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Dielectric Relaxation Studies of Perfluorocarboxylate Polymers

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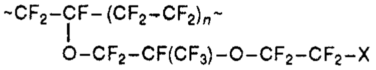
ABSTRACT: Dielectric studies of Nafion[‡] perfluorocarboxylate polymers in the methyl ester, potassium and sodium salt, and carboxylic acid forms over an equivalent weight (EW) range of 950–1334 (15.6–9.8 mol % vinyl ether) uncovered α, α', β, γ, and δ dielectric relaxations. The α relaxations occurred between −20 and +100 °C with activation energies (E_a) between 35 and 110 kcal/mol indicative of the motion of the polar vinyl ether side chains. The β relaxation, observed between −80 and −10 °C, was characterized as the ester rotation with an E_a = 13–26 kcal/mol. The amplitude of the dissipation factor of both the α and the β peaks increased linearly with decreasing equivalent weight indicating that a larger number of side chains (lower EW) resulted in a more intense dielectric response. Furthermore, the area under the β relaxation curves (a measure of the total population of ester groups) increased monotonically with the side-group concentration. The β peak location did not shift as a function of EW but did change depending on the chemical form of the polymer; i.e., lowest temperature for the salt and highest temperature for the acid. A γ relaxation, the crankshaft rotational movement of nonlinear $-CF_2-$ groups along the polymer backbone similar to that in PTFE, was hidden under the more dominant β peak but began to emerge at around −100 °C at frequencies below 10 Hz with an E_a between 10 and 19 kcal/mol; in the acid form, however, the γ peak dominated the β peak. The δ relaxation (E_a = 3–5 kcal/mol), occurring between −200 and −150 °C, was attributed to the highly polar $O-CH_3$, O-K, and O-H groups at the end of the side chain.

Introduction

Perfluorinated carboxylate polymers have been used since the mid-1970's in membrane structures to achieve high ionic selectivity. Used in conjunction with the more highly conductive, yet less selective, sulfonate polymers, membrane composites such as Nafion have achieved excellent performance in many industrial separation processes. The structure of the sulfonate polymer has been studied, and a brief summary of past research is given below. Very few studies have been performed on the carboxylate polymer, and those that have deal mainly with ionic transport through the membrane as opposed to fundamental structure/property relationships of the polymer. This paper is intended to present dielectric, mechanical, thermal, and FT-IR data leading to a better structural understanding of the carboxylate polymer.

Nafion in the carboxylate form is a copolymer of tetrafluoroethylene (TFE) and 2,2,3,3-tetrafluoro-3-[1′,2′,2′-trifluoro-1′-(trifluoromethyl)-2′-[(1″,2″,2″-trifluoroethyl)oxy]ethoxy]propanoic acid, methyl ester, the polymeric structure of which is



$$\begin{array}{l}\sim CF_2-\underset{|}{C}F-(CF_2-CF_2)_n\sim \\ \qquad O-CF_2-CF(CF_3)-O-CF_2-CF_2-X\end{array}$$

where X = CO_2CH_3 (methyl ester form), CO_2K (potassium salt form), or CO_2H (carboxylic acid form). The polymer composition is expressed in terms of the equivalent weight (EW) defined as the weight in grams of polymer containing 1 equiv of acid or, alternatively, the comonomer molecular weight plus 100*n*, where *n* is the number of moles of TFE per mole of comonomer. 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 side groups hinder crystallization.

Extensive work has been performed on the sulfonate polymers where X = SO_2F, SO_3K, or SO_3H. Mauritz and co-workers[1–4] detected a low-frequency dielectric peak indicative of dc conduction or intercluster, long-range ion hopping and a high-frequency peak thought to be due to diffusion-controlled ionic polarization leading to ion transport across clusters in the salt form. Dielectric data were measured at or slightly above room temperature from 5 Hz to 13 MHz. Mauritz et al.[5] presented a model for dipole interactions and critically reviewed the current theoretical models;[6] no true quantitative model presently exists which could be used to predict transport or structure/property relationships for sulfonate polymers.

Yeager and co-workers[7–10] have also studied ionic and water transport mainly to measure diffusion coefficients in Nafion as a function of concentration and temperature.

Some excellent work by Eisenberg and co-workers[11,12] and especially by Hodge and Eisenberg[13] detailed the low-temperature properties of a single sulfonate polymer sample. Specifically, Hodge and Eisenberg detected three sub-glass transition peaks and the T_g at low frequencies for a single sample (EW was not reported). In addition, Eisenberg et al.[14] have recently proposed a new theoretical model based on cluster and multiplet formation to help characterize cationic transport in ionomers.

Starkweather et al.[15,16] examined the degree of crystallinity, crystal size, and water uptake in the sulfonate forms of Nafion.

Most previous work sought to examine the ion-exchange characteristics and structure of Nafion sulfonate membranes. The present work examines the structure and chemistry of perfluorocarboxylate polymers in the various forms to elucidate fundamental relaxation mechanisms of the polymer.

Apparatus and Procedures

Nafion carboxylate samples of varying EW (see Table I) were pressed into 5-mil films, reesterified in trimethyl orthoformate (TMOF) to the methyl ester form, and dried. Gold/palladium was sputtered onto the opposite faces of each film forming two disk electrodes. The film was then sandwiched between disk-shaped backing metal electrodes held in position in thin insulating Teflon plates. The electrode assembly was inserted into a custom-made temperature-controlled chamber. An alternating voltage, applied between two electrodes and across the polymer film,

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[‡] Nafion is a DuPont registered trademark.

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Table I. Polymer Compositions

EW[a] (g/equiv)	n (mol of TFE/equiv)	mol % comonomer
950	5.42	15.58
1070	6.62	13.12
1163	7.55	11.70
1206	7.98	11.14
1334	9.26	9.75

[a] EW = $100n + 408$. All EW values are reported in the acid form.

stimulated the resistive and capacitive components of the polymer, yielding an electrical response from the sample which was measured with a multifrequency LCR meter (Hewlett-Packard, Model 4274-A), whose output was fed to a personal computer (Hewlett-Packard). From the measured values of the sample capacitance and dissipation factor (tan δ), together with the known sample geometry, the dielectric constant (ϵ') and dielectric loss factor (ϵ'') were then computed.

Salt and acid form samples were prepared by first hydrolyzing the methyl ester samples listed in Table I in a mixture of either KOH/DMSO/H_2O to convert to the potassium salt form or NaOH/DMSO/H_2O to convert to the sodium salt form and then acidifying in 10% HNO_3 to convert to the carboxylic acid form.

All samples were dried in a vacuum oven overnight at 110 °C prior to each experiment. During an experiment the temperature was ramped from −190 to +250 °C at 1.5 °C/min. Dielectric properties were measured at 11 frequencies ranging from 10^2 to 10^5 Hz. In addition, for low loss samples, the dielectric properties were measured with a Carl Andeen capacitance bridge (Model CGA-85) over the frequency range of 10^1–10^5 Hz.

Additional low-frequency (10^{-1}–10^5 Hz) experiments were carried out with use of a dielectric analyzer (TA Instruments DEA 2970). Sample preparation was identical to that described above. The temperature range used was from −170 to +150 °C at a scan rate of 5 °C/min. After scanning the 1163 EW polymer in the three forms, the samples were soaked in distilled, deionized water for 1 h and measured again.

A dynamic mechanical analyzer (DMTA; Polymer Laboratories) enabled mechanical measurements of the glass and subglass transitions without ion conduction interferring with the measurements at high temperatures at 1 and 10 Hz from −150 to +100 °C at 3 °C/min. Thermal mechanical analysis (TMA) was performed from −100 to +100 °C at 5 °C/min using 1–5-g loads in the penetration mode to measure thermal transitions. Infrared measurements were performed with a Fourier transform IR spectrometer (Nicolet, Model 730) from 400 to 4000 cm^{-1} to examine the carbonyl, ether, and methyl vibrational motions.

Experimental Results

The ester, salt, and acid forms of the perfluorocarboxylate polymers are first discussed individually and then compared to examine the polymer microstructure.

Methyl Ester Form. Four dielectric relaxations were observed for all Nafion methyl ester carboxylate polymers. The 1163 EW spectra, shown in Figure 1, display a typical set of temperature-dependent dissipation factor and dielectric constant curves at frequencies from 10^{-1} to 10^5 Hz. At all frequencies, a dissipation factor peak (β relaxation) centered between −80 and −10 °C was evident. Two smaller α relaxation peaks (α and α') located between −20 and +10 °C were both observed only at frequencies below 100 Hz. The α and β peaks were also detected in low-frequency (1 and 10 Hz) DMA studies. A shoulder (γ relaxation) on the β peak, present at around −100 °C, was evident at low frequencies. Note that, at high temperatures, the signal increased to very large tan δ values due to the ionic conduction contribution.

Arrhenius plots for the α, β, and γ dielectric relaxations are shown in Figure 2, each curve representing three duplicate polymer measurements. The activation energy (E_a) for the three peaks varies with EW: α between 30 and 60 kcal/mol decreasing with EW, β between 16 and 23 kcal/mol slightly increasing with EW, and γ between 11 and 19 kcal/mol. Note that the α curve is nonlinear. The activation energy for the α relaxation is typical of values measured for polymer glass transitions (T_g),[17] while the β relaxation indicates a movement of or within the side chains; both relaxations will be discussed in detail later in the paper.

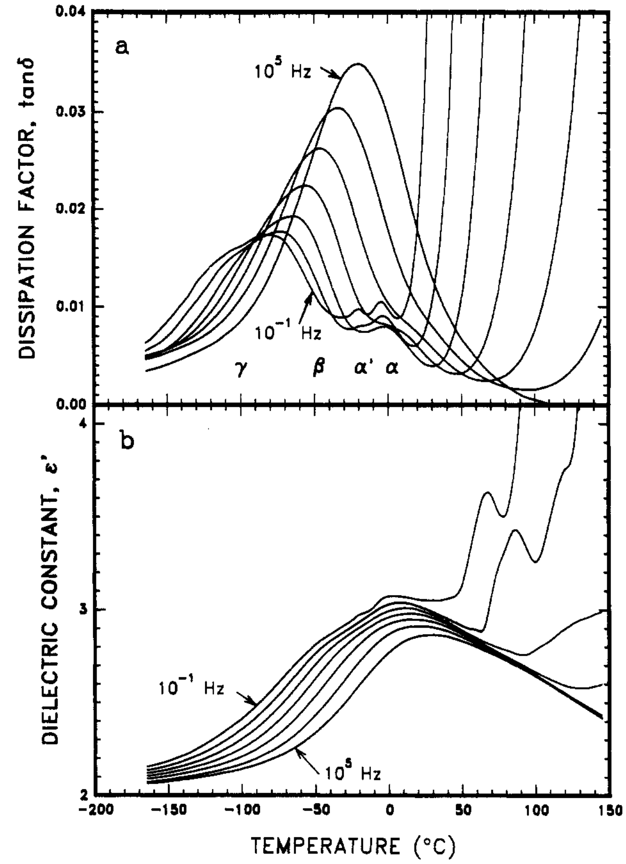


Figure 1. (a) Dielectric dissipation factor and (b) dielectric constant for the methyl ester form (1163 EW) as a function of temperature. The frequency range is 10^{-1}–10^5 Hz.

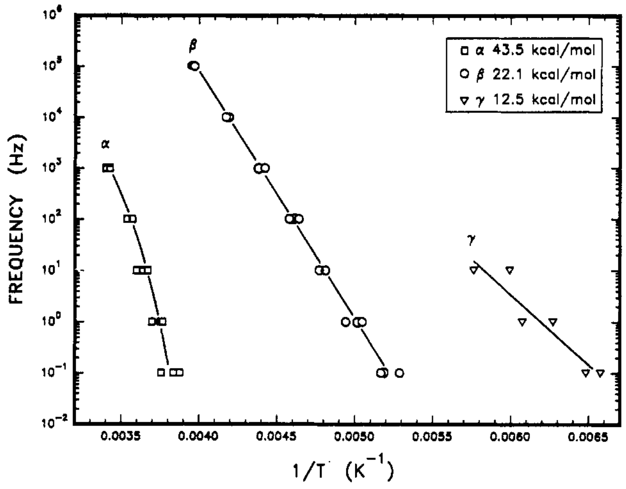


Figure 2. Arrhenius plot of α, β, and γ relaxations for the methyl ester form (1163 EW) polymer.

A modified Cole–Cole plot for the 1163 EW polymer at temperatures between −170 and +50 °C (for clarity, only the −70 to −20 °C curves are labeled) over the 7-decade frequency range is given in Figure 3. The dashed curves represent isotherms, while the solid curves depict constant frequency. The data from Figure 3 and other Cole–Cole plots of each polymer at −50 °C were curve fit at various frequencies to obtain the values of the unrelaxed (ϵ_u) and relaxed (ϵ_r) dielectric constants. A summary of the data is given in Table II.

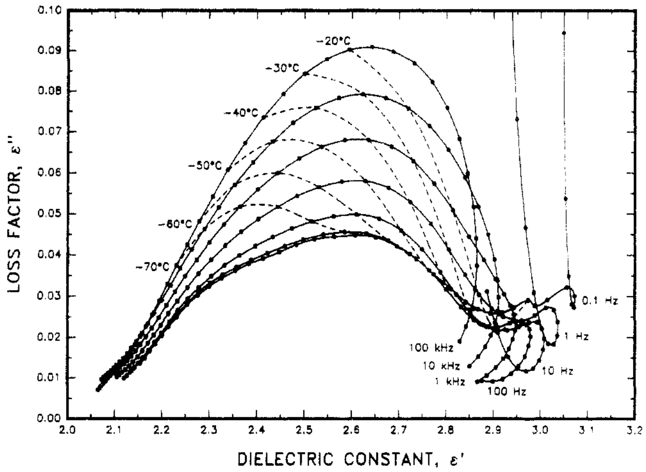


Figure 3. Modified Cole–Cole plot for the methyl ester form (1163 EW) polymer β relaxation from 10^{-1} to 10^5 Hz and between −170 and +50 °C. Dashed curves represent constant temperature, while solid curves represent constant frequency data.

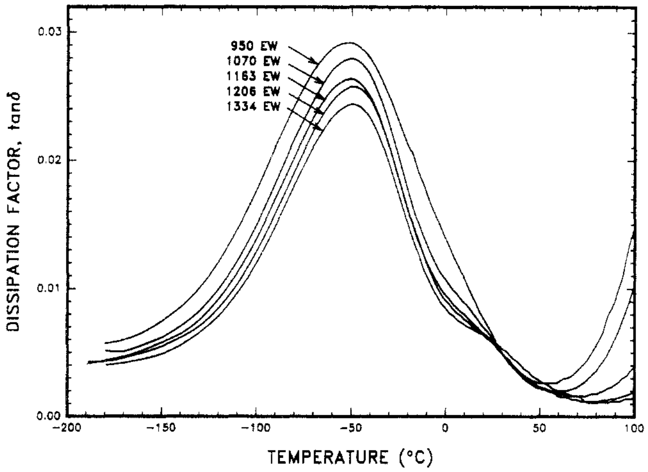


Figure 4. Five isochronal dielectric spectra superimposed to show the influence of EW (methyl ester form) on the β transition at 1000 Hz.

Table II. Computed High- and Low-Frequency Dielectric Constants and β Dipole Moments at −50 °C

polymer EW	heat	ester ϵ_u	ester ϵ_r	salt ϵ_u	salt ϵ_r	μ (D)
950	1st	2.60	3.87			1.67
	1st			2.40	2.57	0.66
	2nd			2.28	2.31	0.27
	3rd			2.27	2.31	0.37
1070	1st	2.42	3.63			1.80
	1st	2.24	3.30			1.76
1163	1st	2.03	3.06			1.90
	1st	2.23	3.19			1.76
	2nd	1.82	2.58			1.73
1206	1st	2.29	3.40			1.89
	1st			2.37	2.59	0.86
	2nd			2.25	2.27	0.27
	3rd			2.22	2.26	0.36
1334	1st	2.30	3.31			1.90
	1st			2.35	2.61	0.98
	2nd			2.26	2.28	0.31
	3rd			2.23	2.26	0.36

Dielectric spectra at 1000 Hz for five polymer samples are shown in Figure 4. The β peak centered at −50 °C represents a dipolar relaxation whose peak height decreases with increasing EW, as shown in Figure 5; i.e., the measured peak dissipation factor is a monotonically decreasing function of EW (hence, a monotonically increasing function of the polar vinyl ether side-group concentration). In general, the dielectric constant also decreased with increasing EW. Note that the mechanical dissipation data from DMA studies show that the tan δ values for the β peak are independent of EW at 1 and 10 Hz, indicating that the side-group motion, active over a given temperature range, can be detected mechanically as well as electrically but the concentration of side groups influences only the electrical impedance and not the absorbed mechanical energy.

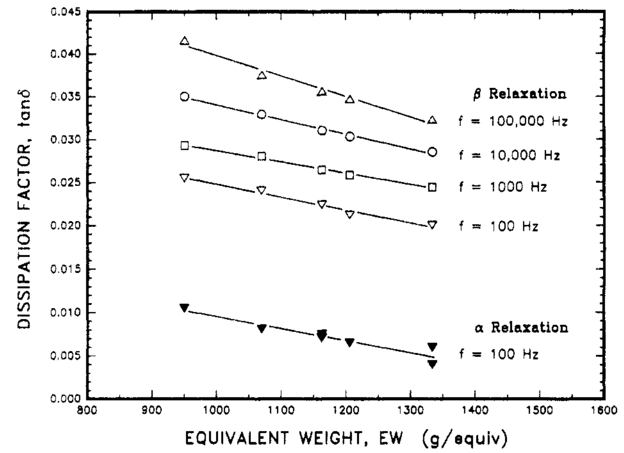


Figure 5. Variation of the peak tan δ with EW for the α and β transitions.

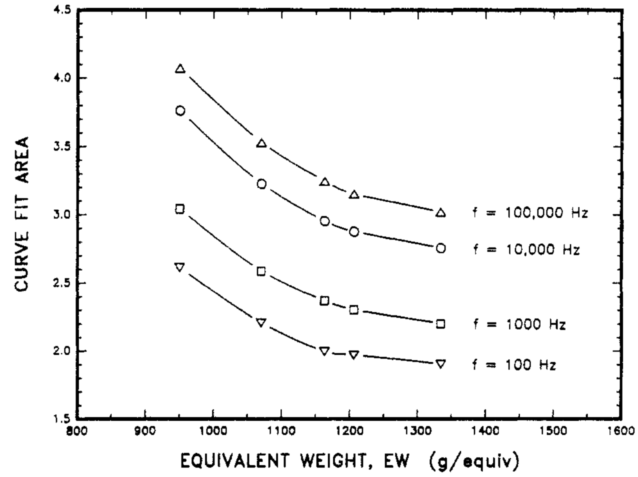


Figure 6. Variation of the computed curve fit areas under the five β peaks in Figure 4 with EW.

Data at all frequencies were curve fit by a nonlinear regression in the range of −100 to +50 °C. The area under the curve, indicating the total concentration of species undergoing the β relaxation, was found to be a monotonically decreasing function of the EW and a function of frequency, as shown in Figure 6.

The β peak temperature, a measure of the threshold limit of the relaxation, did not vary more than 0.1 °C with EW. Even at low EW where the concentration of side groups is high, the interaction between dipoles is negligible (no steric hindrance). It may be expected, though, that if polymers with even lower EW could be made, the maximum temperature would shift to higher values.

The α peak decreases with increasing EW in both dielectric and DMA scans. The β relaxation peak values, however, are independent of EW in DMA scans but strongly dependent on EW in dielectric studies. Figure 5 shows dielectric tan δ values for the α relaxation which compare almost exactly in slope to the β relaxation. The concentration of side chains thus influences both the α and β relaxations, indicating that both transitions represent dipole motions of or within the side chain. In the DMA studies, the α peak tan δ decreases at higher EW

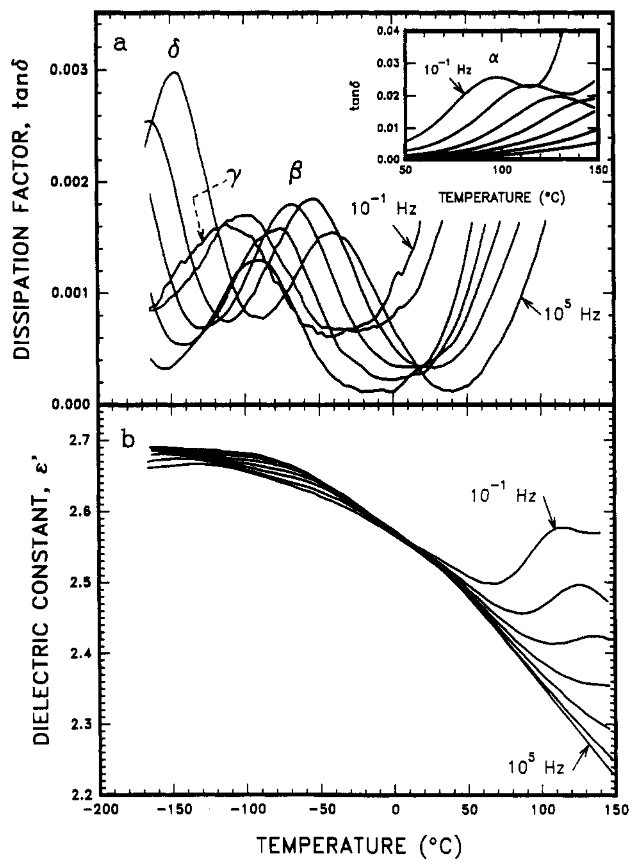


Figure 7. (a) Dielectric dissipation factor and (b) dielectric constant for the potassium salt form (1163 EW) as a function of temperature. The frequency range is 10^{-1}–10^5 Hz. The inset plot shows the α transition.

because the polymer crystallinity increases. The crystallinity, though, does not affect the mechanical β relaxation, indicating that the "secluded" β dipole is positioned along the side chain and far from the backbone so that the changes in crystallinity do not affect the β motion. Note that the temperatures at the peak tan δ values for all relaxations obtained via DMA are 10–30 °C higher than dielectric values yet the activation energies are comparable. This discrepancy between DMA and dielectric measurements has been reported in the literature by Starkweather and Avakian for phenylene polymers.[18]

The tan δ data in the ionic conduction/dipolar region at 100 °C in Figure 4 are also seen to be a direct function of the EW. Since crystallinity is known to increase with EW, at higher EW the free ion motion is impeded by the higher degree of crystallinity.

Salt Form. Dielectric spectra for the potassium salt carboxylate form of Nafion uncovered a low-temperature δ peak, as shown in Figure 7, as well as the β peak seen in the methyl ester data. The γ shoulder began to emerge at the lower frequencies, and the α transition may be observed at around 100 °C.

The α transition, shown in the inset plot in Figure 7, has an order of magnitude greater tan δ value than the β, γ, or δ relaxations and is shifted to higher temperatures than in the methyl ester case. The activation energy for the α transition ranged between 35 and 43 kcal/mol for the Na and K form polymers. No measurable difference was detected between the two salt forms.

The β peak shifted to lower temperatures by approximately 20 °C and displayed a lower range of activation energies (13–16 kcal/mol) than the methyl ester data (16–23 kcal/mol). In addition, the tan δ values are depressed an order of magnitude compared to the ester data. A rough approximation of the β relaxation tan δ was obtained by ratioing the Debye equations and neglecting ionic conduction since $T < T_g$

Table III. β Relaxation Times

	ester			salt		
f (Hz)	T_m (°C)	tan δ	τ (s)	T_m (°C)	tan δ	τ (s)
10^2	−60.1	0.0209	3.68×10^{-2}	−76.4	0.00198	1.43×10^{-2}
10^3	−50.1	0.0258	2.98×10^{-3}	−65.9	0.00217	1.30×10^{-3}
10^4	−40.3	0.0300	2.56×10^{-4}	−53.7	0.00233	1.21×10^{-4}
10^5	−20.2	0.0345	2.22×10^{-5}	−37.3	0.00250	1.13×10^{-5}

$$\tan \delta = \frac{\epsilon''}{\epsilon'} = \frac{(\epsilon_r - \epsilon_u)\omega\tau}{\epsilon_r + \epsilon_u(\omega\tau)^2} \qquad (1)$$

where tan δ = dissipation factor, ϵ'' = dielectric loss factor, ϵ' = dielectric constant, ϵ_r = relaxed low-frequency dielectric constant, ϵ_u = unrelaxed high-frequency dielectric constant, $\omega = 2\pi f$ = frequency (rad/s), and τ = relaxation time (s). Using the data in Table II, the strength of the relaxation $\epsilon_r - \epsilon_u$ in eq 1 is found to be much less for the salt (0.03) than for the ester (1.1) which accounts for the depressed tan δ values in Figure 7 vs Figure 1.

The relaxation time can be computed from eq 1 by solving the quadratic at a specified frequency and using the values for ϵ_r and ϵ_u in Table II. Table III shows some sample results for the 1206 EW polymer relaxation. In all cases, the τ_{ester} is greater than τ_{salt}. Thus, the salt β relaxation is activated with less thermal energy (peak shifted to lower temperature), needs less energy to become active (smaller E_a), and is quicker to relax (smaller τ) than the ester β dipole.

Acid Form. Upon acidification, the carboxylic acid polymer displayed α, β, and γ transitions, as shown in Figure 8. Although many replicate samples were run, the reproducibility of the dielectric data was poor. The tan δ peak values varied between 0.002 and 0.009, while the ϵ' values ranged between 1.9 and 2.4. The cause of the variance is unknown. It was speculated that the scatter could emanate from the equilibrium reaction during conversion from the salt to the acid form, but FT-IR measurements of the polymer after acid washing three times under reflux revealed the carbonyl peak at 1775 cm^{-1}, indicating complete acidification (the salt peak would have appeared at 1680 cm^{-1}).

Figure 8 illustrates a low loss spectra where the α and γ relaxations dominate the spectra. The β relaxation is actually masked by the γ relaxation but begins to appear at the lower frequencies. The α relaxation is shifted to higher temperatures by approximately 50 °C in the acid form relative to the ester form but occurs 50 °C lower than in the salt form. In addition, very low temperature studies performed at frequencies between 10^2 and 10^5 Hz on the 1206 EW acid polymer elucidated a further δ peak located between −200 and −150 °C with a E_a = 3.3 kcal/mol. The magnitudes of all acid tan δ values are comparable to the salt form values and are an order of magnitude lower than the ester data.

The ϵ' values were measured as low as 1.9, comparable to the ϵ' value of PTFE (2.04[19]). The small ϵ' values indicate hydrogen bonding either between side groups or with entrapped water in the acid polymer rigidly hindering the orientation of dipoles at the end of the side chain. This rigid structure may also account for the elevated α peak temperature and the depressed β peak tan δ relative to the ester polymer.

An Arrhenius plot (Figure 9) gives larger α and somewhat larger β activation energies than for the ester but a comparable γ energy. The data plotted in Figure 9 are

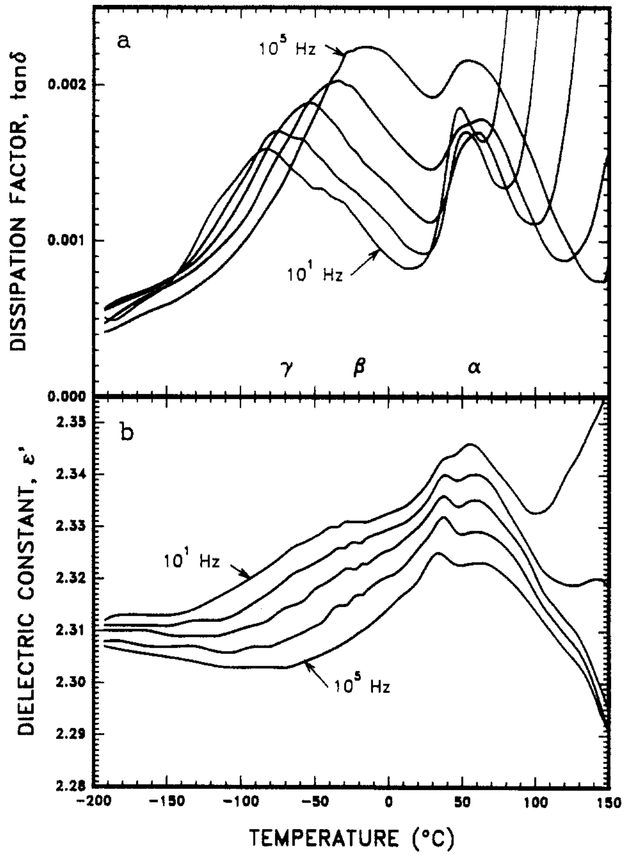


Figure 8. (a) Dielectric dissipation factor and (b) dielectric constant for the carboxylic acid form (1163 EW) as a function of temperature. The frequency range is 10^1–10^5 Hz.

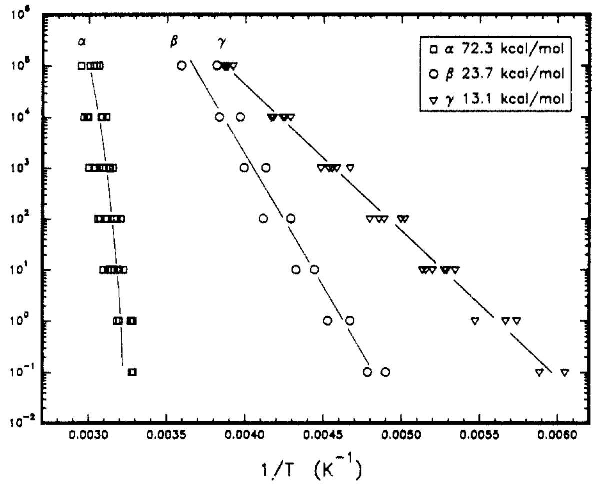


Figure 9. Arrhenius plot of α, β, and γ relaxations for the carboxylic acid form (1163 EW) polymer.

from seven replicate spectra performed on either the DEA or Andeen dielectrometers. The curvature of the α curve is characteristic of a T_g relaxation. Note that the E_a for the α transition cited in the figure is calculated based on all points along the curve; if only points at the lower temperatures were used, the activation energy would be much higher. The activation energies, taken on various acid form samples, indicate that α varies between 70 and 110 kcal/mol, β between 23 and 26 kcal/mol, and γ between 11 and 14 kcal/mol.

Discussion of Results

A summary of the peak assignments is found in Figure 10 and discussed below.

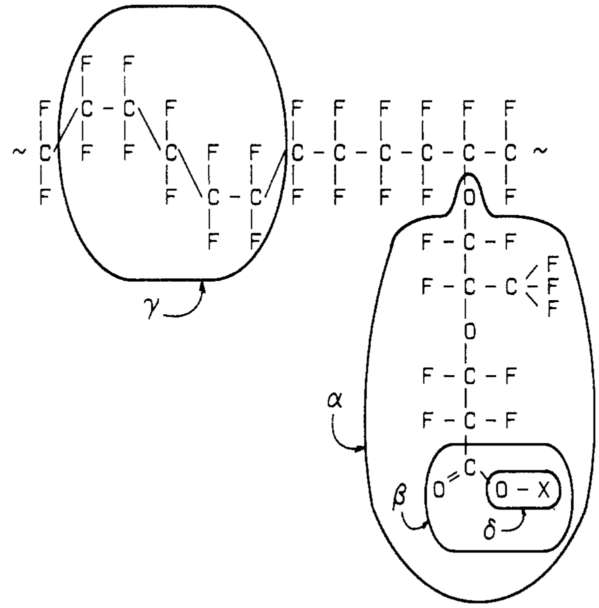


Figure 10. α, β, γ, and δ polymer relaxations.

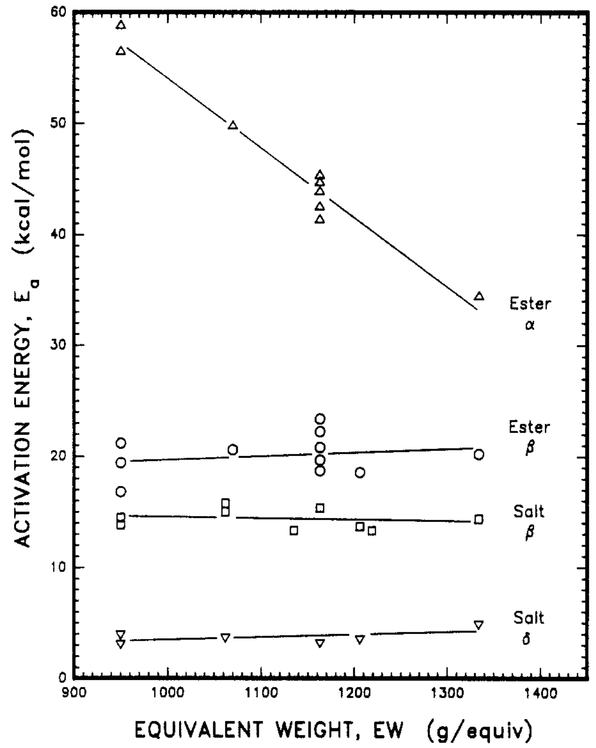


Figure 11. Influence of equivalent weight on the activation energy for the α, β, and δ dielectric relaxations. Note that both Na and K ionic forms were used to generate the salt polymer data.

α and α′ Relaxations. The α peak, observed between -20 and +100 °C, exhibits an activation energy between 35 and 110 kcal/mol which is in the range of the glass transitions of other polymers.[17] This tan δ peak is seen in dielectric, DMA, and TMA studies and decreases in amplitude with increasing EW; thus, the peak is representative of the side chain rather than the backbone motion. The peak was present in the ester, salt, and acid forms. The activation energy for the α relaxation decreased as a function of EW, as shown in Figure 11, implying steric hindrance of the side-chain motion at decreasing EW. The lower temperature relaxation energies were virtually independent of EW. In addition, the peak tan δ for the α transition occurred at the lowest temperature for the ester, higher for the acid, and highest for the salt. The activation energy, however, was lowest for the salt and highest for the acid. The α peak, thus, represents a relatively high temperature, sterically hindered transition, and is attributed to the motion of one or more vinyl ether side chains.

In contrast to the α peak, the α' peak is not well-defined. Since α' only occurs at the lowest frequency, an activation energy could not be obtained. Lower frequency studies are needed to better resolve the α' peak.

β Relaxation. The β relaxation dissipation factor, from Figure 4, decreases with increasing EW, implying the peak represents motion along the side chain. The narrower range and lower values of the activation energies (13–26 kcal/mol) as compared to the α relaxation further implies a local motion along the side chain. The motion is unaffected by the number of neighboring side groups present since the E_a from Figure 11 is constant over the EW range; note that one additional high equivalent weight (1853 EW) salt β data point (not plotted) displayed an E_a = 13.8 kcal/mol, confirming that E_a is independent of EW. The dissipation factor varies with the concentration of side groups present, but the activation energy required to move this dipole is concentration independent. Thus, the dipole is not sterically hindered over the EW range studied, implying that β represent a more "secluded" dipole. The β relaxation is present in both dielectric and DMA studies in all chemical forms but absent in the PTFE electrical and mechanical spectra. The peak does not undergo a temperature shift with EW but does shift in temperature depending on the chemical form of the polymer; the lowest peak temperature occurs in the salt, higher for the ester, and highest for the acid. The same ordering is observed when examining the E_a: lowest for the salt (13–16 kcal/mol), higher for the ester (16–23 kcal/mol), and highest for the acid (23–26 kcal/mol). The only dipoles along the side chain which change with the chemical form of the polymer are at the end of the side chain: ester (–COOX), carbonyl (C=O), or ether (O–X), where X = CH_3 (ester), K (salt), or H (acid).

FT-IR studies were used to examine the C=O and O–X vibrational bands. The C=O band shifts from 1790 cm^{-1} (methyl ester) to 1680 cm^{-1} (salt) and back to 1775 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. Between 1400 and 1450 cm^{-1}, a band characteristic of the O–CH_3 (1444 cm^{-1} for the methyl ester), O–K (1408 cm^{-1} for the salt), and O–H (1443 cm^{-1} for the acid) is present. Again, the ionic salt band requires less energy to vibrate than the other two covalent bonds.

Although one must exercise extreme care when comparing the vibrational motion detected by FT-IR and the rotational motion detected by dielectrics, the two measurements can complement one another. The FT-IR data for the C=O and O–X vibrational motions require the least amount of energy in the salt form and larger energies in the ester and acid structures. The differences in bond strength and the hydrogen-bonding character of the three polymer forms account for the different energy requirements. The rotational motion, detected by dielectrics, is also greatly influenced by these two factors. The β rotation requires the least amount of energy in the salt form, a greater amount in the ester form, and the largest in the acid form. Neither of the FT-IR measured C=O or O–X energies display the energy trend measured by dielectrics and, therefore, do not represent the β relaxation. However, the rotation about the –COOX bond would follow the energy trend: the salt would require the lowest energy due to the weaker ionic bonds, the ester a somewhat higher energy due to longer, possibly hydrogen-bonded groups, and the acid would require the largest energy because of the possible rigid dimer formation. It will be further shown in the Dipole Moment section that the computed dipole moment of the β peak agrees with literature values of the –COOX groups rather than the C=O dipoles, so henceforth the β peak is attributed to the $-COOCH_3$ (ester), –COOK (salt), and –COOH (acid) groups.

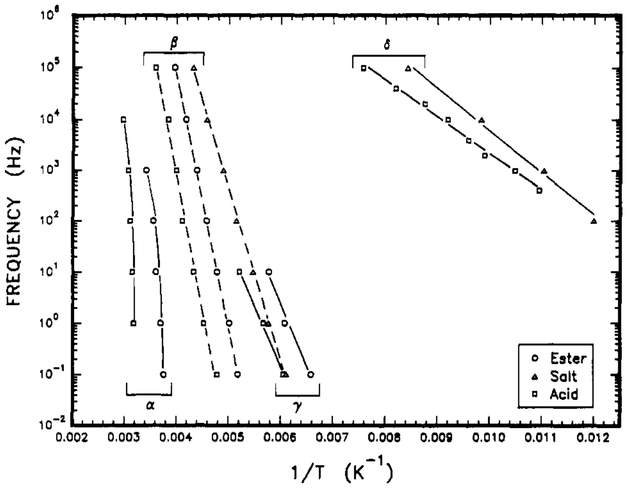


Figure 12. Composite Arrhenius plots for the three forms of Nafion (1206 EW).

γ Relaxation. For the PTFE homopolymer, a crankshaft rotational transition occurs at –100 °C at 1000 Hz[20] but is much smaller in amplitude than the Nafion β peak and is therefore masked by the β peak in the ester and salt form polymers. At very low frequencies (<10 Hz), however, the γ peak begins to appear. The measured activation energies of 10–19 kcal/mol and the peak position agree with measurements made of the crankshaft motion in PTFE.[21] This PTFE peak will henceforth be called a γ relaxation and displays a rotational crankshaft motion along the Nafion backbone similar to the motion in PTFE; i.e., the rotation of four or more $-CF_2-$ groups.

δ Relaxation. The δ relaxation is present in the salt and acid samples but is not observed in the ester form. The low-temperature (–200 to –150 °C) behavior and low activation energy (3–5 kcal/mol) imply a very unconstrained localized motion. The composite Arrhenius plot, shown in Figure 12, indicates that for the δ relaxation the salt has the lowest temperature transition, as in the β relaxation, and a slightly higher E_a for the salt as compared to the acid δ relaxation. From Figure 11, the E_a for the salt δ transition is shown to be independent of EW; the δ transition, like the β relaxation, is, thus, not sterically hindered by adjacent side chains. Note that the ester C=O rotation would be expected to occur at a higher temperature than in the salt form, but an ester δ peak is not observed at any temperature above –200 °C; thus, the motion of the carbonyl group is eliminated from further consideration.

The relaxation of the O–H group in the acid form would be expected to occur at the highest temperature because of the formation of hydrogen-bonded structures holding the hydroxyls in place. The hydrogen bonding could be due to the side groups bonding either to other side groups or to free water. The relaxation for the mobile O–K dipoles in the salt form would occur at lower temperatures due to weaker bonding forces. Finally, the O–CH_3 dipole is very polar and would undergo a relaxation at the lowest temperature. Figure 12 verifies these ideas although the δ transition in the ester state was beyond the lower

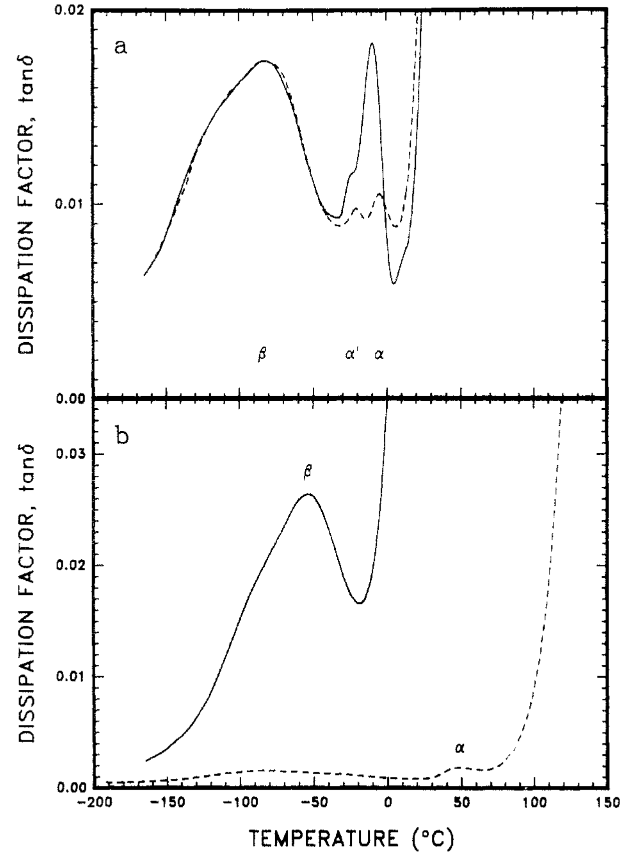


Figure 13. (a) Methyl ester polymer at 10^{-1} Hz. The solid curve represents polymer soaked in water for 1 h; the dashed curve represents dry polymer (data taken from Figure 1). (b) Carboxylic acid polymer at 10^1 Hz. The solid curve represents polymer soaked in water for 1 h; the dashed curve represents dry polymer (data taken from Figure 8).

temperature limit of the present experimental apparatus. Therefore, the δ peak is attributed to the highly polar O–K and O–H dipoles (and probably O–CH_3 at a much lower temperature) at the end of the side groups.

Moisture Studies. In the methyl ester form, water may hydrogen bond to the carbonyl groups, but the effect on the rotation of the ester should be minor. If any hydrogen bonding does occur, it should hinder the bond rotation, thus slightly increasing the peak temperature. This effect is negligible, as shown in Figure 13a. A comparison of the dry and wet ester form polymers at 10^{-1} Hz shows almost no change in the β peak. At higher frequencies, though, there is a slight increase in the peak location. The α peak, however, increased in amplitude and shifted to a lower temperature as if the water either acted to plasticize the polymer or swelled the polymer allowing less hindered side-chain rotation. In addition, the α′ peak grew much less relative to the α peak, indicating that the α′ transition is, thus, unaffected by hydrogen bonding. Note that similar behavior between wet and dry polymers is also evident at higher frequencies, but the α peak is more dominant at low frequencies.

In the acid form, dimers may form in the dry state (thus hindering the normal β rotation); this leads to a depressed β peak height shown in Figure 8. By adding water, the water hydrogen bonds to the side groups and breaks up the dimer structure, increasing the β peak height, as is dramatically observed in Figure 13b at 10^1 Hz. Other frequencies show similar behavior. The α peak also increased in amplitude due to the increased mobility of the side chain. More detailed controlled humidity experiments are needed to fully understand the influence of moisture on the relaxation mechanisms.

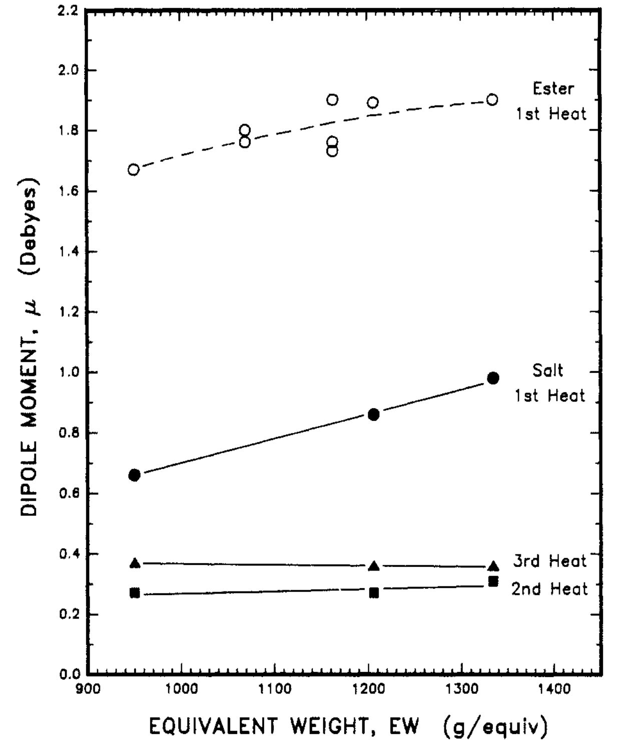


Figure 14. Computed dipole moment from Onsager's equation for the β transition as a function of EW for the ester (open symbols) and salt (filled symbols) forms at −50 °C.

Dipole Moment. The dipole moment of the β relaxation is calculated using the Fröhlich modification of Onsager's equation[22]

$$\mu^2 = \frac{3kT}{4\pi Ng}(\epsilon_r - \epsilon_u)\left(\frac{2\epsilon_r + \epsilon_u}{3\epsilon_r}\right)\left(\frac{3}{\epsilon_u + 2}\right)^2 \qquad (2)$$

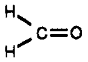
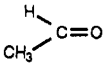
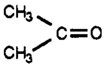
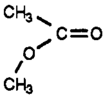
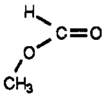
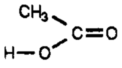
and Table II at −50 °C. In eq 2, μ is the dipole moment (D), *k* is Boltzmann's constant (J/K), *T* is temperature (K), *N* is the concentration of dipoles (mol/cm^3), and *g* is the Kirkwood factor.[23] The value of *N* is computed by dividing the density ($2\ g/cm^3$) by the equivalent weight. The *g*-factor is assumed to be unity for the initial calculation. The dipole moment was found to vary in a manner described in Figure 14.

The dipole moments for the ester form polymers varied between 1.6 and 1.9 D which is consistent with values measured for methyl acetate (1.72 D), methyl formate (1.77 D), and acetic acid (1.74 D),[19] as shown in Table IV. Data taken on the second heating were virtually identical to the first heat data. If the carbonyl group formed the most intense dipole, as in the case of formaldehyde, acetaldehyde, and acetone (refer to Table IV), the computed dipole moment would be between 2.3 and 2.9 D. This argument represents further confirmation that the β relaxation results from the ester motion.

The dipole moment of the salt was considerably lower than the ester. The second and third heating cycles display dipole moments between 0.25 and 0.4 D, much lower than the first heat most likely because some residual hydrolyzing solution was still present during the first heat. Thus, the apparent difference between the ester and salt dipole moments is almost an order of magnitude. The acid form polymer data (not plotted) ranged from 0.25 to 0.3 D, thus comparable to the salt form data. The low values of the salt and acid dipole moments are most likely due to the molecular symmetry for the salt resonance and the formation of dimer structures for the acid polymer.

For the initial calculation, the *g*-factor in eq 2 was taken to be unity for all polymer forms. Since ionic clustering

Table IV. Dipole Moments

chemical name	chemical structure	dipole moment μ (D)
formaldehyde		2.33
acetaldehyde		2.69
acetone		2.88
methyl acetate		1.72
methyl formate		1.77
acetic acid		1.74

is known to occur in the salt form (and may occur to some extent in the ester form due to attraction of the like polar side groups) and hydrogen bonding occurs in the acid form, the g-factor may deviate significantly from unity. Consider, for instance, if the actual dipole moments for the ester and salt forms were identical. By writing eq 2 for both forms, equating the equations, and solving for the ratio of the g-factors, the result is $g_{\mathrm{salt}}/g_{\mathrm{ester}} = 0.04$.

Conclusions

The perfluorocarboxylate polymers display up to five dielectric relaxations depending on the chemical form between −200 and +200 °C. The α transition, corresponding to the T_g, relates to the motion of the vinyl ether side chain. The β relaxation is due to the ester motion at the end of the side chain. The γ transition relates to a crankshaft motion of CF_2 groups along the polymer backbone. The mobile $O-CH_3$, O–K, and O–H ends of the side group produce the low-temperature δ relaxation.

A physical model, based on the results presented in this paper, is proposed and illustrated in Figure 15. The model asserts that dipole–dipole interaction between the side groups is present in all three polymeric forms, not just in the salt form as proposed previously.[24]

In the methyl ester form, the vinyl ether side chain is sterically hindered as evidenced by the increase in E_a with increasing side-group concentration (lower EW); however, the more localized dipoles along the side chain are unaffected by the concentration of neighboring side groups. Hydrogen bonding between the carbonyl on one side group and the methyl on another side group may cause the clustering in the nonionic form. Whether neighboring side chains form nonionic clusters in the ester form or side chains from different segments of the chain interact is currently under study; Figure 15 illustrates the latter case. In either case, the extent of side-chain interaction in the unhydrolyzed polymer will influence the degree and rate of ionic cluster formation and other polymer properties during subsequent hydrolysis. For instance, if the side chains in the methyl ester form strongly interact with other segments forming a "cross-linking" structure, as illustrated in Figure 15, the polymer may not even have to rearrange to form the ionic clusters in the salt form.

In the salt form, ionic clusters attenuate the dielectric dissipation factor of the lower temperature relaxations, indicating more steric hindrance and ionic interaction of the side groups than in the ester form. Furthermore, the ionic conduction portion of the spectrum is shifted to much lower temperatures than in either the ester or acid forms. The δ peak (not seen in the ester samples but thought to be present at extremely low temperatures) is present in the salt and describes the O–K dipole. This assignment, though, is complicated by the resonance between the double and single carbon–oxygen bonds and the transport of cations through the polymer in the presence of the ac electric field. The measured δ relaxation, therefore, represents some complex average over the time scale of the measurement.

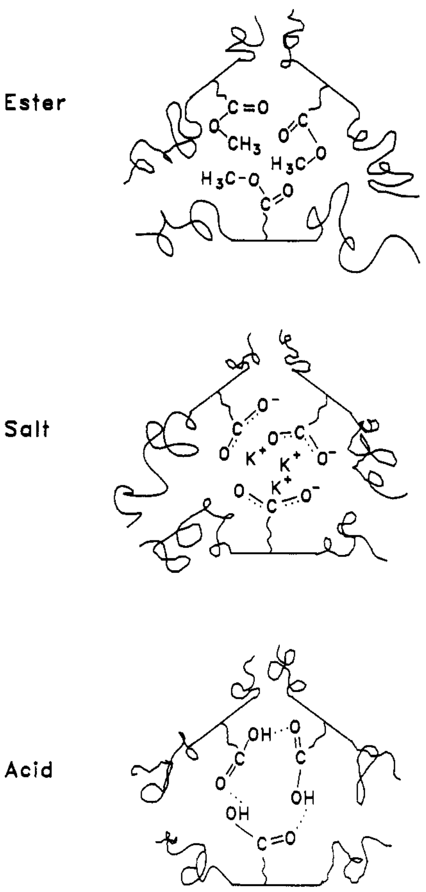


Figure 15. Model for dipole interaction in the three carboxylate forms. Bond angles are not drawn to scale.

The acid polymer forms dimers and trimers which lead to tightly bound C═O and C–OH dipoles, as illustrated in Figure 15. The dissipation values are extremely small and similar to the salt form values, indicating that the dimer and trimer structure hinders the motion of both the β and δ relaxations. This is evidenced by the β and δ transition temperatures in the acid being the highest of the three polymer forms. Also, the calculated dipole moments of the β transition for the acid and salt polymers are very similar and much smaller than the ester β moment. The acid form is most dramatically affected by the presence of water; the water breaks up the dimer structure by interfering with the hydrogen bonding as evidenced by the low peak dissipation temperature and large dissipation values as compared to the dry sample.

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