	$1000/EW$
(mequiv/g)	Acid	$1000/EW$	$1000/EW$
Mole %	Unhydrolyzed	$[1 + (EW\text{-}446)/100]^{-1} \times 100$	$[1 + (EW\text{-}422)/100]^{-1} \times 100$
	K^+ Salt	$[1 + (EW\text{-}482)/100]^{-1} \times 100$	$[1 + (EW\text{-}446)/100]^{-1} \times 100$
	Acid	$[1 + (EW\text{-}444)/100]^{-1} \times 100$	$[1 + (EW\text{-}408)/100]^{-1} \times 100$
Weight %	Unhydrolyzed	$(446/EW) \times 100$	$(422/EW) \times 100$
	K^+ Salt	$(482/EW) \times 100$	$(446/EW) \times 100$
	Acid	$(444/EW) \times 100$	$(408/EW) \times 100$

elucidated segmental long range rotational and translational motions of the polymer leading to modeling the microstructure. Thermal techniques, such as DSC, TGA/MS, TMA, and DMA, have yielded knowledge of the polymer crystallinity, thermal transitions, and thermal stability while XPS, NMR, SEC/GPC, NIR, rheological, and many other techniques have given a host of interesting and useful analytical data on Nafion®.

The use of infrared radiation to study the vibrational motions in fluoropolymers dates back to the early work on polytetrafluoroethylene (pTFE) in the 1950s. Robinson and Price[3] and Liang and Krimm[4] did some of the first IR studies on pTFE. A landmark paper was published by Moynihan[5] in 1959 where he examined both the amorphous and crystalline regions in pTFE as well as made many of the band assignments which are still valid today.

The earliest published IR studies of Nafion® were done in 1976 by Lopez et al.[6] who examined the sulfonic acid and salt forms of Nafion®. Their studies revealed three main high energy bands indicative of water and C—F bonds; the low wavenumber region of the spectrum was overabsorbed so that no bands attributed to the Nafion® sidechain were observed.

Heitner-Wirguin[7] studied the sulfonic acid form of Nafion® and was the first to perform ATR coupled with transmission FTIR to examine CF_2 bands. The 1060 cm^{-1} band was attributed to the symmetric stretching of the SO_3^- group while the 1720 cm^{-1} peak was attributed to H_3O^+. Lowry and Mauritz[8] studied Nafion® XR in the salt form with ATR and examined the 982 and 1060 cm^{-1} peaks as a function of different cations; they also attributed the 1060 cm^{-1} band to the symmetric stretch of the $-SO_3^-$ group.

Falk[9] did extensive investigations studying the water regions of the Na^+ form Nafion® XR spectrum. He attributed the 1625 cm^{-1} band as a superposition of H—O—H bands and the 1720 cm^{-1} band to the $-CF_2$ backbone. In addition, Falk[10] wrote a review article on the infrared studies performed on Nafion® XR especially related to the polymer's water content.

Mauritz and Gray[11] further examined the O-H region of the IR spectrum to study proton tunneling and were able to distinguish between hydrogen bonded and free water.

Hsu[12] used the $-SO_2F$ and K^+ forms of Nafion® XR at three equivalent weights using pTFE as a control. He found that helical reversal occurs in Nafion® as was previously found in pTFE and other polymers. Equivalent weight did not seem to strongly influence this phenomenon. Hsu attributed the $625/640$ cm^{-1} doublet to this reversal and also found that the 608 cm^{-1} band could be attributed to an $-SO_2F$ group.

Ostrowska and Narebska[13] used N-120 (acid form Nafion® XR) data to curve resolve the O—H region with computer modeling. Quezado et al.[14] also studied the O-H bands in 20 salt forms of Nafion® XR and found that at low water content, the water attaches itself (1) outside the cation-anion pair if the Lewis acid base strengths are well matched or (2) between the cation and anion if the size and charge do not match. They studied the ~ 3500 and 1640 cm^{-1} O—H regions of the IR spectra.

Weber et al.[15] dissolved Nafion® 117 in hexamethylphosphortriamide and carried out XPS, electrochemical, and FTIR measurements. Their studies indicated a close similarity between the solution cast film and the original Nafion® 117 film.

Rieke and Vanderborgh[16] measured the acid form Nafion® XR as a function of temperature. They attributed the 1440 cm^{-1} peak to $-SO_3H$, the 1060 cm^{-1} peak to the symmetric vibration of the dissociated $-SO_3^-$ groups, and the 920 cm^{-1} peak to single-bond S—O vibration of the $-SO_3H$.

Osawa et al.[17] studied the 2075 cm^{-1} band region to examine Pt particles on Nafion®. Zen et al.[18] used Near-IR spectroscopy and a cyanine dye to study thin alcohol solution cast Nafion® 117 films; the dye aided in detecting changes in the hydrophobicity of the polymer. Tsatsas and Risen[19] also used Nafion® XR in the acid form and solution cast films. Far-IR (100–400 cm^{-1}) showed the release of solvent upon heating.

Nandan et al.[20] studied Nafion® XR in the acid and salt forms with transmission and ATR FTIR. They discussed the controversial 982 cm^{-1} peak to which Falk assigned to the C—O—C stretch while Levy et al.[21] assigned this band to a CF$_3$ endgroup. Note that Moynihan never saw a 982 cm^{-1} peak in pTFE. Nandan et al. preferred the CF$_3$ interpretation since they point out that when the membrane is hydrated, the water should hydrogen bond to the ether causing the 982 cm^{-1} band to broaden; broadening was not observed by them but broadening and splitting are observed in the present study. Cable et al.[22] later attributed the 982 cm^{-1} peak to the outermost ether group on the sidechain.

Infrared studies in the literature have mainly concentrated on the sulfonic acid and salt forms of the polymer and on the water absorbance as detected by FTIR. Very little work has been done on the sulfonyl fluoride or carboxylate forms of Nafion® with some notable exceptions.[23–25] In addition, the effects of EW and the correct methods to compute EW are absent from the literature (with the exception of Ref. 25 for the carboxylate polymer) and are discussed in detail in the present paper.

APPARATUS AND PROCEDURES

A Fourier transform infrared (FTIR) spectrometer (Nicolet, Model 730) was used to make all FTIR measurements. Omnic (Nicolet) spectral programming was combined with Visual Basic programs to produce the full range of analyses desired.

To perform most experiments, the polymer sample was cryogenically ground to a fine powder, mixed, and pressed into a film of a thickness dictated by the chase used in the range of 5 to 1000 μm (0.2 to 40 mils). The film was then dried overnight under 20 to 25 in. of vacuum and a nitrogen purge. The drying temperature varied depending on the polymer used but was normally 110°C. The specific sample or instrumentation setup and procedures are described in detail in the respective Discussion of Experimental Results section.

The titration procedure used for Nafion® XR is detailed below. Fifty grams of unhydrolyzed polymer were added to 500 mL of standard hydrolysis solution (30% dimethyl sulfoxide [DMSO], 12% KOH, 58% H$_2$O). This solution was heated to 80 to 90°C

overnight ($\sim$ 18 h). If the EW of the polymer was expected to be below 1000 g/equiv, the DMSO was omitted from the solution. The hydrolysis solution was decanted off and disposed. Deionized water (500 mL) was added to the polymer and heated to 80 to 90°C for 1 h. The H$_2$O was decanted off, and the rinsing was repeated two more times. Five hundred milliliters of 15% HCl was added to the polymer and stirred. This solution and polymer were allowed to set for 30 min. The HCl was decanted and disposed. A second and third acid exchange were completed as above. Deionized water (500 mL) was added to the polymer and allowed to set for 30 min. The water was then decanted off, and the process was repeated until the wet polymer was neutral (using pH paper). The polymer was placed in a vacuum oven overnight at 90°C.

Three grams of hydrolyzed and acid exchanged XR polymer were placed into a 250 mL Erlenmeyer flask with a magnetic stirrer. One gram of NaCl was added with 50 mL of deionized H$_2$O. The flask (with loose fitting top) was heated with stirring at 70 to 80°C overnight ($\sim$ 18 h). One milliliter of bromothymol blue was added to this heated stirring flask, and the titration began using a 50 mL buret and 0.1N NaOH. The end point was when the blue (or green) color remained for 10 min. The time of heating and stirring the polymer + NaCl + deionized H$_2$O was important because the more time allowed, the sharper the end point. The EW was computed using eq. (1).

$$EW = \frac{\text{Polymer Weight (grams)}}{[\text{NaOH (equiv/L)}] \times [\text{NaOH Volume Used (L)}]}$$

(1)

For ATR studies, a KRS-5 (thallium bromoiodide) crystal (50 mm long, 3 mm thick, and 10 mm wide) was used. The crystal had a sufficiently high refractive index (2.35) and transparency throughout the entire mid-IR range. The refractive index of Nafion® XR was measured at the D lines of sodium (about 589 nm) at atmospheric pressure and 25°C to be 1.3413. The ATR sample holder was from Harrick Scientific Corp.

In addition, a Baseline® horizontal ATR (HATR, Spectra-Tech Inc.) with a ZnSe crystal was also used for some studies. This device holds the sample horizontally and directs the beam into the sample with mirrors and can be used for both solid and fluid samples using the proper crystal attachment. It has a clamping device with a rubber pad to push the sample into contact with the crystal if needed. The spectral range available with this device in combination with the Nicolet 730 setup is from 4000 to about 650 cm^{-1}. A variety of polymer films of known titrated EW were pressed under standard conditions and
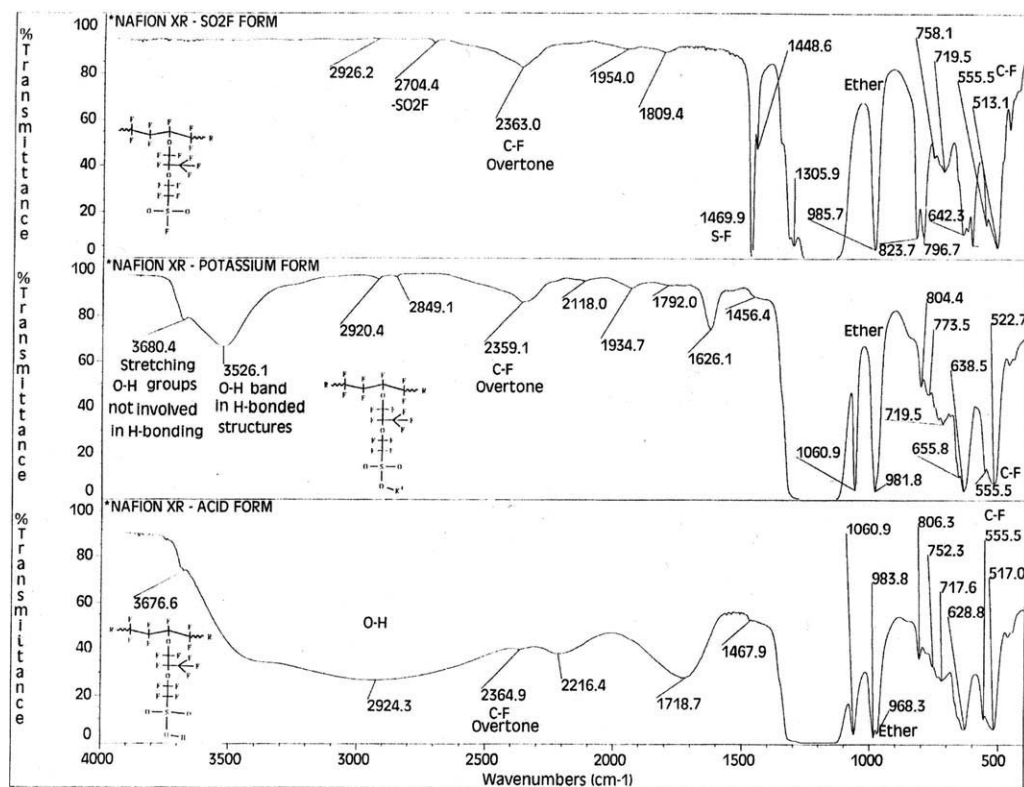
Figure 1 Nafion® sulfonate thin film polymer spectra (sulfonyl fluoride, salt, and acid forms).

each was cut into small strips about 15 mm wide and 60 mm long.

## DISCUSSION OF EXPERIMENTAL RESULTS

Spectral Analysis

Nafion® XR thin film spectra for the unhydrolyzed —SO₂F, salt —SO₃K, and acid —SO₃H polymers are shown in Figure 1. Some of the more prominent peaks are labeled for identification. A complete table of the band assignments made by previous researchers as well as those made during the present work are given in Appendix Table A1.

The ~ 982 cm^{-1} band (in the range of 981 to 986 cm^{-1}) is surrounded by controversy. Levy et al.[21] and later Nandan et al.[20] assigned this peak to the CF₃ endgroup. Falk[9,10] and others believe this peak to be due to the C—O—C ether stretch. The main objection to the ether assignment is that water should hydrogen bond to the ether oxygen and broaden the peak upon hydration; Nandan et al. did not observe any broadening. The present study detects a broadening and splitting of the ~ 982 cm^{-1} band as a function of the form of the polymer. The —SO₂F form is not very hydrophilic and is relatively easy to dry. In this form, the 986 cm^{-1} band is a relatively sharp singlet. The 986 cm^{-1} peak is seen to shift to 982 cm^{-1} in the salt form and become broader. The

salt is known to be more hydrophilic than the sulfonyl fluoride form which may be the cause of the broadening. Alternatively, the change in the end of the sidechain may cause the two ether groups to become dissimilar and the band to split. Heitner-Wirguin[7] also suggested the two ether assignment. In the acid form, hydrogen bonded structures are known to form, further changing the secondary ether linkage resulting in an even greater split of the band.

The ~ 982 cm^{-1} band is assigned to the ether closest to the backbone in the present study and was used to compute the equivalent weight of the thin films while the —SO₂F band, located at 2704 cm^{-1}, was used for the thick film EW measurement. To establish an internal film thickness standard, the major C—F bands, originally described by Moynihan,[5] at 513, 555, 719, ~ 1200, and 2365 cm^{-1} were studied. The 2365 and 555 cm^{-1} C—F bands were found to give the best film thickness accuracy for both the thick and thin film methods, respectively, and were also used in part to measure the EW.

Heitner-Wirguin[7] and Lowry and Mauritz[8] suggested that the 1060 cm^{-1} band in the salt and acid spectra is due to the S-O stretch. Nandan et al.[20] further suggested that this peak is due to hydrogen bonded sulfonate groups. Since the 1060 cm^{-1} band is absent from the —SO₂F spectrum in the present study, the previous assignments need to be examined more closely. The S—O bond energy is different
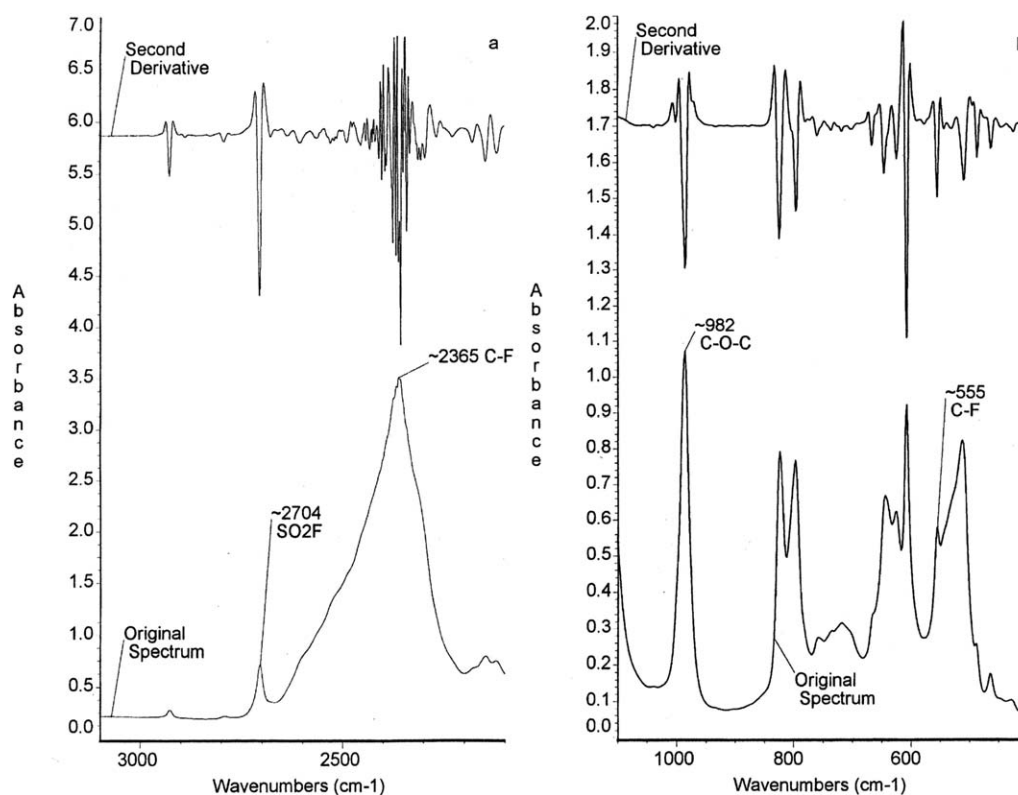
Figure 2 —SO$_2$F polymer derivative spectra: (a) 1087 g/equiv, 40 mil thick film, high wavenumber region; (b) 1076 g/equiv, 0.5 mil thin film, low wavenumber region.

in a —SO$_2$F structure versus a —SO$_3^-$ structure so it is not unreasonable to expect a shift in the 1060 cm^{-1} band. In addition, the band is broader in the acid form than in the salt form indicating the presence of hydrogen bonded structures in the acid form.

An important band in examining the amount of the polymer that is converted to the salt or acid forms is the 1470 cm^{-1} band. This peak is attributed to the S—F motion (unlike Falk who attributed the band to CF$_2$ groups) but could involve a more complex series of bonds. A calibration of this peak ratioed to a C—F band gives the percent hydrolysis during the conversion to the salt form. Likewise, the disappearance of the 2704 cm^{-1} peak would provide similar information although this peak is much weaker than the 1470 cm^{-1} peak.

In the salt spectrum, the O—H groups not involved in hydrogen bonding (free water) can be distinguished from O—H structures involved in hydrogen bonding by the two bands at 3680 and 3526 cm^{-1}. The O—H band broadens considerably in the acid form yet the 3680 cm^{-1} band (now shifted to 3677 cm^{-1}) is still present. The O—H region of the spectrum has been dealt with extensively in the literature.[11]

To check for interference and overlapping bands, the second derivative was taken of the SO$_2$F spectrum, as shown in Figure 2 for both thick (a) and thin (b) films. For the thin film, the $\sim$ 982 cm^{-1} ether and 555 cm^{-1} C—F bands are relatively clean with only two small side lobes present on the ether band; therefore, an EW derived from these peaks should be devoid of other compositional interference. For the thick film spectrum, the 2704 cm^{-1} SO$_2$F band is very clean, but the 2365 cm^{-1} C—F broad band is composed of a series of combination bands. Within these multiple peaks, a band at 2550 cm^{-1} was chosen to minimize the distortion of other surrounding peaks which is discussed in greater detail in the following sections.

Standards

The most important starting point for all FTIR equivalent weight measurements is the development of calibration standards upon which all subsequent data are compared. To this end, sulfonate polymers were first made over the widest possible equivalent weight range, from 700 to 1800 g/equiv. All samples were pressed into films and measured on the FTIR. To check for homogeneity, a few films were dissolved[26] in a Flutec PP-11 (Rhone-Poulanc) solvent and remeasured with the FTIR. The spectra and EW values obtained for the mixed versus dissolved samples were in good agreement.

Titration is the most accurate and reproducible method of measuring the EW and was used here to determine the absolute EW of all sulfonate polymers. Unfortunately, titration is very time consuming and labor intensive which is why the technique is not used routinely. The titration procedure detailed in the Apparatus and Procedures section was followed. A thorough check was made of any potential errors that could have occurred during the titration procedure such as inadequate washing, incomplete hydrolysis, inexact endpoint detection, incomplete acid treatment, and inaccurate dry sample weight determination; however, none of these possible sources of error (or any combination of these errors) could produce an error of more than 30 g/equiv. From experiments, however, titration has been found to measure the EW to within ±5 g/equiv.

Note that since titration gives the EW in the acid form, all EW values quoted in the present the paper, regardless of what form the measured polymer is in, are stated as if the polymer were in the acid form. To convert the acid form EW (EW_{acid}) to either the sulfonyl fluoride (EW_{SO_2F}) or potassium salt (EW_{SO_3K}) EW, use eqs. (2) and (3).

$$EW_{SO_2F} = EW_{acid} + 2 \qquad (2)$$

$$EW_{SO_3K} = EW_{acid} + 38 \qquad (3)$$

To check the accuracy of the titration method and to provide an independent absolute means of calibrating the data, the equivalent weight was measured with fluorine-19 NMR at melt temperatures between 250 and 340°C. All polymers were cryogenically ground to a fine powder, mixed, pressed into films, dried in a vacuum oven, and measured. The NMR data were taken by increasing the temperature until the temperature reached a point (generally 340°C) where the instrument readings were internally consistent. The measured EW can vary over a wide range in this temperature region. Note also that the NMR reports EW data in the SO_2F form, so that 2 g/equiv were subtracted from the NMR EW values to convert them to the SO_3H EW as measured by FTIR and titration. The NMR values show a good correlation with titration EW data in Figure 3 ($r^2 = 0.998$) over the EW range of 700 to 1800 g/equiv

$$EW_{NMR} = 0.95019\,EW_T + 35.76422 \qquad (4)$$

where, EW_T = equivalent weight (g/equiv) based on a titration measurement and EW_{NMR} = equivalent weight (g/equiv) based on a NMR measurement.
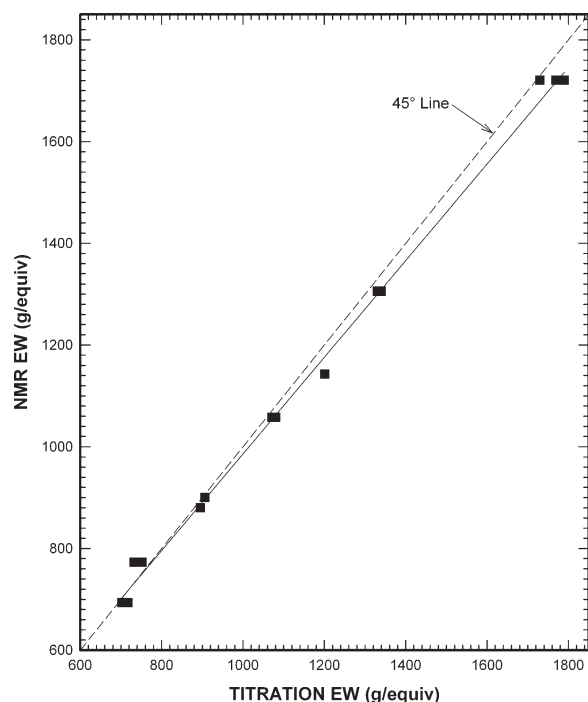
Figure 3 Equivalent weight determination by NMR and titration for Nafion® XR.

Equivalent weight determination

Thin films

A thin ($\sim$ 1 mil) film FTIR method, based on the $\sim$ 982 cm^{-1} ether band measurement, was developed to compute the EW of all chemical forms of Nafion®. The thin film technique requires measuring the absorbances A($\sim$ 982), A($\sim$ 555), and a baseline at A($\sim$ 900) and computing the band ratio (*BR*) defined in eq. (5).

$$BR = \frac{A(\sim 555) - A(\sim 900)}{A(\sim 982) - A(\sim 900)} \qquad (5)$$

where, $A(\tilde{\nu})$ = absorbance at a peak-picked wavenumber near wavenumber $\tilde{\nu}$. The calibration standards are plotted in Figure 4. The best fit to the data (lower graph) was found to be a sigmoidal regression given by

$$EW = c - d\,\ln\left(\frac{b}{BR - a} - 1\right) \qquad (6)$$

where, $a = 0.265$, $b = 0.905$, $c = 1353.135$, and $d = 265.175$. Note that many other regression fits were attempted, but the sigmoidal regression gave the most consistent and accurate results.

The reason for the deviation from linearity at the EW extremes may be caused by differences in the polymer morphology. At low EW, the rotational motion of the sidegroups is sterically hindered by
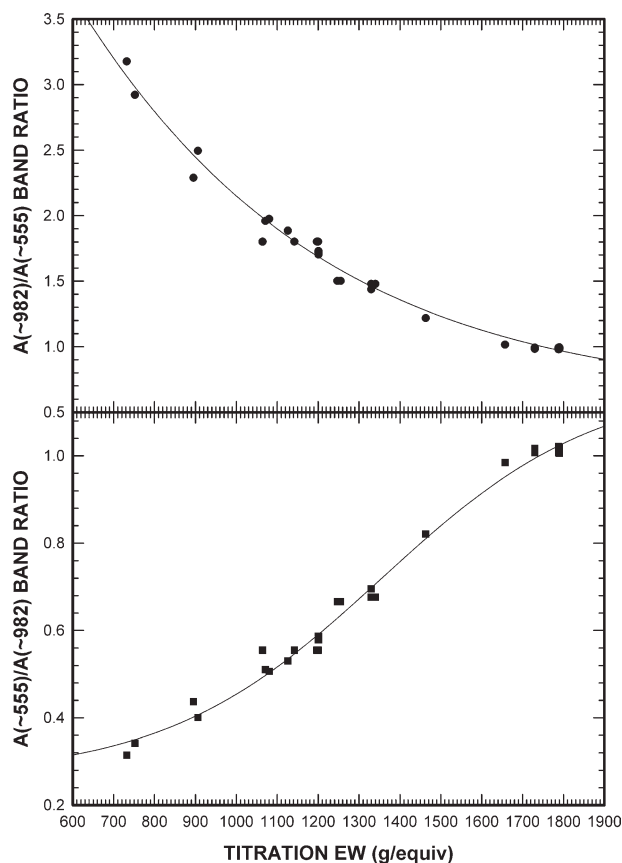
Figure 4 $\sim 555 / \sim 982 / \sim 900$ thin film Nafion® XR sigmoidal calibration curves.

neighboring sidegroups[1]; the vibrational motion may also be affected by steric considerations. At high EW, the increasing crystallinity suppresses the motion of the sidegroup bands. In the mid EW region, steric and crystallinity phenomena are less important, and classical Beer's law behavior is observed.

One problem encountered using the thin film method was that in measuring EW values less than ~ 850 g/equiv, the 555 cm^{-1} band became difficult to measure due to the competing effects of C—F groups along the sidegroups versus those along the backbone. In addition, at these low EW values, the films had to be pressed much less than 0.5 mils which caused handling problems. Despite these limitations, the method provides an excellent way to obtain very accurate, quantitative information on Nafion® XR polymers.

Thick films

As an alternative to the thin film technique described above, a thick film technique was developed. For thick films, the ether band is overabsorbed and cannot be used in the measurement. Alternatively, the —SO$_2$F band at high energy is used which

prohibits measurements of hydrolyzed or acidified samples. The thick film method uses a ~ 15 mil film to examine the —SO$_2$F peak relative to a shoulder on the C—F peak. The technique is valid for any dried, unhydrolyzed Nafion® XR polymer. Numerous thick films were pressed at about 270°C using a 15 mil chase from the polymers used in the thin film analysis. An optimum wavenumber along the C—F peak was determined to be 2550 cm^{-1} with a 2745 cm^{-1} baseline.

The band ratios (defined in Table II) were computed for each film and fit to sigmoidal and other regressions. The best fit to the data is given by the sigmoidal regression [eq. (6)] and the A(2550)/A(~ 2704) band ratio with a A(2745) baseline (Method 2b in Table II), as shown in Figure 5 and defined below.

$$BR = \frac{A(2550) - A(2745)}{A(\sim 2704) - A(2745)} \qquad (7)$$

The parameters resulting from this regression are given in Table II. The A(2550)/A(~ 2704) band ratio represents the best fit curve ($r^2 = 0.99227$) of all the correlations tested for Nafion®. Note that the band ratio represents the C—F band (proportional to the amount of polymer measured or the film thickness) in the numerator and the —SO$_2$F band (corresponding to the amount of sidegroups) in the denominator. This relationship is similar to quoting moles or grams of polymer per sidegroup (equivalent) which is the definition of equivalent weight.

One variable that has not been explored in depth is the influence of water on the —SO$_2$F band. For the thin film EW technique, the ether band was not affected by water (except possibly for a slight broadening), and the water and ether peaks were spaced far away from one another so that no peak overlap occurred. For the thick film analysis, the O—H band is very close to the —SO$_2$F band and may indeed affect the EW measurement if the two bands begin to overlap when the water concentration is large.

The equivalent weight calibrations, designated by a * in Table II, were programmed into the FTIR using Omnic (Nicolet) linked via DDE commands to Visual Basic. In the program, a spectral library was established to allow identification of unknown samples. The comparison between the sample spectrum and the library spectra is performed by taking the first derivative of all spectra, comparing all library derivatives at each wavenumber to the sample derivative, and arriving at the best match.

A 15 mil XR film is required to make the EW measurement. If a film is pressed outside of a 10 to 20 mil range, the measurement will be in error. The thick film calibration yields an EW with a reproducibility within 10 g/equiv (due to the sample

TABLE II
Band Ratio Correlations for Perfluorosulfonate Polymers

	File Parameters				Sigmoidal Fit: $BR = a + b / \{1+exp[(c-EW)/d]\}$ or $EW = c - d * ln\ [b/(BR-a) - 1]$				
Number	Polymer Wavenumbers	Thin/ Thick Film	EW Range (g/equiv)	XR/CR	a	b	c	d	r^2
1a	$\sim 982/\sim 555/\sim 900$	Thin	700–1800	Nafion XR	0.59830699	27.297703	−508.26823	−537.02837	0.98692
1b[a]	$\sim 555/\sim 982/\sim 900$	Thin	700–1800	Nafion XR	0.26502961	0.90509793	1353.1347	265.17477	0.99203
2a	$\sim 2704/2550/2745$	Thick	700–1800	Nafion XR	0.26037777	3.9863106	−592.08646	−690.92426	0.98792
2b[a]	$2550/\sim 2704/2745$	Thick	700–1800	Nafion XR	1.0350967	1.8480534	1266.7245	306.66756	0.99227
3a	$\sim 2704/\sim 2365/\sim 2760$	Thick	700–1800	Nafion XR	0.086251715	0.20545741	1027.5923	−274.2471	0.9839
3b	$\sim 2365/\sim 2704/\sim 2760$	Thick	700–1800	Nafion XR	3.8542183	6.9191212	1319.4055	206.68261	0.99142
4a	$\sim 2704/2300/\sim 2760$	Thick	700–1800	Nafion XR	0.1846261	0.21593909	1140.6572	−205.35975	0.94203
4b	$2300/\sim 2704/\sim 2760$	Thick	700–1800	Nafion XR	2.6228448	2.6380564	1281.5682	162.59511	0.97103
5a	$\sim 2704/2559/\sim 2760$	Thick	700–1800	Nafion XR	0.28902245	3.8374168	−468.35362	−673.79487	0.98683
5b	$2559/\sim 2704/\sim 2760$	Thick	700–1800	Nafion XR	0.9611614	1.6597207	1263.0416	298.72527	0.99156
6a	$\sim 982/\sim 555/\sim 900$ [25]	Thin	900–1900	Nafion CR	0.57978547	51.770268	−780.1816	−464.23247	0.92941
6b[a]	$\sim 555/\sim 982/\sim 900$ [25]	Thin	900–1900	Nafion CR	−1.0103218	8.8602837	3528.7614	1685.5439	0.96601
7a	$\sim 2704/2550/2745$	Thick	400–1200	Dow XR	0.54716429	7.6884831	−56.184899	−257.93812	0.99844
7b[a]	$2550/\sim 2704/2745$	Thick	400–1200	Dow XR	0.15206513	1.6835696	656.53909	255.53364	0.99727

[a] Calibrations currently used for EW measurements.

inhomogeneity) and an accuracy within 10 to 15 g/equiv (due to the calibration). The FTIR instrument (reproducibility) error is less than 1 g/equiv, but the calibration (due to slight inhomogeneities in the Nafion® standards) has a greater error. The range of the calibration should be more than adequate for the lowest EW catalysis or fuel cell polymer applications to tracking startup conditions during plant production which may yield very high EW polymer.

The advantages of the thick film technique are (1) the ease of handling 15 mil films compared to 1 mil films, (2) the lower EW measurements possible with 15 mil films, and (3) the less rigid thickness tolerances with the 15 mil technique (1 mil films had to be pressed from 0.5 to 1.1 mils whereas 15 mil films can be pressed from 10 to 20 mils). Note that in all cases the peak area can be used instead of the peak height. No discernable improvement in accuracy or reproducibility, however, was achieved using peak areas.

Film thickness determination

It was realized early in the present research that the film thickness would be an important variable in measuring the polymer chemical properties. One could take the approach of specifying the same film thickness for every analytical measurement; however, this is impractical given the inability to press the exact same film thickness over a range of EW values even if the same pressing chase is used. The varying crystallinity and EW distributions among Nafion® samples dictate differences in pressing temperatures resulting in varying viscosities which in turn lead to a range of flow properties producing various film thicknesses. Since even small variations in the film thickness dic-

tate large differences in the measured EW, it was decided to develop a technique that would factor out the thickness dependence. The FTIR method would then be independent of film thickness.
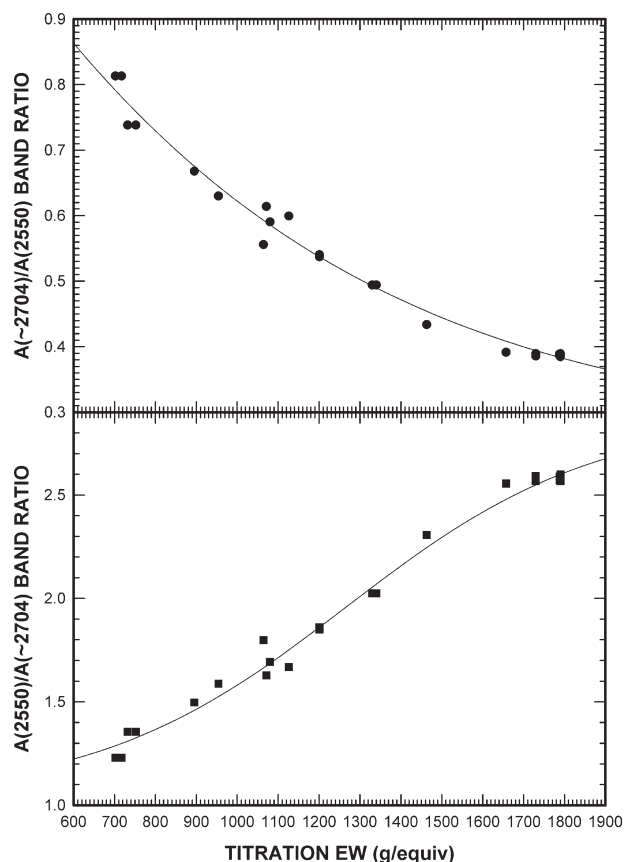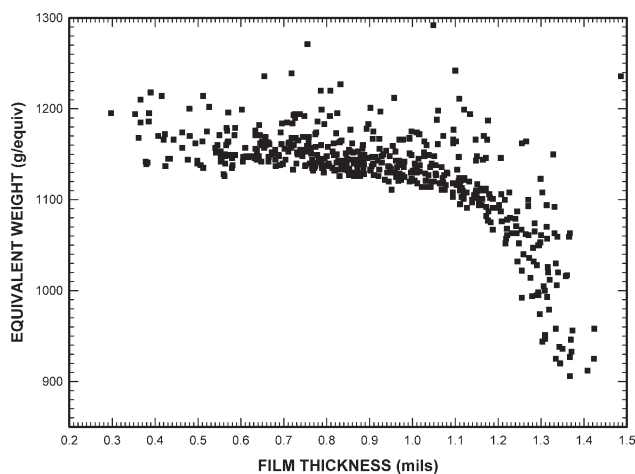

Figure 5 2550/$\sim$ 2704/2745 thick film Nafion® XR sigmoidal calibration curves.

Figure 6   Thin film EW dependence on film thickness for a blended 1080 g/equiv sulfonyl fluoride polymer.

As a first attempt to eliminate the effect of the film thickness on the final computed EW, an internal thickness standard was established as is normally done in quantitative infrared studies. For thin films, Figure 3 in Reference[25] can be used as a thickness calibration for sulfonate as well as carboxylate fluoropolymers. Using this correlation, at film thicknesses less than 1 mil, the computed EW is virtually independent of thickness. Films greater than 1 mil thick tend to bias the computation toward a lower EW value, as shown in Figure 6. For thick films, this simple thickness correction was inadequate since the computed thickness was found to strongly depend on the EW of the polymer.

To account for this thickness dependence, two polymers with vastly different EW values were measured over a thickness range of 5 to 22 mils. To analyze the data and obtain an equation which relates the EW, film thickness, and thickness band height, the data were correlated in a manner described in the Appendix. The methodology developed for the 2550/∼ 2704 band ratio was also found applicable to the alternative band ratios given in Table II. To illustrate this mathematical procedure, consider the high and low EW regressions obtained for thick films from the data shown in Figure 7. The following two correlations ($r^2 = 0.99$ for both regressions)

$$1076 \; EW: \qquad T_m = 45.903554 \, T_f - 1.083527 \qquad (8)$$

$$1789 \; EW: \qquad T_m = 48.013476 \, T_f - 0.300765 \qquad (9)$$

are in the form of eqs. (14) and (15) in the Appendix, where $y = T_m$, $x = T_f$, $z = EW$, and the numerical values represent the parameters c, d, e, and f. Note that T_m = mechanically measured thickness (mils) and $T_f = A(2550) - A(2745)$.
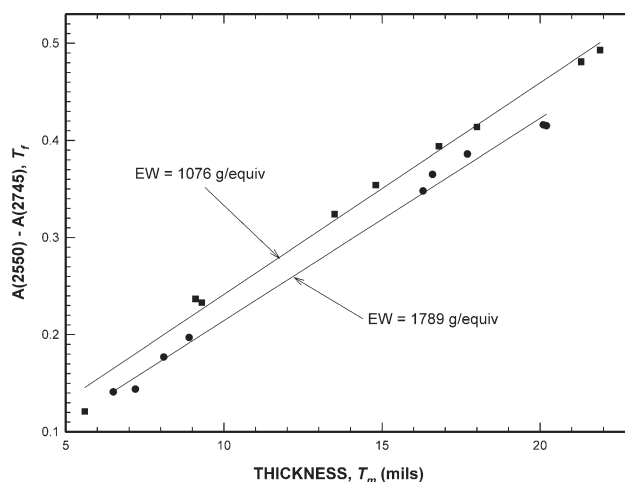

Figure 7   A(2550) film thickness calibration for two thick Nafion® XR films of different EW.

After obtaining the linear regression for each sample, interpolation between the two curves was performed so that the EW dependence on thickness could be computed for any future sample. Substituting eqs. (8) and (9) into eq. (20) gives

$$T_m = [-0.002959217 \, (EW_i - 1076) + 48.013476] \, T_f$$
$$-0.001941504 \, (EW_i - 1076) - 0.300765 \qquad (10)$$

As an example, if the EW is measured to be 1200 g/equiv and the thickness band is given by $T_f = A(2550) - A(2745) = 0.3$, then from eq. (10), $T_m = 13.86$ mils.

To check experimentally the EW dependence on film thickness, the mechanically measured film thickness is plotted against the band ratio in Figure 8 for a series of thick films. The goal was to minimize the influence of thickness on the EW measurement or, to state this as a different way, to make the slopes in Figure 8 nearly zero, as shown by the regressions in eqs. (11) and (12).
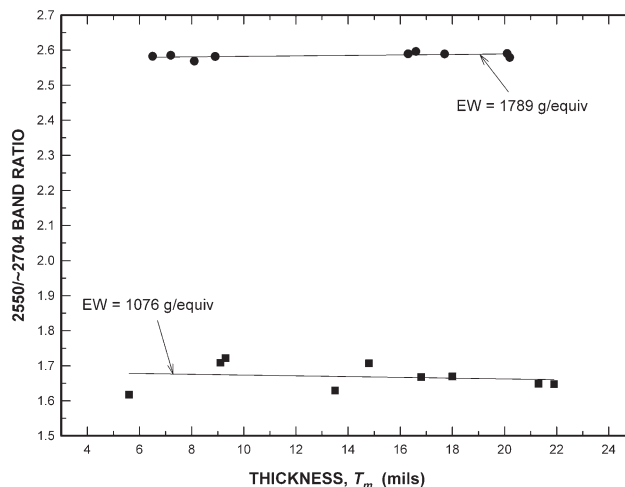
Figure 8   2550/∼ 2704 band ratio dependence on film thickness for Nafion® XR.

$$1076 \; EW: \qquad BR = -0.0011 \, T_m + 1.6846 \qquad (11)$$

$$1789 \; EW: \qquad BR = 0.00067 \, T_m + 2.5756 \qquad (12)$$

The correlations are good; however, data scatter for the 1076 g/equiv polymer may reflect inherent inhomogeneities or broadness of the EW distribution for this polymer.

At this point, some discussion must be included as to the validity of using the C—F band as a thickness gauge. Specifically, is the film thickness proportional to a C—F band and is the band ratio which uses a C—F band accurate?
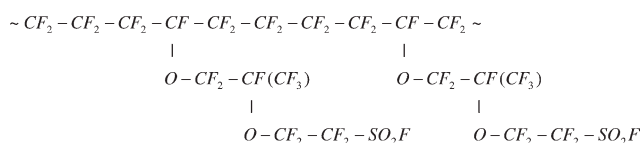
Consider two polymer films of exactly the same thickness (T_m) but different EWs:

1. Low EW sample with EW = EW_{low}
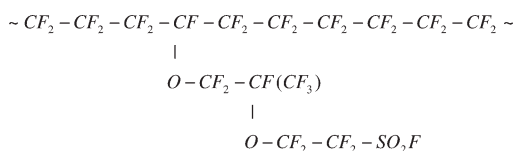2. High EW sample with EW = EW_{high}

In the IR beam, the measurement area is constant so that the volume of each sample measured (product of the area and T_m) is constant. Assuming the density does not change with EW, the mass of polymer being measured in both cases is identical. Also assume that the chains can pack together to the same extent (actually the higher EW sample should be able to pack or crystalize to a greater extent) in both samples and that the average length of chains is constant (same molecular weight) for the two samples.

Consider one hypothetical chain from each polymer (of equal chain length) as shown below.

Low EW:

$$\sim CF_2 - CF_2 - CF_2 - CF - CF_2 - CF_2 - CF_2 - CF_2 - CF - CF_2 \sim$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad |$$
$$O - CF_2 - CF(CF_3) \qquad\qquad O - CF_2 - CF(CF_3)$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad |$$
$$O - CF_2 - CF_2 - SO_2F \qquad O - CF_2 - CF_2 - SO_2F$$

High EW:

$$\sim CF_2 - CF_2 - CF_2 - CF - CF_2 - CF_2 - CF_2 - CF_2 - CF_2 - CF_2 \sim$$
$$|$$
$$O - CF_2 - CF(CF_3)$$
$$|$$
$$O - CF_2 - CF_2 - SO_2F$$

Counting the number of C—F and CF_2 groups along the backbone and sidegroup for each chain results in the values shown in Table III. Therefore, whether C—F or CF_2 groups are counted, the low EW sample always has more total groups.

Now consider the hypothetical spectrum in Figure 9. Peak a decreases in amplitude (from sample 1 to 2) due to either (i) fewer groups being present on the sidegroup, (ii) fewer groups being present on the backbone, or (iii) fewer total groups. Conversely, peak b increases in amplitude (from sample 1 to 2)

TABLE III
**C—F and C—F$_2$ Concentrations for Hypothetical Polymers**

	Low EW polymer	High EW polymer
Backbone # of C—F Groups	18	19
Sidegroup # of C—F Groups	20	10
Total # of C—F Groups	38	29
Backbone # of C—F$_2$ Groups	8	9
Sidegroup # of C—F$_2$ Groups	6	3
Total # of C—F$_2$ Groups	14	12

due to (i) more groups being present on the sidegroup, (ii) more groups being present on the backbone, or (iii) more total groups. Taking the two peaks together either (i) one must be the sidegroup and the other must be the backbone or (ii) much more complex reason (as described below).

It is well known that as the polymer thickness increases (all other properties being equal), the overall spectrum increases in amplitude. This phenomenon, however, does not allow a distinction to be made between bands primarily influenced by C—F groups along the sidechain and those groups along the backbone.

Figure 10 presents scans of five different Nafion®—SO$_2$F XR polymers with equivalent weights ranging from 775 to 1657 g/equiv and all pressed to ~ 0.6 mils thick. The amplitude of the ether band at ~ 982 cm^{-1}, the S—O band at 608 cm^{-1}, and the 805 cm^{-1} band (possibly due to CF$_2$ sidechain bonds) increase with decreasing EW as expected. The 824 cm^{-1} band is as yet unassigned but is the only band strongly present in the —SO$_2$F form implying a S-O assignment; this band also increases in amplitude with decreasing EW. Most of the other bands are due either to the C—F groups along the sidechain and/or backbone.

Since a lower EW polymer produces more sidechain and total C—F bonds per unit volume (as shown in Table III), peaks that increase in amplitude
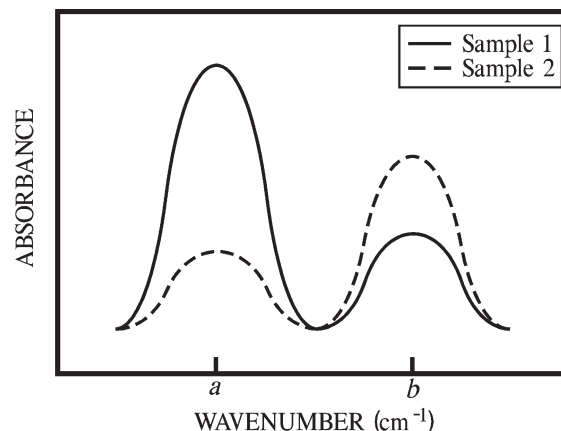
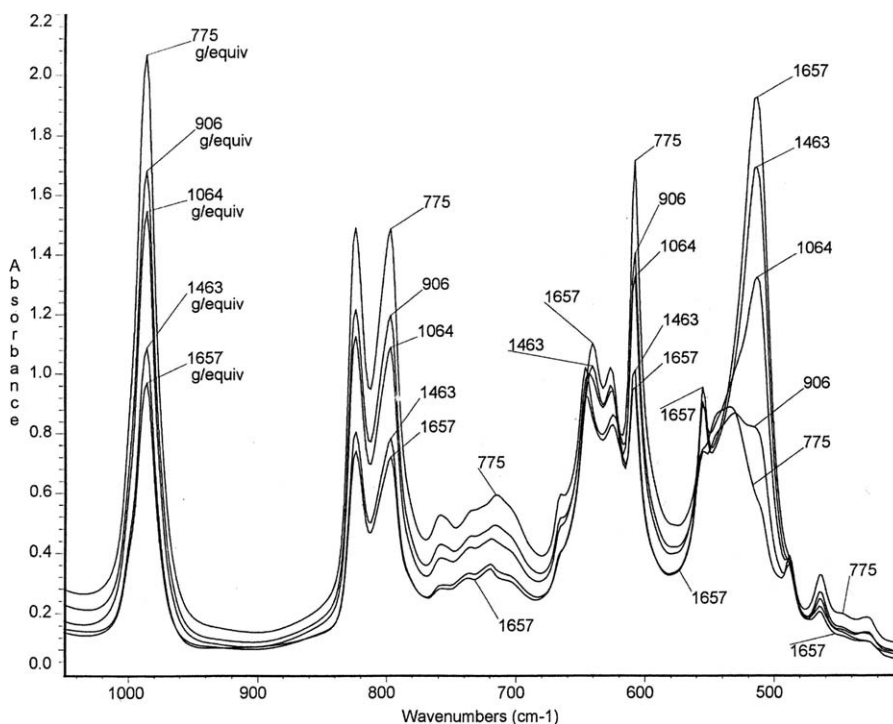**Figure 9** Hypothetical spectra of two polymer samples.

Figure 10 Spectral changes as a function of equivalent weight for thin SO_2F Nafion® films.

with EW must deal only with species exclusively along the backbone. These peaks in Figure 10 are located at 510 and the 627/639 cm^{-1} doublet which have previously been identified as C—F bands.[5,12] This indicates that a C—F bond on the backbone may have sufficiently different character than C—F groups on the sidechain to produce these peaks. The 555 cm^{-1} peak seems to be a combination band of both sidechain and backbone C—F groups. Below a certain EW value ($\sim$ 900 g/equiv), the 555 cm^{-1} and the larger 510 cm^{-1} peak become less defined. At this point the vibrational motion of the C—F groups along the backbone could possibly be affected in some manner by the larger number of sidechains.

The bands appearing at 464, 700–720, and 805 cm^{-1} all increase in amplitude with decreasing EW. The 1306 cm^{-1} band (not shown in Fig. 10) also increases in amplitude with decreasing EW but has not been identified as a C—F; it is believed by the author to be due to the pendant —CF$_3$ on the sidechain. All these bands (except the 1306 cm^{-1} band) are known to be due to C—F motions[5,10] in pTFE. For these bands to increase in amplitude with decreasing EW indicates that these bands are mainly influenced by the sidechain C—F groups. Please note that the peak amplitude of these bands is the summation of the backbone and sidechain C—F groups, but since they increase in amplitude with decreasing EW, the sidechain motions must overshadow the backbone motions.

Also, note that the CF/CF$_2$ region at 1200 cm^{-1} and the combination band at 2365 cm^{-1} (used by the

thick film FTIR method) increase in amplitude with decreasing EW. Since these CF/CF$_2$ peaks have been identified in the pTFE homopolymer[5] along with the 555 cm^{-1} band, they must represent the total C—F groups along the sidechain plus backbone.

The present definition of equivalent weight now comes into question. The EW presently represents the grams of polymer per mole of repeat units (or the grams of polymer in a repeat unit per one sidechain). The sidechain concentration can be measured precisely with either of the —SO$_2$F bands. The weight of the polymer, though, is most accurately given by the total C—F concentration (sidechain + backbone). Both thin and thick film measurements use the total C—F concentration as measured by the $\sim$ 2365 and $\sim$ 555 cm^{-1} bands; therefore, the EW dependence on thickness is accurately quantified using these thickness bands to compute the EW.

It is not inconceivable to redefine the EW in terms of the backbone C—F concentration or to even define an equivalent volume (EV) based on the total C—F groups. To be of use, these new ways of defining the EW would have to be coupled with the measurement of other properties of the Nafion® polymers.

ATR studies

In theory an ATR method for measuring polymer films would circumvent the film thickness problem. Since the apparent crystal size in the polymer (30 to 60 Å, as measured by X-ray diffraction) is much smaller than
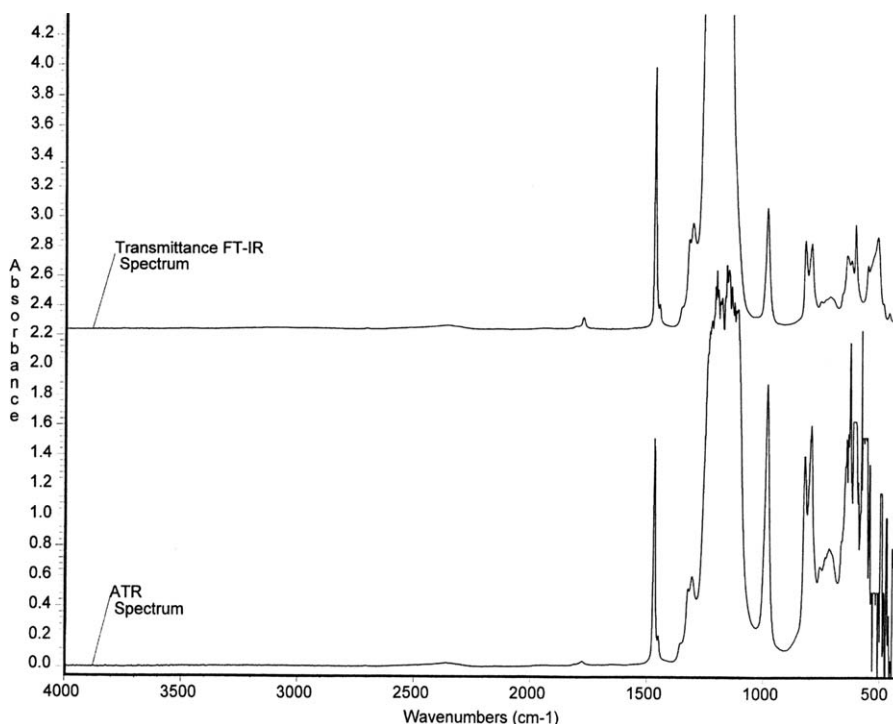
Figure 11 ATR versus transmittance spectra for a 1076 g/equiv —SO$_2$F form Nafion® polymer.

the wavelength of the IR beam (2.5 to 25 μm), no scattering should occur and, therefore, the beam should penetrate the same distance into each polymer sample; thus no thickness correction is needed. This method would also be useful for bifilms, laminates, or very thick films where transmission analysis is prohibited.

A typical ATR spectrum is shown in Figure 11. The 1200 cm^{-1} C—F region is slightly clearer using ATR. In addition, the peak locations are similar to the transmission spectrum although the relative intensities vary. A number of sulfonyl fluoride polymer samples in the equivalent weight range of 1050 to 1800 g/equiv were measured with ATR. The 982 cm^{-1} (ether) peak and the 1467 cm^{-1} peak (attributed to the —SO$_2$F group at the end of the sidechain) were measured with baselines at 900 and 1390 cm^{-1}, respectively. The peak heights of each of the two bands were correlated with EW values obtained from titration, but the data were not sufficiently reproducible or steady to allow an accurate EW calibration.

Endgroups

The polymerization and processing of Nafion® produces a variety of endgroups along the polymer backbone. To eliminate the potential reactive nature of these endgroups, all Nafion® sulfonate polymers are fluorinated to convert the endgroups to stable structures. A measure of the composition and con-

centration of endgroups is needed, however, to control polymerization and postprocessing of the polymer.

A standard 1070 g/equiv, ∼ 15 mil, unfluorinated Nafion® polymer was first analyzed by FTIR; the resulting spectrum in the carbonyl region is shown at the top of Figure 12. All peaks are peak-picked by the computer. The spectrum displays two distinct peaks at 1807.4 and 1776.6 cm^{-1}. Both peaks are thought to be due to the carboxylic acid endgroup
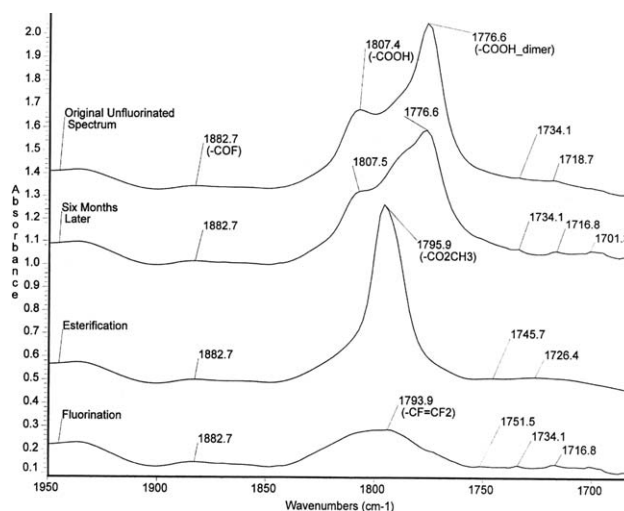

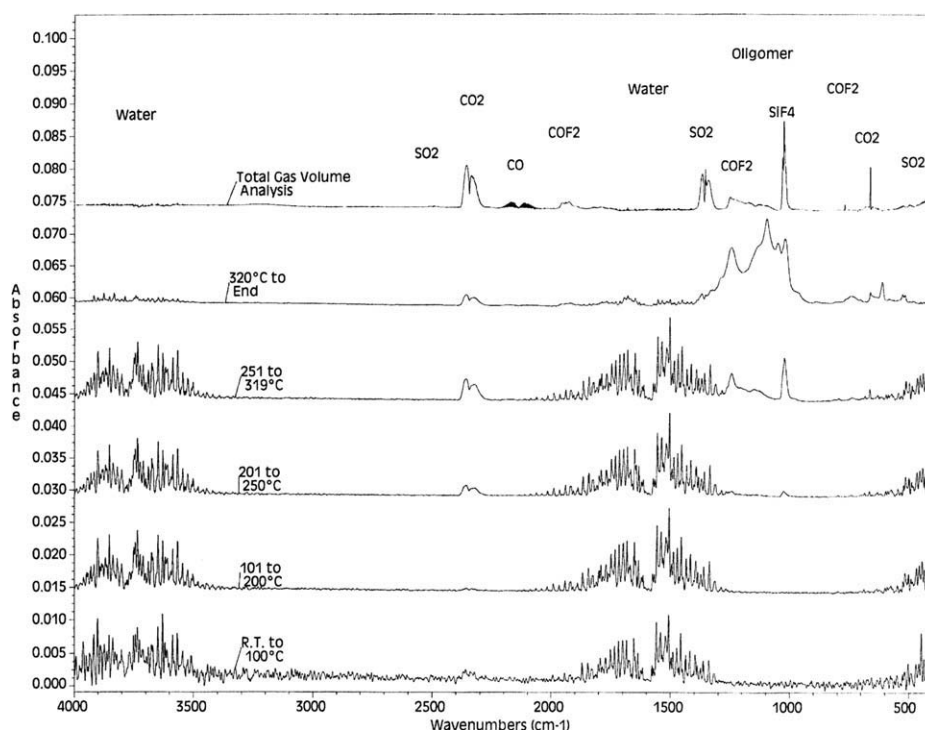**Figure 12** Fluorination and esterification of the carboxylic endgroups of Nafion® XR.

Figure 13 TGA-IR spectra for sulfonic acid form Nafion®.

arising from polymerization. In particular, the 1776.6 cm^{-1} peak occurs in the carboxylic acid form of Nafion® and is due to the acid carbonyl band;[25] this endgroup peak in Figure 12 is also due to the carbonyl in the —COOH dimer while the 1807.4 cm^{-1} band is due to the —COOH. The very small peak at 1882.7 cm^{-1} is due to carbonyl fluoride (—COF) endgroups; under certain conditions, such as during the production of extremely low EW polymers where two vinyl ether monomers can react with one another, this —COF band can be dominant in the spectrum.

The second spectrum in Figure 12 was taken on the same polymer film exposed for six months to ambient air at room temperature. The film swelled with time thus raising the baseline, but the concentration of endgroups actually decreased with time. The acid fluorides given off may tend to further fluorinate the polymer although a band in the 1777 to 1807 cm^{-1} range cannot be discerned.

As a next step, the six-month-old polymer was methylated (esterified) with trimethyl orthoformate (TMOF) to convert the —COOH endgroups to the methyl form to gain some further insight to these peak assignments. The resulting spectrum is shown as the third spectrum in Figure 12. The methylated sample spectrum indicates that the —COOH groups were converted to —CO_2CH_3 groups indicated by the peak at 1795.9 cm^{-1}. The methyl ester carbonyl occurs at 1790 cm^{-1} in the ester form of Nafion® very close to the 1796 cm^{-1} shown in the present spectrum.[25] In addition, the -COF endgroup at

1882.7 cm^{-1} did not change during the esterification which is reasonable.

Finally the polymer was fluorinated with fluorine gas which converted all the endgroups to vinyl —CF $= CF_2$ (or —COF) groups. The broad band centered at $\sim$ 1794 cm^{-1} represents the fluorinated vinyl group while the —COF is still present at 1882.7 cm^{-1}.

TGA-IR

Thermogravimetric analysis coupled with infrared spectroscopy (TGA-IR) is a useful extension of FTIR technology to examine the off-gases from a heated polymer. This technique was employed to observe if the polymer loses functionality at temperatures below its decomposition temperature.

The sulfonic acid form Nafion® polymer was sealed under nitrogen in a quartz tube and placed in a TGA-IR chamber. The sample was then heated from room temperature to about 350°C. The evolved gases flowed through a 20 cm IR gas cell and were scanned continuously by the FTIR yielding an off-gas spectrum every 30 s. All gases were collected in a polyvinylfluoride gas bag, and at the end of the experiment, the total quantity of gas collected was measured with FTIR.

The results are plotted in Figure 13 and described below. From room temperature to 200°C only water came off the polymer. CO_2 was also present in all the spectra. From 201 to 250°C, water and CO_2 are still present; in addition, a peak at 1030 cm^{-1}

indicated the presence of SiF_4 which would result from HF (in the polymer) etching away at the glass components in the chamber. From 251 to 319°C, water, CO_2, and SiF_4 are still present (the SiF_4 peak has grown significantly); also, other peaks in the 1100 to 1300 cm^{-1} region are beginning to form. In any FTIR scans of Nafion® films, this region is always strongly absorbing and is attributed to a combination band involving all —CF_2— groups. In this instance, most likely some low MW oligomers (not monomers) began to be detected in the off-gases. From 320 to ~ 350°C, water, CO_2, and SiF_4 (SiF_4 is very large) are all still observed. Also, the bands for the oligomers have grown tremendously. In addition, two new combination bands are observed due to COF_2 (possibly from the endgroups on the main chain) and SO_2 (from the end of the sidegroup). This is the first indication of sidegroup degradation. The analysis of the total gases collected revealed water, CO_2 (1.7 mg/g), SiF_4 (1.4 mg/g), CO (1.3 mg/g), SO_2 (4.8 mg/g), and COF_2 (0.8 mg/g). Possibly some oligomers were also present. Note that neither the 920 nor the 1440 cm^{-1} peaks, seen in the Rieke and Vanderborgh[16] study, are observed in the present study.

The —SO_3H on the sidegroup is the first part of the Nafion® to start degrading which only occurs above 320°C. This slow rate of decomposition seems to be due to the minor loss of weight from the —SO_3H groups between 300 and 350°C before the bulk of the sidegroup and backbone start degrading around 400°C. Therefore, at normal use temperatures (25 to 100°C), no loss of functionality should occur.

Monomer

Perfluoro-2-(2-sulfonyl ethoxy)-propyl vinyl ether (PSEPVE) and tetrafluoroethylene (TFE) are polymerized to make Nafion® XR. The structure of PSEPVE is shown below.

$$O$$
$$|$$
$$F-S-CF_2-CF_2-O-CF(CF_3)-CF_2-O-CF=CF_2$$
$$|$$
$$O$$
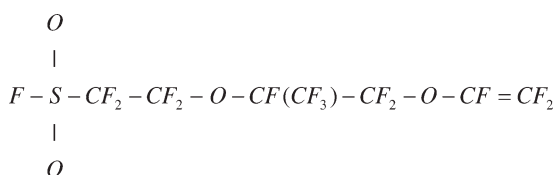
If the polymer is not post-treated correctly, some PSEPVE may remain in the polymer which in turn will affect the EW measurement as well as processing the resin. Therefore, it is critical to at least identify the peaks attributed to the PSEPVE in the polymer to develop a concentration calibration.

Nafion® XR was pressed into a thin film and measured on the FTIR. The film was then soaked in PSEPVE overnight and remeasured. The two spectra are plotted in Figure 14. The only major difference between the two spectra (aside from a thickness var-
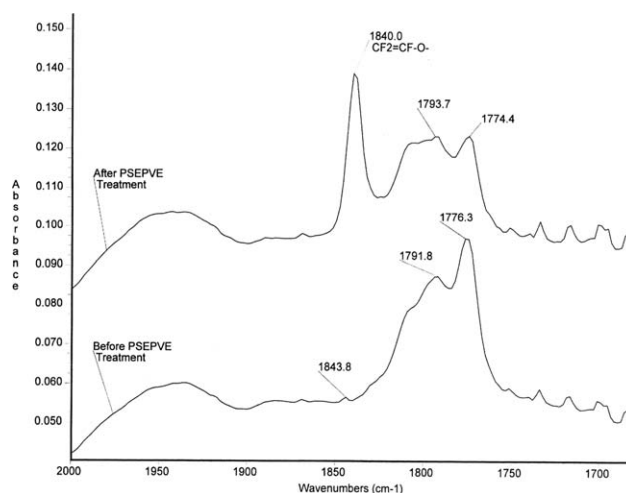

Figure 14 PSEPVE-soaked sulfonyl fluoride form Nafion® FTIR spectra.

iation) is present around 1800 cm^{-1}. A peak at 1840 cm^{-1} is attributed to the vinyl (CF_2=CF—O—) group in the PSEPVE. The double bond disappears upon polymerization so is not present in the final polymer. The appearance of this 1840 cm^{-1} peak will indicate if PSEPVE is present. To calibrate the peak height or area with the PSEPVE concentration, a group of standards would have to be prepared and measured. A suitable baseline may be the trough at ~ 1900 cm^{-1} or a connected baseline between ~ 1860 and ~ 1830 cm^{-1}.

Short sidechain polymers

FTIR EW calibrations can also be developed for shorter sidechain polymers such as those made by Dow Chemical Company. The structure of the Dow sulfonyl fluoride polymer is

$$\sim CF_2-CF-(CF_2-CF_2)_n \sim$$
$$|$$
$$O-CF_2-CF_2-SO_2F$$
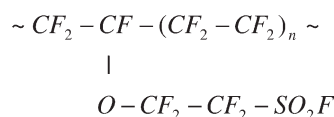
The same IR bands used to measure Nafion® (~ 2704 cm^{-1} —SO_2F, 2550 cm^{-1} C—F shoulder, 2745 cm^{-1} baseline for thick films and ~ 982 cm^{-1} ether, ~ 555 cm^{-1} C—F, and ~ 900 cm^{-1} baseline for thin films) were also found applicable for the Dow polymer measurement.

Polymerized Dow monomer as well as commercial polymer were used in this study. All reference EW values were measured by NMR; the EWs of a few samples were confirmed by titration. Numerous thick films were pressed at temperatures between 190 and 220°C, temperatures much lower than those used for Nafion® yet the resulting films had excellent structural integrity possibly because of the high crystallinity due to the shorter sidechain length. The analytical bands for the samples were measured
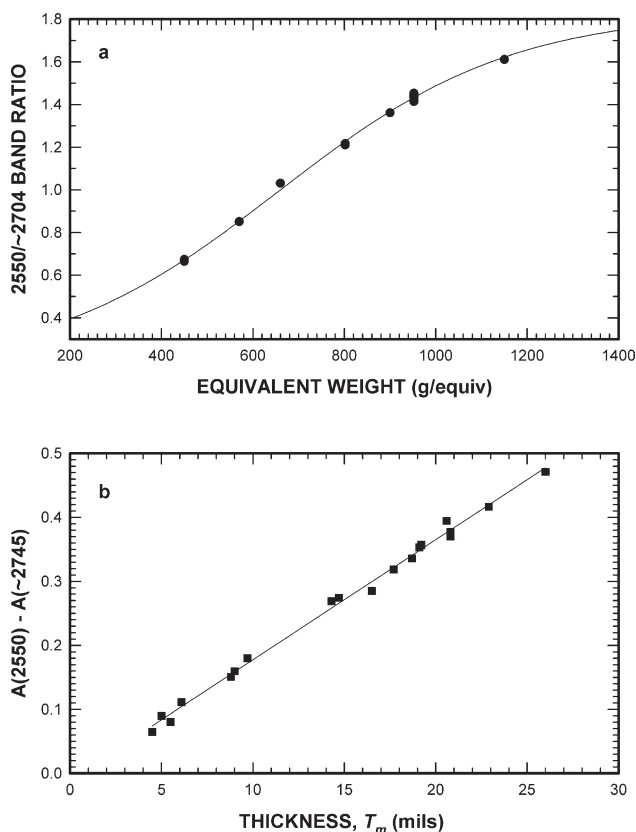
Figure 15 Dow sulfonyl fluoride polymer FTIR: (a) sigmoidal calibration curve and (b) linear film thickness calibration.

with FTIR. A 2550/$\sim$ 2704 band ratio was determined using eq. (7).

Data taken on the various films are plotted in Figure 15. The upper plot (a) is the calibration between the NMR measured EW and the FTIR measured band ratio. The data were fit to a sigmoidal regression ($r^2 = 0.997$) given in eq. (6) where the constants for thick films are given in Table II (7b). A thin film calibration is also possible.

Films of various thicknesses were pressed and measured with a micrometer. The mechanically measured thickness is plotted versus the C—F "thickness" band in Figure 15(b). A linear regression was used to fit the points resulting in the following correlation ($r^2 = 0.998$)

$$T_m = 53.4759 \, T_f + 0.5417 \tag{13}$$

The technique uses the —SO$_2$F peak (located at 2705 cm^{-1} for the Dow polymer versus 2703–2704 cm^{-1} for Nafion®) ratioed to a C—F shoulder at 2550 cm^{-1} with a 2745 cm^{-1} baseline. The calibrations cover the EW range of 400 to 1200 for film thicknesses of 4 to 26 mils.

Longer sidechain polymer

Detailed TGA, DSC, FTIR, and NMR studies of Aciplex sulfonate polymer (Asahi Chemical) and

Nafion® revealed differences in the thermal and structural properties of the two polymers. Specifically, Aciplex has at least one extra —CF$_2$— group along the sidechain, adjacent to the sulfonate group. The Aciplex sulfonate structure is

$$\sim CF_2 - CF - (CF_2 - CF_2)_n \sim$$
$$|$$
$$O - CF_2 - CF(CF_3) - O - CF_2 - CF_2 - (CF_2)_m - SO_2F$$
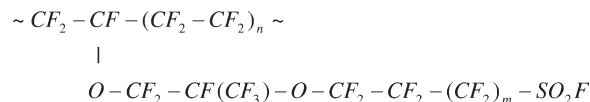
Note that all the data contained in this section refer to Aciplex made prior to 1994. In 1994, Asahi Chemical changed the composition of their sulfonate polymer to a chemical structure identical to Nafion® XR. The FTIR spectra of the carboxylate layers of Aciplex and Nafion® were and still are virtually identical indicating extremely similar polymers.

The FTIR spectra of the Aciplex, Dow, and Nafion® sulfonate polymers are compared in Figure 16. The Aciplex (a) and Nafion® (d) sulfonyl fluoride polymer spectra are nearly identical. The differences in the polymer structure become clear only when the salt forms (b and e) are examined. Most noticeable are the two peaks in the Aciplex spectrum at 870 and 936 cm^{-1} which are absent in the Nafion® spectrum. In addition, many of the other Nafion® peaks are shifted to lower energy (lower wavenumber). It is conceivable that the presence of these extra peaks and the shifting of other peaks are related to the extra —CF$_2$— groups, but the interpretation may be more complex. A —CH$_2$— peak is known to occur at 876 cm^{-1}, but proton NMR showed no evidence of hydrocarbon structures. The Dow spectrum (c) is also very similar to the unhydrolyzed Aciplex and Nafion® spectra. The $\sim$ 982 cm^{-1} peak shifts to
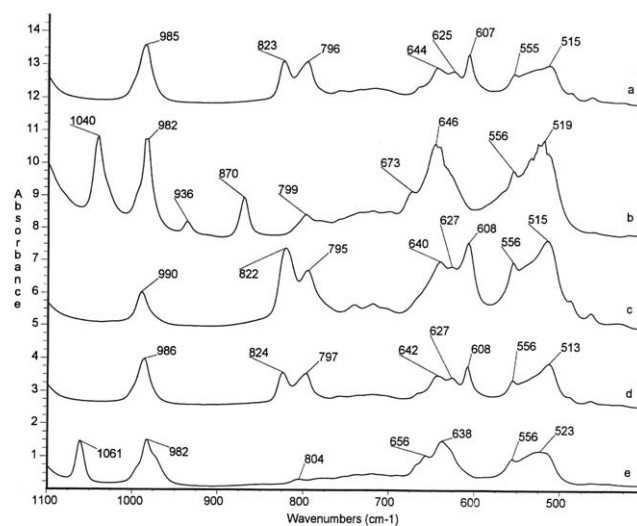
Figure 16 Comparison of Aciplex, Dow, and Nafion® sulfonate FTIR spectra: (a) Aciplex sulfonyl fluoride, (b) Aciplex salt, (c) Dow sulfonyl fluoride (952 g/equiv), (d) Nafion® sulfonyl fluoride (1180 g/equiv), (e) Nafion® potassium salt.

higher energy as the sidechain becomes shorter, an increase of 1–2 cm^{-1} per —CF$_2$ sidechain linkage.

CONCLUSIONS

FTIR Spectroscopy provides an accurate and reproducible method for determining the equivalent weight, salt content, endgroups, impurities, water content, and many other properties of ionomer films, bifilms, and membranes for the sulfonyl fluoride, salt, and acid form fluoropolymers. The calibrations presented are valid for the sulfonate form of Nafion® over the EW range of 700–1800 g/equiv for films between 0.2 and 40 mils thick.

To advance the present study, hydrolyzed standards need to be developed to use the methods presented to create a degree of hydrolysis calibration. The technique could be based on either the 608, 1061, 1470, or 2704 cm^{-1} bands. In addition, the FTIR data should be compared with other analytical data to study structure/property relationships of Nafion®. FTIR coupled with dielectric spectroscopy, thermal methods, rheological techniques, mechanical measurements, and other techniques will help to gain further insight into the polymer properties.

APPENDIX: FILM THICKNESS ANALYSIS

Consider the case where $y = f(x,z)$, as shown in Figure 17. The subscript u represents the upper value and L represents the lower value. Each of the two original lines has a
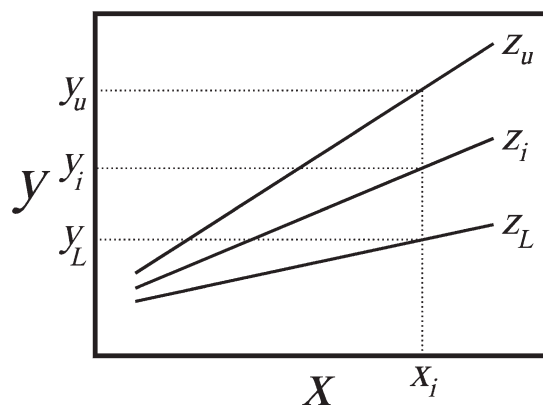

Figure 17 Three variable correlation.

linear relationship of the form

$$z_u : \qquad y_u = c\,x_u + d \qquad (14)$$
$$z_L : \qquad y_L = e\,x_L + f \qquad (15)$$

If it is desired to obtain the y value (y_i) at some x_i and z_i in between the upper and lower bounds, and if a linear relationship is assumed between the variables, the Lever Arm Rule can be used to obtain the following two equations.

$$\frac{a}{b} = \frac{y_i - y_L}{y_u - y_L} \qquad (16)$$

$$\frac{a}{b} = \frac{z_i - z_L}{z_u - z_L} \qquad (17)$$

Combining eqs. (16) and (17) gives

$$\frac{y_i - y_L}{y_u - y_L} = \frac{z_i - z_L}{z_u - z_L} \qquad (18)$$

APPENDIX TABLE AI
Infrared Active Bands and Assignments

Peaks	SO$_2$F	SO$_3$K	SO$_3$H	Assignment
419		VW		
428	*VW*			
443		VW	VW	
461		VW		
464	W	VW	VW	CF$_2$ [10]
488	*VW*			
515	S	VS[a]	VS	CF$_2$ Rock or Twist [5]
529		VS[a]		CF$_2$ + S—O [7]
556	S	S	S	CF$_2$ [5]
608	*S*			—SO$_2$F [12]
627	S		S	CF$_2$ Wag or Scissor [5,12][j]
639	S[c]	VS	S[b]	CF$_2$ Wag [5,12][j]
644	S[c]			CF$_2$ Wag [5]
656		*S*		CF$_2$ Wag [5]
691		W		
719	W[d]	VW	VW	CF$_2$ Amorphous [5]
735	W[e]	VW	VW	C—C Amorphous [7]
753		VW	VW	
758	VW			
774		VW	VW	

APPENDIX TABLE AI. *Continued*

Peaks	SO$_2$F	SO$_3$K	SO$_3$H	Assignment
797	S			
805		VW	W	CF$_2$ [5]
825	S			SO$_2$F
968			VS[f]	C—O—C Sym. Stretch [7]
984	VS	VS	VS[f]	C—O—C Sym. Stretch [7]
1038	VW			
1061		VS	VS	S—O Stretch [7]
1140				CF$_2$ [7]
1152				Sym. C—F Stretch [5]
∼ 1200	VS	VS	VS	C—F Bands
1213				C—F [5]; —SO$_3^-$ Stretch
1242				C—F [5]
1302			VS	
1306	S			Sidechain CF$_3$
1321	*S*			
1352	VW			
1420	VW	VW	VW	CF$_2$ (203+1213=1416) [5]
1437		VW	VW	
1449	W		VW	CF$_2$ (203+1242=1445) [5]
1456		VW	VW	
1469	VS		W	CF$_2$ [10], S—F
1489			VW	
1497		VW	VW	
1507	VW	VW	VW	Water?
1522	VW	VW	VW	Water?
1534	VW	VW	VW	Water?
1541	VW	VW	VW	
1559	VW[g]	VW[g]	VW	Water?
1570	VW	VW	VW	Water?
1576	VW	VW	VW	Water?
1616	VW	VW		H—O—H Water Bend [10]
1624	VW	W		H—O—H Water Bend [10]
1636	VW	VW		Water?
1647	VW	VW		Water?
1653	VW	VW	VW	Water?
1663	VW	VW		Water?
1670	VW	VW		Water?
1676	VW	VW		Water?
1684	VW	VW	VW	Water?
1701	VW	VW	VW	CF$_2$ (1152+553=1705) [5]
1718	VW	VW	S	CF$_2$ [10], H$_3$O$^+$ [7]
1733	VW	VW	VW	
1757		VW		
1774	VW	VW		
1776	VW			—COOH Dimer Endgroup
1790	VW[h]	VW		C=O in —CO$_2$CH$_3$ CF$_2$ (638+1152=1790) [5]
1794	VW			—CF=CF$_2$ Endgroup
1808	VW[h]			—COOH Endgroup
1844	VW	VW		
1869	VW	VW		
1883	VW			—COF Endgroup
1935	VW[i]	VW		CF$_2$ (553+1380=1933) [5]
1942	VW[i]	VW		
2075	VW			
2115		VW		CF$_2$ [10]
2120	VW	VW		
2147	VW	VW		
2216			*W*	
2342		W[k]		
2365	W	W[k]	VW	CF$_2$ (1152+1213=2365) [5]
2704	VW			—SO$_2$F
2797	VW			
2863		VW		
2924			W	

APPENDIX TABLE AI. *Continued*

Peaks	SO$_2$F	SO$_3$K	SO$_3$H	Assignment
2926	VW			
2934		VW		
2963		VW		
2969	VW			
3003		VW		
3007	VW			C—F?
3090	VW	VW		
3097	VW			
3194	VW			
3255	VW			
3339	VW			
3397			S	
3476	VW			
3528	VW	W		O—H Water Stretch [10]
3558	VW			
3567	VW	VW		Water?
3588	VW	VW		Water?
3609	VW	VW		Water?
3619	VW	VW		Water?
3630	VW	VW	VW	Water?
3650	VW	VW	VW	Water?
3657	VW	VW		Water?
3670	VW	VW	VW	O—H Water Stretch [10]
3677	VW	VW	VW	Free Water [7]
3689	VW	W	VW	Water?
3711	VW	VW	VW	O—H Water Stretch [10]

Notes

a Peak shifts from 515 (at high EW) to 529 (at low EW).

b A doublet forms at high EW.

c Peak shifts from 640 (high EW) to 642 (mid EW) to 644 (low EW).

d Peak shifts from 720 (high EW) to 720 (mid EW) to 718 (low EW).

e Peak shifts from 737 (high EW) to 735 (mid EW) to 735 (low EW).

f Doublet.

g High EW polymer absorbs less water than low EW (cleaner 1500-1700 region at high EW).

h Coupling between 1790 and 1808 bands.

i Coupling between 1935 and 1942 bands.

j Doublet involved in helical reversal.

Spectra Used in the Analysis

—SO$_2$F Spectra: 1076 g/equiv, 0.5 mil.

1180 g/equiv, 0.6 mil.

1769 g/equiv, 0.9 mil.

—SO$_3$K Spectra: 1076 g/equiv, 0.6 mil.

1180 g/equiv, 0.6 mil.

1769 g/equiv, 0.9 mil.

—SO$_3$H Spectra: 1076 g/equiv, 0.8 mil.

1180 g/equiv, 0.7 mil.

1333 g/equiv, 1.0 mil.

Band Intensities

Very strong absorption: VS > 1.0.

Strong absorption: 1.0 > S > 0.3.

Weak Absorption: 0.3 > W > 0.1.

Very weak absorption: 0.1 > VW.

All absorption values are given after subtraction of the appropriate baseline.

The notation *X* indicates a single isolated peak/band.

Now the only unknown variable is y_i. Rearranging eq. (18) gives

$$y_i = \left(\frac{z_i - z_L}{z_u - z_L}\right)(y_u - y_L) + y_L \qquad (19)$$

or by substituting into eq. (19) the original eqs. (14) and (15) where $x_i = x_u = x_L$ gives

$$y_i = \left[\left(\frac{z_i - z_L}{z_u - z_L}\right)(c - e) + e\right]x_i + \left(\frac{z_i - z_L}{z_u - z_L}\right)(d - f) + f \qquad (20)$$

Equation (20) was used to obtain a correlation between the mechanically measured thickness (T_m), the EW_i, and thickness band (T_f).

References

1. Perusich, S. A.; Avakian, P.; Keating, M. Y. Macromolecules 1993, 26, 4756.
2. Hodge, I. M.; Eisenberg, A. Macromolecules 1978, 11, 289.
3. Robinson, T. S.; Price, W. C. Proc Phys Soc (London) B 1953, 66, 969.
4. Liang, C. Y.; Krimm, S. J Chem Phys 1956, 25, 563.
5. Moynihan, R. E. J Am Chem Soc 1959, 81, 1045.
6. Lopez, M.; Kipling, B.; Yeager, H. L. Anal Chem 1976, 48, 1120.
7. Heitner-Wirguin, C. Polymer 1979, 20, 371.
8. Lowry, S. R.; Mauritz, K. A. J Am Chem Soc 1980, 102, 4665.
9. Falk, M. Can J Chem 1980, 58, 1495.
10. Falk, M. ACS Symposium Series 1982, 180, 139.
11. Mauritz, K. A.; Gray, C. L. Macromolecules 1983, 16, 1279.
12. Hsu, W. Y. Macromolecules 1983, 16, 745.
13. Ostrowska, J.; Narebska, A. Coll Polym Sci 1984, 262, 305.
14. Quezado, S.; Kwak, J. C. T.; Falk, M. Can J Chem 1984, 62, 958.
15. Weber, J.; Janda, P.; Kavan, L.; Jegorov, A. J Electroanal Chem 1986, 199, 81.
16. Rieke, P. C.; Vanderborgh, N. E. J Mem Sci 1987, 32, 313.
17. Osawa, M.; Nakane, T.; Ito, K.; Suetaka, W. J Electroanal Chem 1989, 270, 459.
18. Zen, J.-M.; Lipowska, M.; Patonay, G. J Appl Polym Sci 1992, 46, 1167.
19. Tsatsas, A. T.; Risen, W. M. J Polym Sci: Part B: Polym Phys 1993, 31, 1223.
20. Nandan, D.; Pushpa, K. K.; Kartha, V. B.; Wahi, P. K.; Iyer, R. M. Indian J Chem A 1994, 33, 395.
21. Levy, L. Y.; Jenard, A.; Hurwitz, H. D. J Chem Soc, Faraday Trans I 1982, 78, 29.
22. Cable, K. M.; Mauritz, K. A.; Moore, R. B. J Polym Sci: Part B: Polym Phys 1995, 33, 1065.
23. Greso, A. J.; Moore, R. B.; Cable, K. M.; Jarrett, W. L.; Mauritz, K. A. Polymer 1997, 38, 1345.
24. Robertson, M. A. F.; Mauritz, K. A. J Polym Sci: Part B: Polym Phys 1998, 36, 595.
25. Perusich, S. A. Macromolecules 2000, 33, 3437.
26. Perusich, S. A.; Tuminello, W. H.; Banerjee, S. U.S. Patent 5,273,694 (1993).