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Fourier Transform Infrared Spectroscopy of Perfluorocarboxylate Polymers

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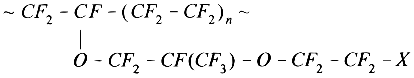
ABSTRACT: Perfluorocarboxylate polymers in the carboxylic methyl ester, potassium salt, and carboxylic acid forms have been analyzed by Fourier transform infrared (FT-IR) transmission and attenuated total reflectance (ATR) spectroscopy. Band assignments were made for most of the dominant peaks. An absorbance band ratio, comparing the 555 cm^{-1} C−F band to the 982 cm^{-1} C−O−C ether band, was found to be a direct measure of the equivalent weight of the polymers. In addition, the transition from the methyl ester form to the acid form was determined by examining the 2969 cm^{-1} methyl ester band versus the broad ∼3200 cm^{-1} acid band. Quantitative expressions are presented to enable the computation of equivalent weight and acid content based on FT-IR thin-film absorbance measurements.

Introduction

Nafion 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] propanoic acid, the polymeric structure of which is shown in Structure **1**, where $X = CO_2CH_3$ (methyl ester form), CO_2K (potassium salt form), or CO_2H (carboxylic acid form) and *n* is the average number of consecutive $-(CF_2-CF_2)-$ groups along the polymer backbone. Nafion CR is the common name for this group of fluoropolymers which are alternatively referred to as TFE/methyl perfluoro(5-methyl-4,7-dioxa-8-nonenoate) copolymer.



$$\sim CF_2-CF-(CF_2-CF_2)_n\sim \quad \text{with } CF \text{ bearing } O-CF_2-CF(CF_3)-O-CF_2-CF_2-X$$

I

The quantity traditionally used in ion-exchange membrane technology to describe the polymer functionality is the equivalent weight (EW in grams/equivalent) which is the molecular weight of the polymer repeat unit. The present paper evaluates the infrared-active bands in Nafion CR and details a methodology to determine the equivalent weight of the polymer. Another paper[1] will describe the sulfonate fluoropolymers (Nafion XR). Almost all infrared studies of Nafion in the literature have been performed on the salt or acid forms of the sulfonate polymer with only two exceptions described below.

Levy et al.[2] grafted carboxylate groups from poly(acrylic acid) onto Teflon FEP and pTFE to form carboxylic acid-type fluoropolymers. They further converted these carboxylated polymers to the Na^+ form. Their studies investigated the polymer as a function of drying (water content), and they proposed models for the high-energy peaks on the basis of hydrogen-bonded structures. Their polymers, though, were devoid of ether linkages so no 982 cm^{-1} bands were present, although C═O, O−H, and C−F peaks were still observed.

Yeager et al.[3] actually did examine the Nafion CR polymer and compared its diffusional, water absorption, and clustering phenomena to Nafion XR. They specifically studied the O−H region of the salt form polymers with FT-IR and found that the carboxylate structure has a greater degree of hydrogen bonding for water than does the sulfonate structure.

The function of the carboxylate film layer in a Nafion membrane is to severely hinder or eliminate the transport of hydroxyl anions in a chlor−alkali cell, thus providing selectivity for the membrane; the sulfonate layers provide the high membrane conductivity. Characterization of the carboxylate polymer from a structural and chemical view is thus essential to understanding and improving the function of the membrane.

In the present paper, a quantitative determination of the equivalent weight of the carboxylate polymer is given which represents a direct measure of the tradeoff between high anionic selectivity (high EW) and good conductivity (low EW). In addition, the various chemical forms of the carboxylate fluoropolymer are studied with FT-IR to yield knowledge of band assignments and conversion between these polymer forms.

Apparatus and Procedures

A Fourier transform infrared (FT-IR) spectrometer (Nicolet, model 730) with Omnic 2.0 software was used to make all FT-IR measurements. A Visual Basic Windows-based program was written to perform the analyses. A spectral library was developed from calibration standards and includes custom spectra of all forms of Nafion. 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 determining the best match.

FT-IR measurements were made by first measuring an open-beam background spectrum and then measuring the polymer sample. Both background and polymer measurements were performed under identical conditions: N_2 purge, 32 scans, 4 cm^{-1} spectral resolution, Happ-Genzel apodization, DTGS KBr detector, and KBr beam splitter.

For transmission studies, polymer samples were cryogenically ground to a fine powder, physically mixed, re-esterified with trimethyl orthoformate (TMOF), and pressed into thin films measuring less than 1 mil thick. The films were dried overnight under 20−25 in. of vacuum and a nitrogen purge at 110 °C.

For attenuated total reflectance (ATR) studies, films were pressed at 270 °C between Kapton release sheets with about 10 000 pounds pressure on the ram. The resultant films were

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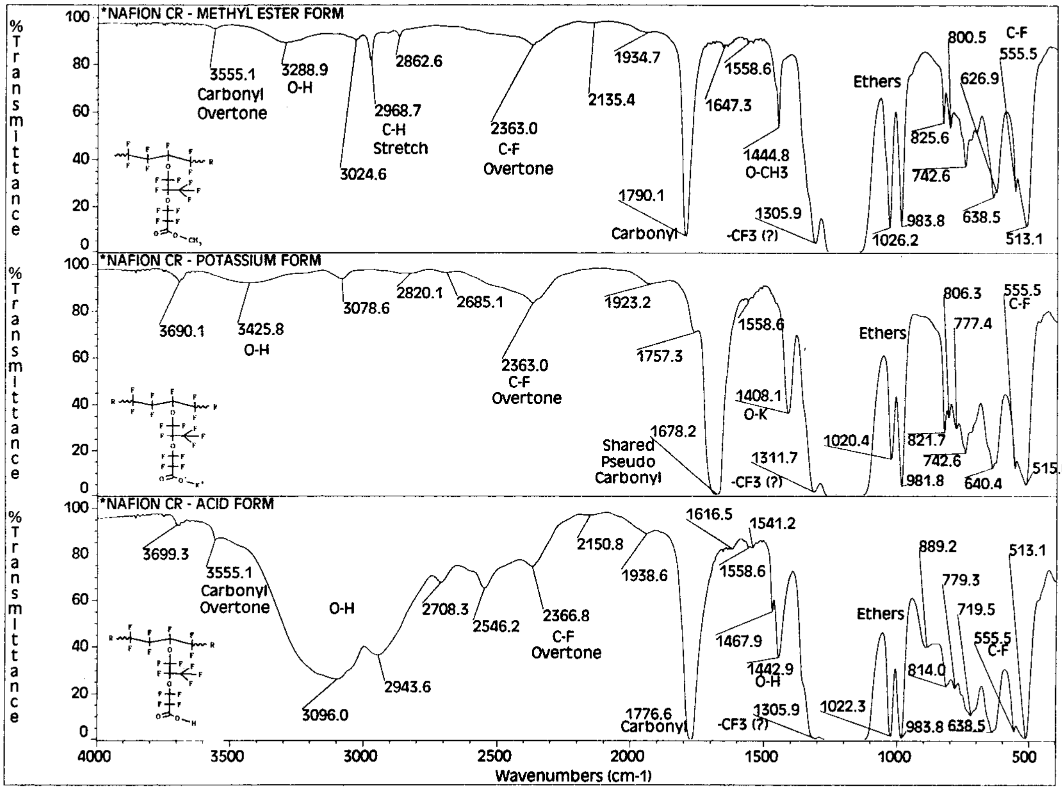


Figure 1. Nafion CR spectra (methyl ester, salt, and acid forms); 4 $\mathrm{cm^{-1}}$ spectral resolution.

slightly thicker than those used for transmission/absorbance spectra, making them easier to handle. Each film was cut into a number of strips about 15 mm wide and 60 mm long. After measurement of the "as is" films, the samples were re-esterified in TMOF and remeasured. Treated films were less tacky than the untreated films which may have an effect on the sample/crystal contact. Two types of ATR crystals were used. A KRS-5 (thallium bromoiodide) crystal (50 mm long, 3 mm thick, and 10 mm wide) allowed measurements from 400 to 4000 $\mathrm{cm^{-1}}$. The refractive index of the crystal was measured to be 2.35. The sample holder used was from the Harrick Scientific Corporation. In addition, a second ATR apparatus (Spectra-Tech Inc. Baseline HATR) was used with a ZnSe crystal over the frequency range from 650 to 4000 $\mathrm{cm^{-1}}$. The apparatus has a clamping device with a rubber pad to push the sample into contact with the crystal if needed. Although the samples were clamped at various pressures to the crystal, it was found that the results were virtually independent of the clamping pressure. In fact, the films could be put in intimate contact with the crystal without applying pressure by forcing out the air bubbles and relying on the inherent tack of the polymer. The entire surface of the crystal can be covered this way, but entrapped dust, less tacky samples, and other factors may decrease the effectiveness of the contact. The two ATR crystals gave virtually identical spectra over the 900−2100 $\mathrm{cm^{-1}}$ wavenumber range studied in the present work.

All polymers were titrated by at least one of two methods. The "standard" technique involved grinding the polymers to less than 20 mesh prior to re-esterification and drying. The methyl ester form powder was then treated by hydrolyzing the polymer to the potassium salt form, adding an excess amount of perchloric acid (converting to the acid form) forming $\mathrm{KClO_4}$, and back-titrating the excess perchloric acid with potassium acid phthalate. For the "direct" titration, the polymers were ground, re-esterified, hydrolyzed, rinsed, acidified in 50% nitric acid, and dried. Each sample was then converted to the salt form in excess NaOH. The sample was washed with distilled water, and the resultant NaOH solution was back-titrated with HCl.

Discussion of Experimental Results

Spectral Analysis. The mid-IR spectra for the methyl ester, salt, and acid forms of Nafion CR are shown in Figure 1. The wavenumbers of all major peaks are labeled and identified whenever possible. Some of the peak identifications are debatable but are assigned the identifications based on the best evidence available at the present time. A complete listing of absorption bands and assignments is tabulated in Tables 1−3. Note that the saturated regions of the spectra are never used in any quantitative analyses in the present paper.

The main bands used for the thin-film EW analysis are the ether band (the ether close to the polymer backbone) at ~982 $\mathrm{cm^{-1}}$ and the C−F band at ~555 $\mathrm{cm^{-1}}$ with a baseline chosen around 900 $\mathrm{cm^{-1}}$. Alternate C−F bands could also have been chosen. These bands are extremely sharp, free of interference from adjacent bands, very strong (prompting the necessity of using thin films), and are present in each chemical form of the polymer. Both the ~982 and ~555 $\mathrm{cm^{-1}}$ bands along with other C−F bands are discussed in detail elsewhere.[1]

Note that throughout this paper $\sim\tilde{\nu}$ represents a wavenumber which has been picked within a specified wavenumber range by the computer; in this way, any peak shifts are measured as well as their influence on the computed values. In addition, the absorbance at wavenumber $\tilde{\nu}$ is designated $A(\tilde{\nu})$ while the absorbance around a wavenumber $\sim\tilde{\nu}$ is designated $A(\sim\tilde{\nu})$.

The 1026 $\mathrm{cm^{-1}}$ band in the methyl ester form is immersed in controversy. Some researchers believe that the band is due to the second ether band toward the end of the side chain while others believe it is due to C−F bonds. Note that in the sulfonyl fluoride polymer, only one ether linkage was observed.[1] Perhaps the two ether peaks in the sulfonate polymer lie on top of one

Table 1. Infrared Active Bands and Assignments

peaks	CO$_2$CH$_3$	CO$_2$K	CO$_2$H	assignment
419	VW	VW	VW	
461		W		
515	VS	VS	VS	CF$_2$ rock or twist[4]
556	S	S	S	CF$_2$[4]
627	S	S	S	CF$_2$ wag or scissor[4,a]
639	S	S	S	CF$_2$ wag[4,a]
702	*W*			CF$_2$ amorphous[4]
719	W	W	W	CF$_2$ amorphous[4]
743	W	W		C$-$C amorphous[6]
753			W	
758	VW			
778		W	W	CF$_2$ amorphous[4]
801	W			
805		W		CF$_2$[4]
814			W	
822		*S*		
825	W			
889			W	
984	VS	VS	VS	C$-$O$-$C sym. stretch[6]
1020		S		C$-$O$-$C
1025	VS		VS	C$-$O$-$C
1140				CF$_2$[6]
1152				sym. C$-$F stretch[4]
~1200	VS	VS	VS	C$-$F bands
1213				C$-$F[4]; $-$SO$_3^-$ stretch
1242				C$-$F[4]
1306	VS		VS	side chain CF$_3$
1312		VS		
1408		*S*		O$-$K or sym. COOK stretch
1420	VW			CF$_2$ (203 +1213 = 1416)[4]
1444	W		S	C$-$O$-$CH$_3$, COOH
1456		VW	VW	
1468		VW	S	CF$_2$[7], C$-$O$-$H
1489		VW		
1497		VW	VW	
1507	VW	VW	VW	water?
1522	VW	VW	VW	water?
1534		VW	VW	water?
1541	VW	VW	VW	
1559	VW	VW	VW	water?
1570	VW	VW	VW	water?
1576	VW	VW	VW	water?
1616	VW		VW	H$-$O$-$H water bend[7]
1624	VW		VW	H$-$O$-$H water bend[7]
1636	VW		VW	water?
1647	VW		VW	water?
1653	VW		VW	water?
1663	VW		VW	water?
1670	VW		VW	water?
1676	VW	VS	VW	salt shared $-$CO$_2$-
1684	VW		VW	water?
1701	VW		VW	CF$_2$ (1152+553 = 1705)[4]
1718	VW		VW	CF$_2$[7], H$_3$O$^+$ [6]
1757		W		
1774			S	acid C=O
1790	VS			ester C=O, CF$_2$ (638 +1152 = 1790)[4]
1844			VW	
1869			VW	
1923		W		
1935	W			CF$_2$ (553+1380 = 1933)[4]
1942			W	
2058		VW		
2115		VW		CF$_2$[7]
2135	VW			
2155	VW	VW	VW	
2164			VW	
2342		W[b]	W[b]	
2365	W	W[b]	W[b]	CF$_2$ (1152+1213 = 2365)[4]
2546			*W*	
2697		VW		
2708			W	
2814		*VW*		
2863	W	VW		
2908	*VW*			
2934		VW		
2944			*S*	
2969	W			
3025	*W*			
3079		*W*		
3090	VW			
3097	VW		S	
3114	VW			
3313	*W*[c]			
3420		*W*		
3503			W[d]	
3555	W	VW	VW	C=O overtone
3558	VW	VW	VW	
3567	VW	VW	VW	water?
3588	VW	VW	VW	water?
3609	VW	VW	VW	water?
3619	VW	VW	VW	water?
3630	VW	VW	VW	water?
3650	VW	VW	VW	water?
3657	VW	VW	VW	water?
3670	VW	VW	VW	O$-$H water stretch[7]
3677	VW	VW	VW	free water[6]
3689	VW	W	W	water?
3711	VW	VW	VW	O$-$H water stretch[7]

[a] Doublet involved in helical reversal. [b] Doublet present at high EW; 2342 peak converts to a shoulder at low EW. [c] Peak shifts from 3314 (high EW) to 3312 (mid EW) to 3289 (low EW). [d] Only present for high-EW polymers.

Table 2. Spectra Used in the Analysis

$-$CO$_2$CH$_3$ spectra:	1022 g/equiv, 0.5 mil
	1169 g/equiv, 0.8 mil
	1194 g/equiv, 0.9 mil
$-$CO$_2$K spectra:	1022 g/equiv, 0.8 mil
	1169 g/equiv, 0.6 mil
	1194 g/equiv, 1.2 mil
$-$CO$_2$H spectra:	1022 g/equiv, 1.0 mil
	1169 g/equiv, 0.4 mil
	1194 g/equiv, 0.8 mil

another and the two ether linkages behave identically; in the carboxylate polymers, the vibrational motion of the ether linkage close to the end of the side group may be hindered and shifted to higher energy (higher wavenumber). It is interesting to note from Figure 1 that the amplitude of the 1026 cm^{-1} band decreases and shifts to lower energy in the salt form; however, in the acid form, the original amplitude is reestablished, and the peak position lies between the wavenumbers for the methyl ester and salt forms. Slight broadening is observed upon hydrolysis, which lends more credibility to the ether assignments.

Table 3. Band Intensities[a]

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

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

The high-energy C$-$H stretch (2969 cm^{-1}) relative to the 2365 cm^{-1} C$-$F broad band was studied using thick films. The 2365 cm^{-1} band is a combination overtone from the 1152 and 1213 bands.[4] The neighboring acid band (3289 cm^{-1}), which interferes and eventually overwhelms the methyl band, introduced a significant error in the EW determination and was rejected from further consideration for the present FT-IR analysis. A detailed discussion of the acid band is given by Yeager et al.[3]

The C=O and COOX vibrational bands were also studied. The C=O band shifts from 1790 (methyl ester) to 1678 (salt) and back to 1777 cm^{-1} (acid). The salt form requires the least energy (lowest wavenumber) to vibrate since the electrons are shared between the two oxygen atoms and a resonance is established. The carbonyl double bonds in the ester and acid forms require a higher energy to vibrate because of the more rigid double-bond structure. Between 1400 and 1450 cm^{-1}, a band characteristic of the $O-CH_3$ or CH_3 bending (1445 cm^{-1} methyl ester), O−K or COOK symmetric stretch (1408 cm^{-1} salt), and COOH stretch (1443 cm^{-1} acid) is present. Again, the ionic salt band requires less energy to vibrate than the other two bonds. The COOX bands may be used to determine the percent conversion from the methyl ester to the salt form. Note that the COOX shift has also been observed by use of dielectric spectroscopy.[5] The differences in bond strength and the hydrogen-bonding character of the three polymer forms account for the different energy requirements.

Standards. To accurately calibrate the FT-IR for equivalent weight determination, a set of Nafion CR standards was created. The ultimate standards must have a homogeneous and precisely known EW as obtained from independent measurements on various instruments. The standards were titrated by two techniques described in the Apparatus and Procedures section to determine the precise EW. The samples were measured with FT-IR using thin (<1 mil thick) and thick (10−40 mil thick) films. For the thick-film measurement, the high-energy acid band overlapped the methyl band in all but extremely acid-free (<0.5% acid) polymers; perhaps a technique could be developed to account for the overlap, but the low-energy ether band provided an unencumbered method so that the thick-film technique was not considered further.

The titration data were found to be accurate to within ±2 g/equiv. Any divergence of the titration data was consistent with theory. For the standard titration, if all of the side groups were not converted to the acid form upon adding perchloric acid, the measured EW would be too high. For the direct titration, if the NaOH was not completely washed out of the sample, it would appear that the sample took up more Na^+ than had actually occurred, and the measured EW value would be too low. In practice, however, the two titration methods were very consistent.

Alternative methods, such as dielectric spectroscopy, NMR, and radioisotope tagging, could be used to characterize the polymer samples. Dielectric spectroscopy[5] and NMR, like IR, will measure the total number of side groups present, whereas radioisotope tagging, like titration, will only measure the side groups accessible to ion exchange.

Equivalent Weight Determination. Both the acid (~3200 cm^{-1}) and methyl ester (~2970 cm^{-1}) groups at high energy as well as the ether linkage close to the backbone at low energy (~982 cm^{-1}) in Nafion CR were considered as possible measures of the equivalent weight and acid content. A comparison of the two measurements gives an indication of decarboxylation or other degradation of the polymer.

All polymer films were first titrated and then measured with the FT-IR. The ~982 cm^{-1} ether peak and the ~555 cm^{-1} C−F band were peak-picked using the FT-IR software, and the absorbances were subtracted from a peak-picked baseline at ~900 cm^{-1}. The band ratio (BR) is computed as either the backbone absorbance at ~555 cm^{-1} over the side group absorbance at ~982 cm^{-1} or the reciprocal, as illustrated below.

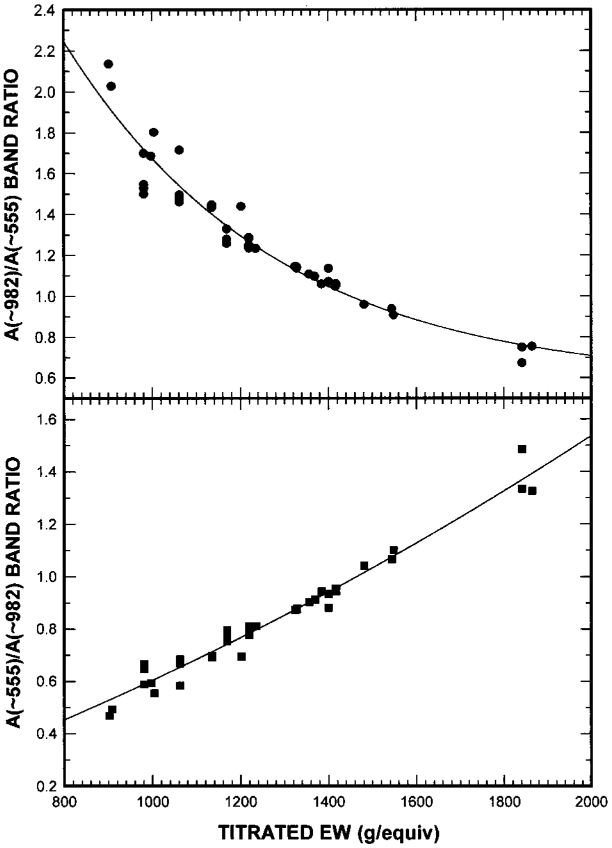


Figure 2. Nafion CR thin-film FT-IR calibration curves.

$$\mathrm{BR} = \frac{A(\sim 555) - A(\sim 900)}{A(\sim 982) - A(\sim 900)} \tag{1}$$

Note that the band ratio in eq 1 represents grams of polymer (C−F thickness band) per side group equivalents (ether absorbance) which is the definition of equivalent weight. A sigmoidal regression (as well as 10 000 other fits using the software TableCurve) was fit to the band ratio versus titrated EW data, as shown in Figure 2. For Nafion CR, the sigmoidal regression gave the best fit using the band ratio described in eq 1 yielding an r^2 equal to 0.97. The regression curve is given by eq 2

$$\mathrm{EW} = c - d \ln\left(\frac{b}{\mathrm{BR} - a} - 1\right) \tag{2}$$

where, $a = -1.010\,321\,8$, $b = 8.860\,283\,7$, $c = 3528.7614$ g/equiv, and $d = 1685.5439$ g/equiv. Note that all EW values are quoted as if the polymer were in the acid form, and all EW values reported from the FT-IR are in the acid form irrespective of what form is being measured. To convert from the acid form ($\mathrm{EW}_{\mathrm{acid}}$) to either the methyl ester ($\mathrm{EW}_{\mathrm{ester}}$) or K^+ salt ($\mathrm{EW}_{\mathrm{salt}}$) forms for Nafion CR, use the following equations.

$$\mathrm{EW}_{\mathrm{ester}} = \mathrm{EW}_{\mathrm{acid}} + 14 \tag{3}$$

$$\mathrm{EW}_{\mathrm{salt}} = \mathrm{EW}_{\mathrm{acid}} + 38 \tag{4}$$

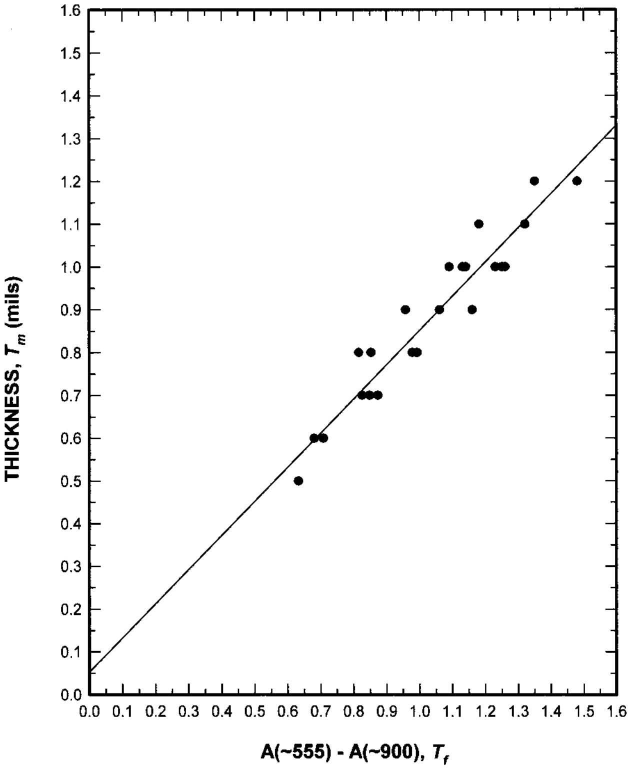


Figure 3. Thin-film thickness calibration.

The film thickness was determined using the absorbance at ~555 cm^{-1} designated $A(\sim555)$ relative to a baseline $A(\sim900)$. Several films were measured with a micrometer (T_m) and calibrated to the FT-IR measured "thickness" (T_f), as shown in Figure 3, where

$$T_f = A(\sim555) - A(\sim900) \tag{5}$$

A linear regression gave the following correlation

$$T_m = 0.799\,172 T_f + 0.05332 \tag{6}$$

The bands dependent on the side group concentration will increase in amplitude for decreasing EW. Scans of four polymers of varying EW but of nearly identical thickness (ranging from 0.91 to 0.96 mil) are shown in Figure 4. The 1790, 1444, 1306, 1025, 984, and other smaller bands are dependent on the side group concentration. The C−F bands at 639, 627, and 515 are strongly dependent on the backbone C−F linkages. The only complex peak is the 555 cm^{-1} band which is almost independent of EW. The 1160 g/equiv sample is 0.04 mil thinner than the other samples which could account for the depressed amplitude of the 555 cm^{-1} peak. Even though the dependence is very weak, the 555 cm^{-1} peak does tend to increase in amplitude with decreasing EW, implying that the band represents C−F groups at least in part along the side group. Since Moynihan[4] did observe this band in the pTFE homopolymer, the band must be due to both backbone and side chain C−F groups, which makes it an ideal peak for an EW and thickness calibration.

In addition to the transmission studies detailed above, the carboxylate polymer was also analyzed by reflectance using an FT-IR microscope (Nicolet NicPlan) attached to a Nicolet Magna750 FT-IR. The beam diameter was 100 μm, and the depth of penetration was less than 1 mil. The spectra obtained are much more noisy than the transmission spectra, but "Nafion peaks" are readily apparent, especially the carbonyl at ~1700 cm^{-1}, the C−F stretch at ~1250 cm^{-1}, and the ether band at ~980 cm^{-1}. Because of the noise, an EW could not be obtained directly, but an indication of the EW homogeneity was approximated by measuring the height of the ether 982 cm^{-1} peak relative to a 990 cm^{-1} baseline. Assuming that the depth of penetration is constant for the polymer films (which is accurate since the wavelength of incoming light is much greater than the crystal size causing negligible scattering), the ether band need not be ratioed to a C−F band to obtain a measure of the EW. However, since a calibration is needed to get the true EW, the ether peak height will only provide a relative EW. Although some differences in peak heights were observed, the noise from the reflectance measurements was too large to obtain an accurate EW calibration.

Acid Analysis. The method detailed in this section allows for the determination of percent acid in Nafion CR with the FT-IR. The percent acid represents the percent of side groups converted to the acid form; it does not represent a mole or weight fraction of acid present in the polymer. The percent acid is used to evaluate the processability of the CR polymer; if the acid content is too high, extrusion is very difficult if not impossible due to the strong hydrogen bonding of the acid groups.

An FT-IR spectrum for a 0.5 mil, 1022 g/equiv Nafion CR film is shown in Figure 5, where the relevant peaks for the acid computation are cited in the figure. In general, the acid peak (A, normalized to thickness T) is ratioed to the total number of side groups (methyl M + acid A, normalized to thickness T) to compute the percent acid in the polymer

$$\%\ \text{acid} = \frac{K\left(\frac{A}{T}\right)}{\left(\frac{M}{T}\right) + K\left(\frac{A}{T}\right)} \times 100 \tag{7}$$

where K is an empirically derived constant. Note that in determining the percent acid, the thickness dependence cancels in the ratio so that after the initial calibration the thickness band need not be measured during routine use to determine the acid content.

The thickness band was evaluated from the shoulder of the CF$_2$ overtone (centered at 2365 cm^{-1}) to eliminate any interference from the CO$_2$ peak present between 2300 and 2400 cm^{-1}. The actual wavenumber chosen for the thickness measurement was 2300 cm^{-1}. Although the CO$_2$ interference should be minimal under normal FT-IR operation, the 2300 cm^{-1} wavenumber was used to avoid any accidental CO$_2$ interference. The absorbance at 2080 cm^{-1} was used as a baseline. Therefore, the acid film thickness (T_{acid}) is given by

$$T_{acid} = A(2300) - A(2080) \tag{8}$$

To compute the acid and ester contributions, the baseline for the acid peak was chosen at ~3850 cm^{-1} and the ester band baseline was chosen at the trough around ~3000 cm^{-1}. Thus,

$$A_{acid} = A(\sim3200) - A(\sim3850) \tag{9}$$

and

$$A_{ester} = A(\sim2970) - A(\sim3000) \tag{10}$$

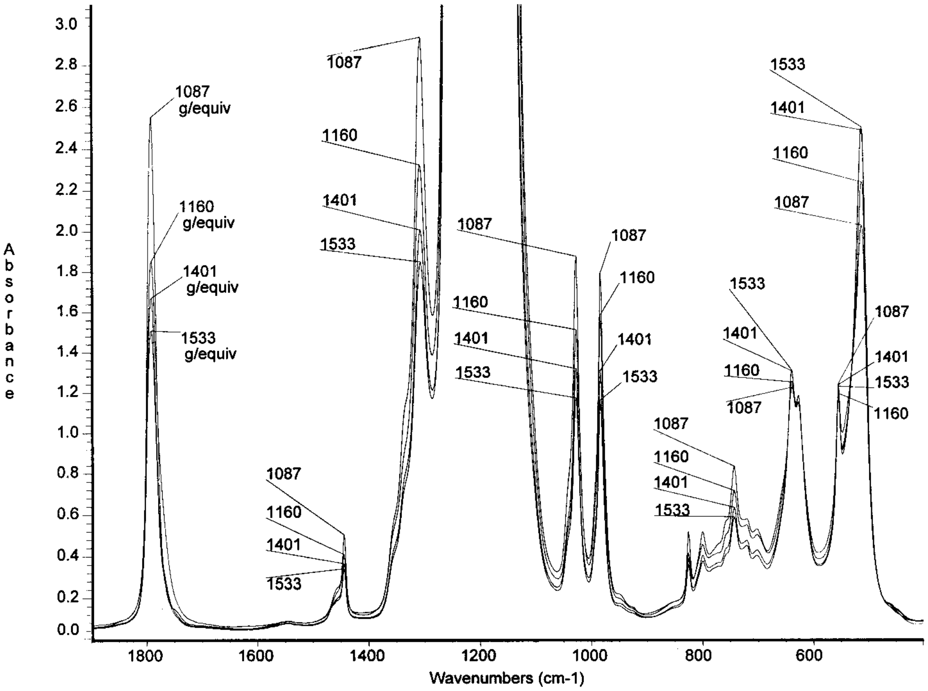


Figure 4. Spectral changes of methyl ester form polymers as a function of equivalent weight; film thicknesses ranged from 0.91 to 0.96 mil (23.1 to 24.4 μm).

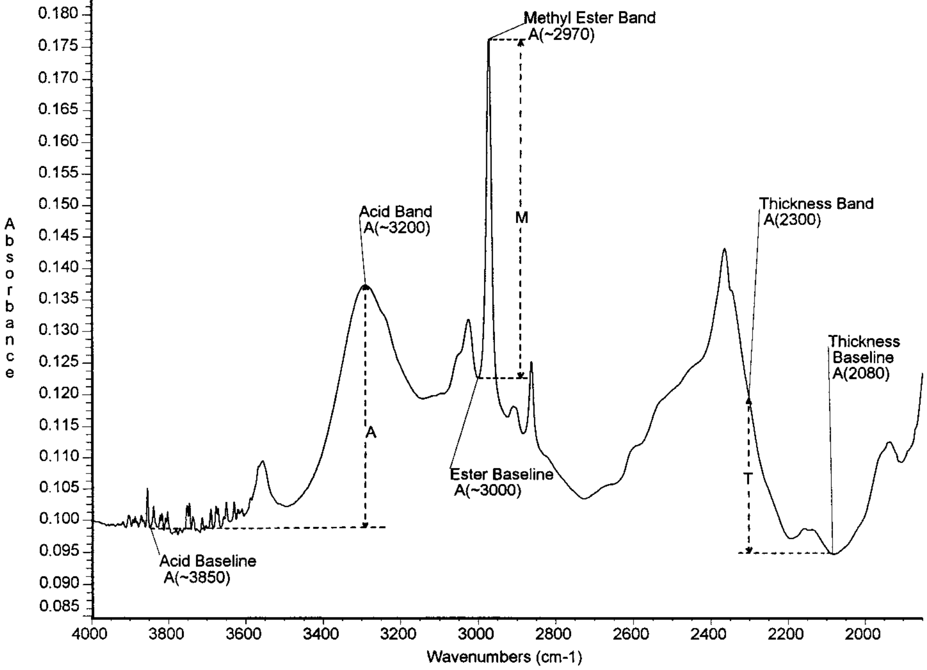


Figure 5. Acid, methyl, and C−F bands used for acid analysis of Nafion CR.

Many alternate baselines were evaluated, but the straightforward method outlined here was found to provide comparable or improved accuracy over the more complex methods.

To determine the *K* value in eq 7, the following procedure was used. Two different EW Nafion CR standards were pressed into films. All films were re-esterified with trimethyl orthoformate. The films were then acidified in 5% HNO_3 for 0.5, 1, 2, 3, 4, and 5 h or longer, taking samples out of the bath at prescribed times. All samples were then dried at 110 °C overnight under vacuum. FT-IR spectra were obtained for each film, and the absorbances in Figure 5 were measured. The ratios A_{ester}/T_{acid} and A_{acid}/T_{acid} were computed using eqs 8−10, and one ratio was plotted versus the other, as shown in Figure 6. The linear regressions yield the slope *K*, which varies with EW; the dashed line represents a regression through all the points irrespective of EW. The average *K* value obtained was 0.303, which was the value used for all acid computations.

Finally, the percent acid is then calculated by eq 11.

$$\%\ \text{acid} = \frac{KA_{acid}}{A_{ester} + KA_{acid}} \times 100 \qquad (11)$$

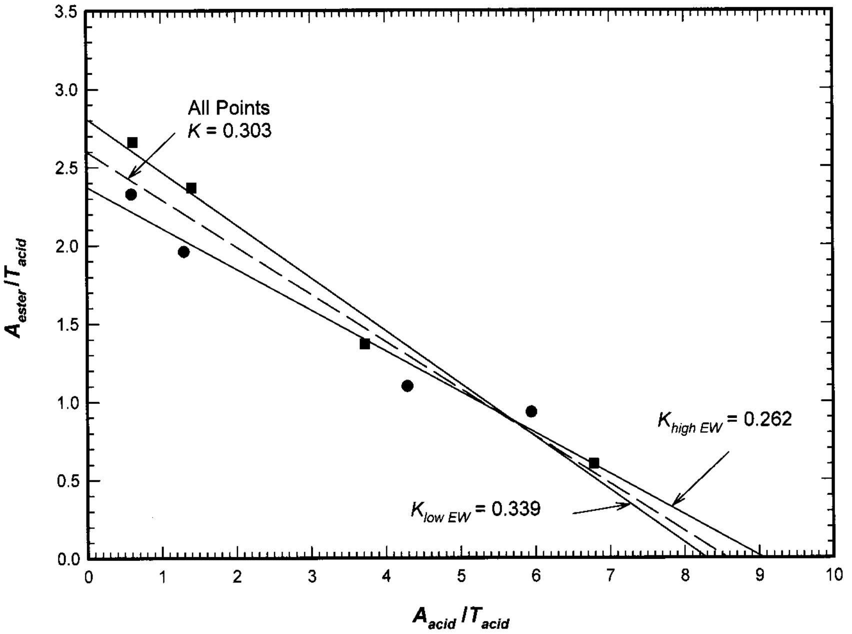


Figure 6. Percent acid determination (*K*) using 1022 (squares) and 1194 (circles) g/equiv carboxylate polymers. The dashed line represents a regression for all of the points.

To observe the conversion from the methyl ester to the acid polymer, a long-term (273 days) experiment was carried out. Two polymers with equivalent weights of 1022 and 1194 g/equiv were pressed into films. Each film was cut in half, yielding a total of four films. One high-EW and one low-EW film were placed in a vacuum desiccator while the remaining two films were left exposed to ambient air. The air temperature and humidity were constantly monitored. All four films were measured on the FT-IR daily. The relatively slow acidification process was thus observed over a long period of time.

Several spectra taken over the time frame of the experiment for the 1022 g/equiv film exposed to ambient air are shown in Figure 7. The same trends discussed below for the 1022 g/equiv sample are also present for the 1194 polymer. Figure 7 presents the data in the acid region for selected spectra over the time scale of the experiment (273 days). All spectra are shown with a common scale so that quantitative differences can be observed. The film absorbed moisture over time, as indicated by the elevated baseline. The methyl band at ~2970 cm^{-1} decreased with time but did not shift in wavenumber to any measurable extent. The broad acid band, however, grows with time and shifts from 3320 cm^{-1} initially to 3220 cm^{-1} after about 50 days, remaining there until 273 days. In addition, the carbonyl overtone (~3555 cm^{-1}) smoothly shifts from 3561 cm^{-1} initially to 3500 cm^{-1} at the end of the experiment. An interesting point to note concerning the ~3555 cm^{-1} band is that its amplitude is comparable to the amplitude of the acid band until ~84 days (~90% acid). At this point, the carbonyl sharply decreases in absorbance until at ~181 days only a shoulder remained, which persisted until the end of the experiment. Perhaps a resonance is being established between the two oxygens as was observed for the salt form. The primary carbonyl band, as seen in Figure 8, gradually shifts from 1790 to 1786 cm^{-1} from 0 to 41 days and then abruptly shifts to between 1772 and 1776 cm^{-1} after ~45 days. Likewise, the ether at the end of the side chain also shifts abruptly from 1026 cm^{-1} up to ~50 days to 1024 cm^{-1} after 50 days; the ether close to the backbone only slightly shifts from 983.8 cm^{-1} initially to 983.5 cm^{-1} at the end of the experiment.

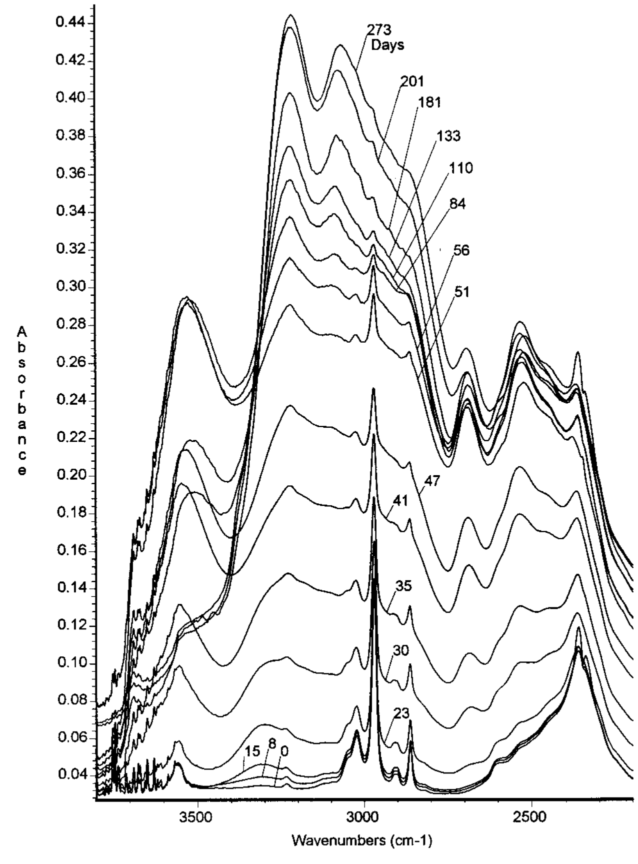


Figure 7. Acidification of the carboxylic methyl ester polymer (1022 g/equiv) in ambient air over time: acid region.

The acid peak height as well as the computed percent acid (as evaluated from the ratio of the acid and ester bands) transients over time are shown in Figure 9. For the films exposed to air, the majority of the conversion to the acid takes place in the first 100 days although the curves truly level off beyond 200 days. Note that at

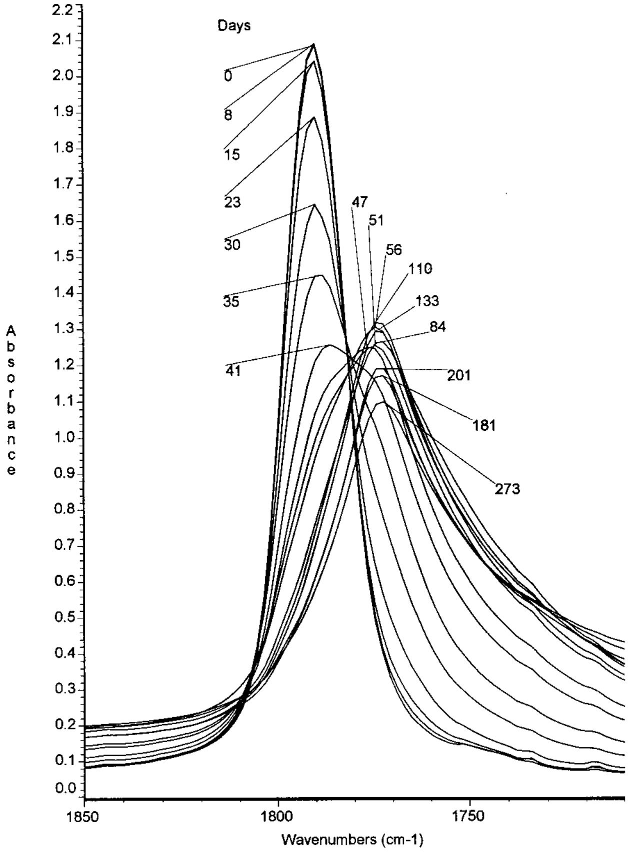


Figure 8. Acidification of the carboxylic methyl ester polymer (1022 g/equiv) in ambient air over time: carbonyl region.

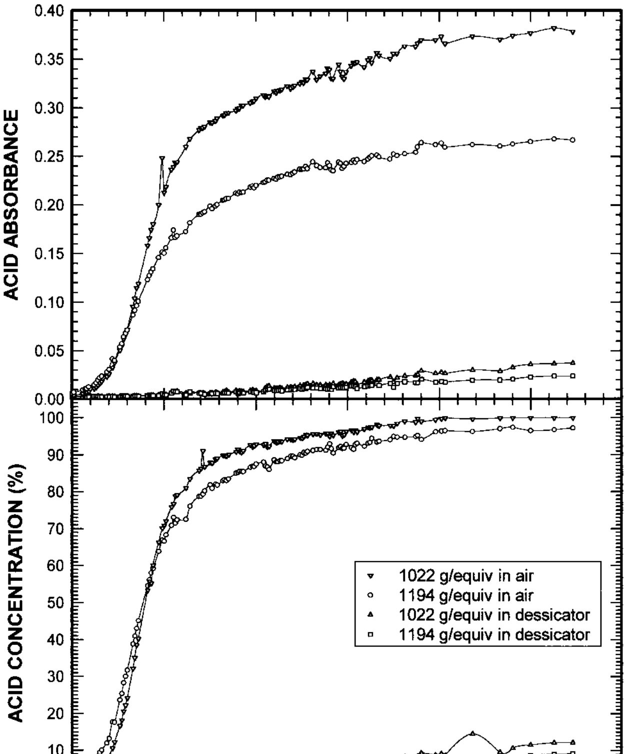


Figure 9. Acidification as measured by the acid band (top graph) and acid content (bottom graph).

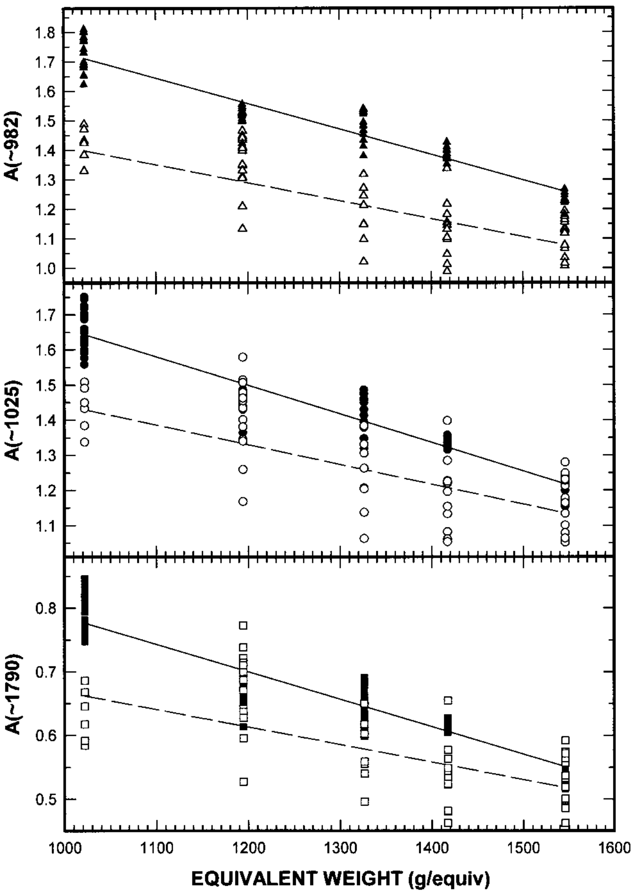


Figure 10. Attenuated total reflectance equivalent weight correlation to various peak heights. No band ratios involving the C−F thickness band were used. Filled symbols represent polymers with some acid content and unfilled symbols represent low-acid polymers after esterification with TMOF.

50 days (~80−90% acid conversion) the curves begin to level off. At this point, the majority of the abrupt peak shifts occur. The higher the EW, the higher the crystallinity, which accounts for the long-term acid concentration in the higher EW polymer being lower than in the low-EW polymer. The polymers sealed in the desiccator showed very little conversion to the acid form. What small conversion did take place could be due to the exposure to ambient air during the daily measurements. The sigmoidal curves in Figure 9 illustrate the initial small surface reaction converting the $-CH_3$ groups plus water to −H groups and CH_3OH. Once the water diffuses into the polymer, the reaction is much more extensive, as evidenced by the sharp increase in the acid content. Finally, after ~100 days, during which greater than 90% of the groups have been converted to the acid form, diffusion of the water around the crystalline regions and into the interior structure takes place over an extremely long time. A higher temperature could be used to promote an acceleration of both the diffusion and reaction.

ATR Studies. ATR measurements of Nafion films should conceivably yield a correlation for EW determination as did the transmission measurements. Measurements of bifilms, surface structure, and laminates, which were not possible with transmission measurements, should also be obtainable with ATR. In addition, since the penetration depth of the evanescent wave propagates the same distance into each polymer film (assuming that the change in EW and therefore crystal-

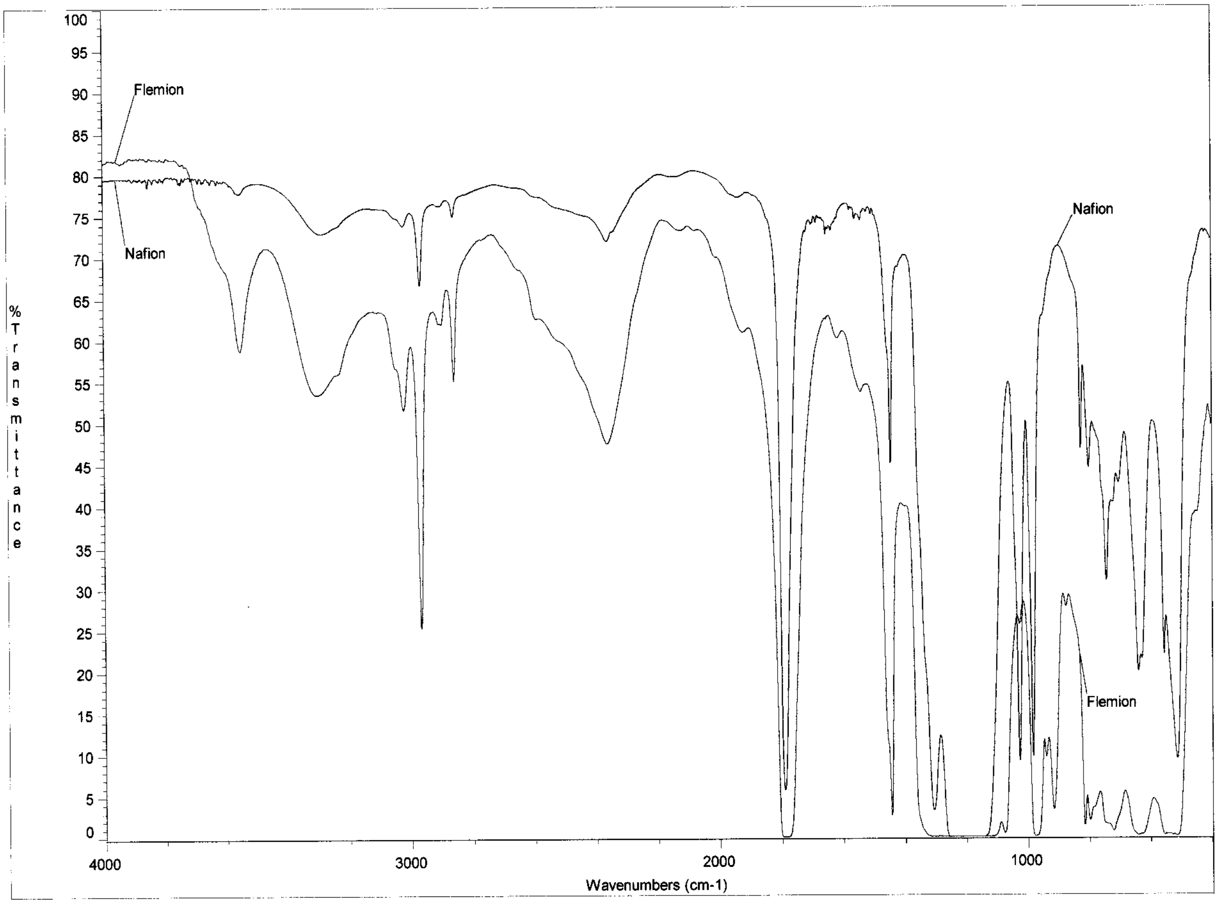


Figure 11. Flemion methyl ester carboxylate polymer FT-IR spectrum compared to the longer side chain Nafion methyl ester polymer.

linity does not significantly alter the path length), the EW measurement should be independent of film thickness. A series of experiments, using five samples from the transmission studies, are detailed below to investigate the potential of developing an ATR method for EW determination.

In ATR, the "effective path length" is the product of the depth of penetration and the number of internal reflections in the crystal. The crystals used in this study yield 16 internal reflectances at the incident angle of 45°. The depth of penetration is defined as the depth at which the field strength of the evanescent wave falls to 1/*e* of the initial magnitude at the edge of the sample. Equation 12 shows the direct dependence of the penetration depth on wavelength

$$d_{\mathrm{p}} = \frac{\lambda}{2\pi(\sin^2\theta - n_{\mathrm{sp}}{}^2)^{1/2}} \qquad (12)$$

where, d_{p} is the penetration depth (cm), λ is the wavelength in the crystal (cm), θ is the incident angle, and n_{sp} is the ratio of the refractive index of the sample-to-refractive index of the crystal.

What is not evident from eq 12 is that the refractive index is itself dependent on wavelength. Most published numbers for refractive index are not pertinent for use at infrared wavelengths, and their use would be misleading and inaccurate. In addition, the refractive index changes drastically at an absorption band, making the evaluation of eq 12 at the relevant wavelengths complex. However, for a rough estimate, the measured value of 1.3413 for the sample refractive index was used so that $n_{\mathrm{sp}} = 1.3413/2.35 = 0.570\,77$ and $\theta = 45°$ were used over the $\lambda = 2.5-25$ μm range to yield a d_{p} equal to 0.95−9.5 μm.

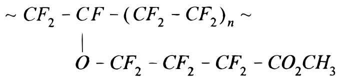
Samples were first measured "as is" with acid contents ranging from 18 to 24%. The samples were then re-esterified with TMOF and measured again, which reduced the acid content to less than 1%. Several replicates of each polymer batch were run by pressing numerous films. Three absorbance bands in each sample were measured and correlated to the titration EW, as shown in Figure 10. The ~982 (due to the proximal ether bond), ~1025 (the distal ether bond), and ~1790 cm^{-1} (due to the carbonyl bond) bands were chosen for these correlations. The reference baseline for the ether bands was ~900 and ~2100 cm^{-1} for the carbonyl band.

For each correlation, it is apparent that the absorbance decreases with increasing EW since less ether or carbonyl structures are present. In addition, the TMOF-treated (low-acid) samples consistently yield a smaller absorbance and a slightly smaller slope than those of the untreated samples possibly due to extraction of some low-EW oligomers during re-esterification or from breaking up the hydrogen-bound acid structures. The scatter in the replicate data samples is, however, disturbing. It is not clear that a linear regression is appropriate for these correlations but is included in Figure 10 in an attempt to separate the data. The scatter could be due to differences in film contact with the crystal or an inhomogeniety in the polymer samples. In either case, more refinements must be developed before an ATR method could compete with the accuracy of the transmission method.

Table 4. Flemion−Carboxylic Methyl Ester Form

band/wavenumber	Flemion (methyl ester)	Nafion (methyl ester)
C=O overtone	3554	3555
O−H	3309	3289
	3024	3025
C−H	2968	2969
	2860	2863
C−F combin.	2366	2363
C=O	1790	1790
O−CH_3	1444	1445
CF_3		1306
C−F	∼1200	∼1200
	1076	
C−O−C	1028	1026
C−O−C	974	984
	916	
		826
	816	
	798	801
C−C	∼740	743
CF_2	721	721
		702
CF_2 wag	640	639
CF_2 wag		627
C−F	555	555
CF_2 rock	515	513

Shorter Side Chain Polymer. The carboxylate form of Flemion, manufactured by Asahi Glass, is made by copolymerizing tetrafluoroethylene (TFE) and the methyl ester of perfluoro(5-oxa-6-heptenoic acid) having the chemical formula $CF_2{=}CF{-}O{-}CF_2CF_2CF_2{-}CO_2CH_3$ resulting in the polymeric structure shown in Structure 2. The sulfonate form of Flemion is identical in chemical structure to the sulfonate form of Nafion. A representative spectrum of Flemion (methyl ester form, 700 g/equiv, thin film) is shown in Figure 11 and is compared to a Nafion methyl ester thin film spectrum. The peak assignments for the carboxylic methyl ester form of Flemion are listed and compared to the Nafion CR methyl ester peak assignments in Table 4.



$$\begin{array}{l}\sim CF_2-\underset{|}{CF}-(CF_2-CF_2)_n\sim\\ \qquad\quad O-CF_2-CF_2-CF_2-CO_2CH_3\end{array}$$

The greatest differences between the carboxylate forms of Flemion and Nafion are seen in the low-energy portion of the spectrum. The ether linkage close to the backbone is present at 984 cm^{-1} for Nafion but is shifted 10 wavenumbers to lower energy in Flemion presumably because the shorter side chain has less electron-drawing power. In addition, both ether peaks at 984 and 1026 cm^{-1} are present in the Nafion spectrum, but only one strong ether is present for Flemion (a very weak 1028 peak is included in the table for completeness, but is not believed to be a second ether). The 1306 cm^{-1} band, believed to be the $-CF_3$ group on the side chain, is present in the Nafion spectrum but absent in the Flemion spectrum, which adds more credibility to this assignment. In addition, some of the peaks in the low-energy "fingerprint" region are different or shifted between the two spectra.

Note that since the Flemion carboxylate polymer is a different structure than Nafion CR, neither the EW nor acid content of Flemion can be measured with the Nafion calibration curves. A calibration curve could be generated for Flemion on the basis of either the ether (974 cm^{-1}) or C−H (2968 cm^{-1}) peaks using the procedures detailed in this paper.

Conclusions

An FT-IR method has been developed to enable quantitative determination of the equivalent weight and acid content of perfluorocarboxylate polymers. Both transmission and reflectance studies revealed a correlation between the EW obtained from titration to the ether and carbonyl absorbances to enable EW evaluation over the range of 800−1900 g/equiv. The conversion of the carboxylic methyl ester to the acid form involved the diffusion of water into the polymer thus causing swelling followed by reaction at the methyl ester sites; crystallinity hindered the complete acidification of the polymer. Polymers stored in a vacuum attained negligible acidity. The FT-IR techniques described in this paper represent a versatile method to measure the equivalent weight, acid and salt content, impurities, water, and many other properties of carboxylate films, bifilms, and membranes in the unhydrolyzed, salt, or acid forms.

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