

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/231703612>

Dielectric and Mechanical Relaxations in a Nafion Precursor

ARTICLE *in* MACROMOLECULES · MARCH 1978

Impact Factor: 5.8 · DOI: 10.1021/ma60062a002

CITATIONS

47

READS

15

2 AUTHORS, INCLUDING:



I.M. Hodge

Independent Researcher

44 PUBLICATIONS 3,282 CITATIONS

SEE PROFILE

Dielectric and Mechanical Relaxations in a Nafion¹ Precursor

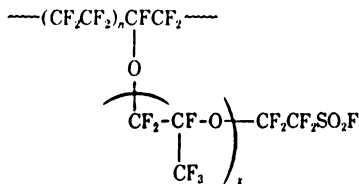
I. M. Hodge and A. Eisenberg*

Department of Chemistry, McGill University, Montreal, PQ, Canada H3A 2K6.
Received February 28, 1977

ABSTRACT: The dielectric and mechanical properties of a Nafion precursor have been determined from -196 to $+80^\circ\text{C}$. The material is a partly crystalline perfluorinated polymer containing a SO_2F group at the end of each perfluorinated ether side chain. Four relaxations are observed, labeled γ , β' , β'' , and α in order of increasing temperature. The two β relaxations can be partially resolved only at very low frequencies (ca. 0.1 Hz). The γ relaxation is assigned to motion of the SO_2F group, β' to backbone $(-\text{CF}_2)_n-$ motions, β'' to side chain motions $(-\text{CF}(\text{CF}_3)\text{OCF}_2)_n-$, and α to the glass transition.

The effect of ionic forces on the properties of polymers has received considerable attention in recent years.^{2a} Despite this effort, however, a number of factors have still not been elucidated completely, either because of the inherent difficulty of the problem (such as clustering of the ionic groups in media of low dielectric constant) or because of the difficulty of obtaining an ionic polymer of varying ion contents which has a structurally exact nonionic analogue. The latter is needed in order to be able to separate clearly the effects of ionic interactions alone from those due to other factors such as molecular weight, sequence distribution, etc. In the case of copolymers containing acidic groups, the ion content can be varied by utilizing different degrees of neutralization of the carboxylic acid groups^{2b–6} and by esterification.⁷ However, the unique properties of the proton in general, and its participation in hydrogen bonding in particular, confer special properties onto the acidic analogues of these ionomers which may invalidate any direct comparison with the salts.

This paper concerns itself with an investigation of a non-ionic material which is the chemical precursor of the family of ionic polymers known as Nafions, developed by Du Pont for use primarily as electrolyte separators. It consists of a tetrafluoroethylene backbone, with a perfluorinated ether side chain which is terminated by an SO_2F group (I)



where x may be as low as 1. Clearly, no ionic interactions nor hydrogen bonding can occur in this material. These are introduced only when the terminal fluorine is replaced with O^-M^+ to give the Nafion salt, which may be acidified to give the sulfonic acid.

The dielectric and mechanical properties of Nafion-H, and its Li, Na, K, and Cs salts, all with equivalent weight 1365, have been reported previously from this laboratory.⁸ The relevant findings may be summarized as follows:

The dielectric and mechanical properties of Nafion-H and its salts are, in general, a sensitive function of water content. However, a mechanical loss tangent (γ) peak is found at ca. -100°C at ca. 1 Hz , for all materials at most water contents.⁸ It has a maximum of ca. 10^{-1} , which is inversely proportional to the counterion radius, except for the acid for which it is anomalously low. For the K salt this γ peak has a shoulder at ca. -60°C .

For the Nafion salts a mechanical β peak also appears at ca. 150°C as a shoulder on the larger α peak. The acid also shows a mechanical β peak at ca. 20°C ($\tan \delta_{\text{max}} \sim 10^{-1}$), which shifts

to lower temperatures with increasing water content and eventually merges with the γ peak.⁸ The dielectric loss tangent data exhibit two peaks, the positions of both of which change with water content. Their magnitudes vary but are of the order of $2\text{--}5 \times 10^{-1}$.

Time-temperature superposition for stress relaxation is not valid in the Nafion salts. However, pseudomaster curves can be constructed by overlapping only the short time segments. These are extraordinarily broad, compared with those of nonionic polymers such as styrene, in the glass transition region. This great breadth cannot be accounted for by partial crystallinity, since the Nafions are completely amorphous. Furthermore, styrene-alkali methacrylate copolymers also exhibit very broad stress relaxation master curves.⁹ These data suggest that it is the presence of ions which is responsible in some way for this great breadth. Although it would be of interest to compare these data with nonhydrogen-bonded polar materials, this is difficult since the latter are usually partly crystalline.

The diffusion coefficient of water in Nafion-H is quite high, ca. 10^{-6} at room temperature,⁸ and has an activation energy of 4.8 kcal mol^{-1} .

Experimental Section

The sample was kindly supplied to us by Dr. D. D. Lawson of the Jet Propulsion Laboratories of the California Institute of Technology. It was in the form of a thin colorless, transparent sheet (thickness ca. 0.025 cm) from which samples were cut. For the stress relaxation experiments in the bending mode, thicker samples (ca. 0.1 cm) were required, and these were prepared by compression molding at ca. 130°C . A sample prepared in this way was also run on the torsion pendulum device over the full temperature range, and the data were compared with those taken from the unmolded thin sample. The agreement was excellent, indicating that no serious physical or chemical changes took place during molding. The material is leathery at room temperature and is slightly crystalline, since its x-ray diffraction pattern shows several lines which can be attributed to crystallinity. The material is inert to water, according to weight change determinations.

Measurements of the dielectric, dynamic mechanical and stress relaxation properties of the Nafion precursor are reported here. The dielectric data were taken with a General Radio 1621 capacitance measurement system, with a cell design taken from the literature.¹⁰ They extend from -196 to $+70^\circ\text{C}$ over a frequency range of 2×10^1 to 10^5 Hz . Because of experimental problems associated with the low losses, their magnitude at 10^5 Hz is low by an estimated 5–10%. However, the peak positions, insofar as they can be determined at this high frequency (see Results), appear to be unaffected. For the γ and β relaxations, a significant part of the spectrum can be observed in the isothermal frequency domain.

Dynamic mechanical data were taken from -180 ($3.7 \times 10^{-1}\text{ Hz}$) to $+16^\circ\text{C}$ ($8.4 \times 10^{-2}\text{ Hz}$) using a torsion pendulum¹¹ and from -190 ($3.3 \times 10^2\text{ Hz}$) to $+30^\circ\text{C}$ ($5 \times 10^1\text{ Hz}$) using a vibrating reed device. In the latter, the vibrational amplitude was monitored using a laser,¹² thus eliminating the need to attach any foreign body to the sample.

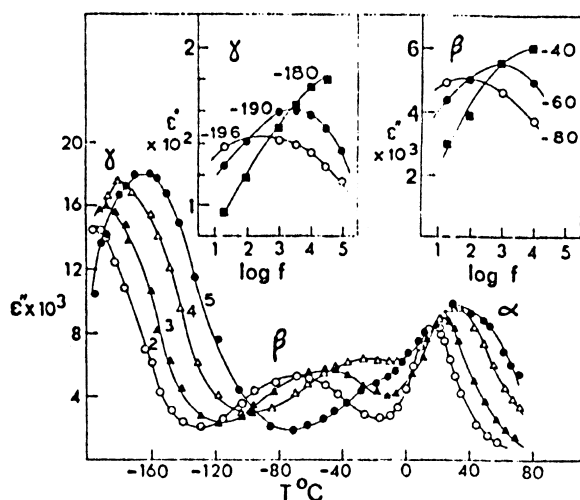


Figure 1. Temperature dependences of the dielectric loss at four frequencies. The curves are labeled with the log frequency of measurement. Isothermal frequency spectra for the γ and β relaxations are shown in the insets.

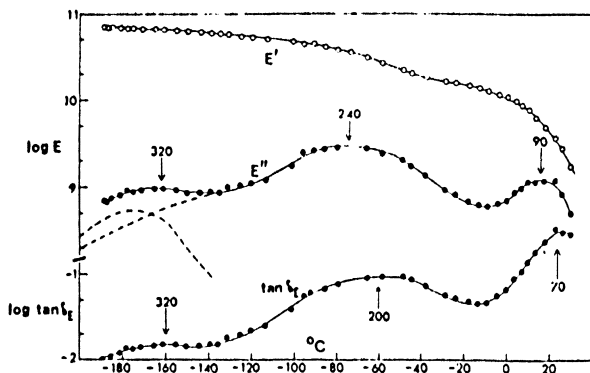


Figure 2. Temperature dependences of the mechanical tensile storage modulus, loss modulus, and loss tangent measured with a vibrating reed. The frequencies in Hz at which the maxima occur are also shown. Moduli are in dyn cm^{-2} .

Stress relaxation data, extending over time intervals of ca. 10^1 to 10^4 s, were taken from ca. -60 to -30°C in the bending mode and from -17 to $+60^\circ\text{C}$ in the stretching mode. During each run, the temperature was usually kept constant to within $\pm 0.05^\circ\text{C}$, although in some cases larger variations ($\pm 0.1^\circ\text{C}$) were tolerated.

For the dynamic measurements, warming rates of ca. 1°C min^{-1} were used for all three techniques, thus allowing a valid comparison of peak positions. It is not known with certainty how much error in temperature was introduced by thermal lag effects, but it probably does not exceed $2-3^\circ\text{C}$. With one possible exception, discussed below, this uncertainty could be much greater and still not affect any of the conclusions which have been drawn from the data. The raw data were converted to the complex response functions using the usual formulas.

The SAXS data were obtained on a Kiessig Vacuum Camera using nickel-filtered copper $K\alpha$ radiation.

Results

The temperature dependences of the dielectric loss, ϵ'' , at the indicated measuring frequencies, are shown in Figure 1. Intermediate frequencies are omitted for clarity. Three distinct peaks are seen and are labeled γ , β , and α in order of increasing temperature. Isothermal frequency spectra of the γ and β relaxations are shown in the insets of Figure 1.

The relative permittivity of this material is about 2 and

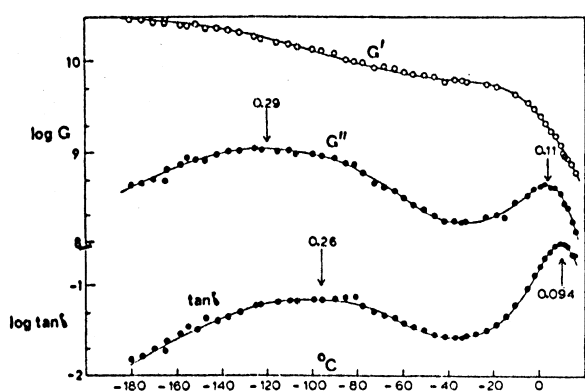


Figure 3. Temperature dependencies of the mechanical shear storage modulus, loss modulus, and loss tangent measured with a torsion pendulum. The frequencies in Hz at which the maxima occur are also shown. Moduli are in dyn cm^{-2} .

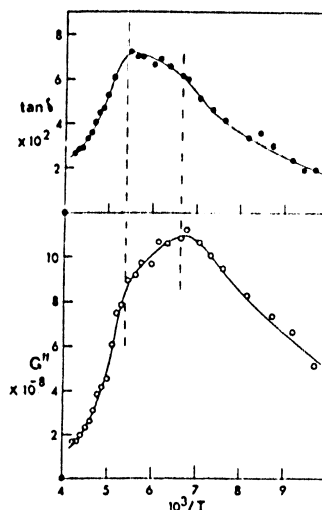


Figure 4. Linear plots of shear loss modulus and loss tangent vs. reciprocal absolute temperature for the β relaxation. Data are the same as those given in Figure 3.

changes by about 10% over the full temperature range. This small dispersion reflects the low intensity of the loss peaks.

The dynamic mechanical spectra obtained from the vibrating reed and torsion pendulum experiments are shown in Figures 2 and 3, respectively. The storage and loss moduli and the loss tangent are plotted logarithmically in these figures, and the frequencies at the peak maxima are also indicated. For reasons which are discussed later, the loss modulus and loss tangent data obtained with the torsion pendulum are replotted, linearly, vs. $1/T$ in Figure 4.

Although the three relaxations are well resolved at most frequencies, considerable overlap does occur. It was therefore important to establish whether or not the peak positions were affected by these overlaps. With the exception of the mechanical γ relaxation (Figure 2) and the dielectric β relaxation at 10^5 Hz (Figure 1), it was found that the peak positions were not altered even by unreasonably large estimates of the adjacent peak edges. For the γ relaxation, correction for peak overlap shifted the mechanical γ relaxation from -165 ± 5 to $-175 \pm 5^\circ\text{C}$. The magnitude of this shift was insensitive to the amount of overlap chosen, to within the quoted uncertainty of $\pm 5^\circ\text{C}$.

Frequency-reciprocal temperature plots for all three re-

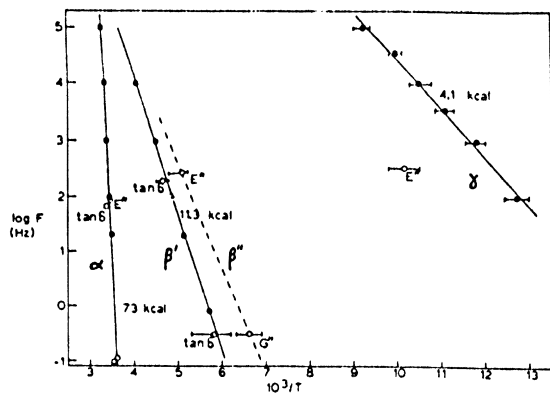


Figure 5. Plot of $\log f$ against $1/T$ for the four observed relaxations. Filled points are dielectric data; open points are mechanical data.

laxations are shown in Figure 5. The peak positions for both the loss moduli and loss tangents are shown in the cases where these differ. Such differences are particularly significant for the β relaxation (see Discussion). For the γ relaxation, the mechanical loss modulus and mechanical loss tangent both go through their maxima at temperatures which are about 15 °C higher than those at which the maximum dielectric losses occur, even after correction for peak overlap. This mechanical relaxation is very weak, however, and occurs near the temperature limit of the vibrating reed device. Thus a systematic experimental error, particularly in temperature, cannot be discounted as a possible source of this discrepancy. The activation energies for the α , β , and γ relaxations are 73 ± 5 , 11.3 ± 0.3 , and 4.1 ± 0.2 kcal mol⁻¹, respectively. It is apparent from Figure 5 that the α and β relaxations would merge together at ca. 10^6 Hz. At 10^5 Hz, the predicted difference in temperatures of maximum loss is about 30 °C. Because of the difference in intensities of these two relaxations, this temperature difference cannot be resolved and the β relaxation at 10^5 Hz is apparent only as a shoulder on the more (dielectrically) intense α relaxation (Figure 1).

Both the temperature and frequency spectra indicate clearly that the peak height increases with increasing temperature. It is also clear, from both the isothermal frequency domain spectra (Figure 1 (inset) and plots of ϵ'' vs. $1/T$ at different frequencies (not shown), that this is due to a narrowing of the distribution of relaxation times with increasing temperature.

This narrowing can be quantified for the γ dielectric relaxation, since for this peak the heights are not significantly affected by peak overlap (this is not true for the α and β relaxations). Due to the low-temperature limit of the experimental apparatus, the complete peaks of the γ relaxation cannot be observed and the full half-widths cannot be determined. However, the width at half height of the high-temperature side of the peak can be determined with a precision which is limited only by the uncertainty with which the temperatures of maximum peak height can be assessed. A crude estimate of the integrated peak intensity can therefore be made by multiplying this width by the peak height. This product is independent of frequency (in the range 10^2 to 3.6×10^4 Hz) within a scatter of $\pm 2\%$, compared with a smooth change in peak height of 50% with respect to the average. This strongly suggests that it is the change in breadth of the distribution function for the γ relaxation which is solely responsible for the temperature dependence of the peak height.

The measured stress relaxation data, and the stress relaxation master curve obtained for overlapping the short time

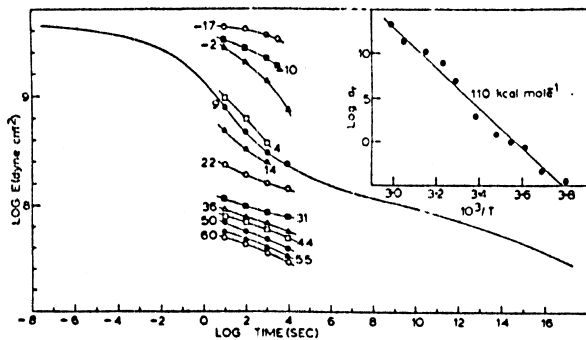


Figure 6. Measured stress relaxation data at the indicated temperatures and the stress relaxation master curve for the Nafion precursor. $T_{ref} = T_g(0.1 \text{ Hz}) = 10^\circ \text{C}$. Many data points have been omitted for clarity. The inset shows a plot of the logarithm of the shift factor against $1/T$.

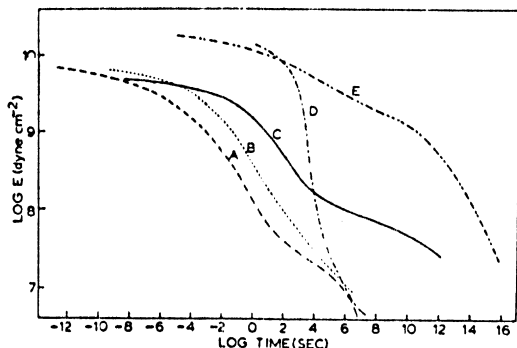


Figure 7. A comparison of the precursor stress relaxation master curve (C) with master curves of other materials: A, Nafion-K ($T_{ref} = T_g = 213^\circ \text{C}$); B, Nafion-H (104°C); C, Nafion precursor (10°C); D, polystyrene (102°C); E, styrene-9.7% sodium methacrylate (130°C).

segments at temperatures above -17°C , are shown in Figure 6. Since the stress relaxation experiments were performed with the intention of characterizing only qualitatively the glass transition region with respect to breadth and apparent activation energy, the temperature increments are somewhat large and the validity of time-temperature superposition cannot be assessed accurately, especially in view of the partial crystallinity of the sample. Nevertheless, superposition to within a scatter of ± 0.1 decades in modulus was observed for data obtained in the stretching mode. In any case, since the sample is partly crystalline, the stress relaxation curves cannot be interpreted unambiguously.

A logarithmic plot of the shift factors vs. reciprocal temperature in the glass transition region is shown in the inset of Figure 6. Over the temperature range studied, corresponding to a change in shift factors of ca. 10, the Arrhenius plot is linear.

Figure 7 shows the stress relaxation master curves for Nafion-H, Nafion-K, and polystyrene, each referenced to their respective glass transition temperatures. The striking similarity of the precursor curve to that of Nafion-K is to be noted.

The temperature dependences of the 10-s moduli for the precursor are shown in Figure 8, together with those for Nafion-H, Nafion-K, a styrene-9% sodium methacrylate copolymer, and polystyrene. Again, the similarity of the precursor and Nafion-K curves is striking, the two being merely displaced as a result of their differing glass temperatures.

The SAXS experiment yielded a weak ring corresponding

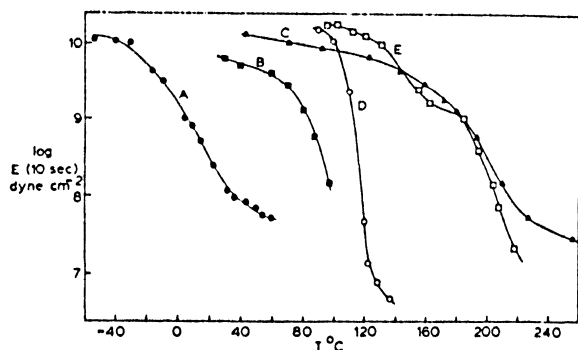


Figure 8. Ten-second tensile modulus vs. temperature for the precursor (A) and other materials: B, Nafion-H; C, Nafion-K; D, polystyrene, E, styrene-9% sodium methacrylate.

to a Bragg spacing of ca. 18 Å and a shoulder at a Bragg spacing of ca. 33 Å. No analysis of the wide-angle lines was attempted beyond the identification of the presence of crystallinity.

Discussion

The α Relaxation and Rubbery Plateau. The α transition, observed in all four experiments, is characterized by a high activation energy (75 kcal mol⁻¹, Figure 5) and a large decrease in mechanical modulus. The transition is therefore unambiguously identified with the glass transition.

The rubbery plateau, the beginning of which is seen in the stress relaxation master curve (Figure 6), has a modulus value of ca. 5×10^7 dyn cm⁻² at 60 °C, and the measured density is 2.13 g cm⁻³ at 20 °C. Insertion of these data into the equation for the rubber modulus gives a value for the molecular weight M_c of segments between cross-links of ca. 3.5×10^3 , which is comparable with the equivalent weight. Therefore, unless the level of crystallinity is determining the value of the modulus, it is possible that the side chains are involved in cross-linking.

Since the SO₂F group is highly polar, it is of interest to explore whether the polarity of that group alone is sufficient to account for the observed cross-linking or if additional factors must be involved. While the dipole moment of the SO₂F group by itself is very large, probably comparable with that of CH₃-SO₂F¹³ (3.880), that of the -CF₂-SO₂F group is much less than this, probably comparable with that of CF₃-SO₂F. The dipole moment of the latter has not been determined, but it can be estimated from the measured values of gaseous CH₃-SO₂F¹³ and CH₃-CF₃¹⁴ and of SO₂F₂,¹⁴ CH₃F,¹⁴ and CH₃CF₃.¹⁴ Both estimates give the same value, ca. 1.1 D, for CF₃-SO₂F.

Using the derived values for the dipole moments of the CF₃ and SO₂F groups (assumed equal to those for CH₃CF₃ and CH₃SO₂F, respectively), a calculation of the electrostatic cohesive energy of two adjacent chain ends is straightforward, and yields a value which is about 10% of that of two ion pairs in the same configuration or about 2–3 kcal mol⁻¹. This would not appear to be sufficient for cross-linking. However, since this material behaves as a highly cross-linked system, it is likely that either the crystallinity determines the value of the modulus or extensive aggregation occurs. The driving forces for such aggregation are most probably dipole-dipole interactions involving not only the terminal group but also the entire side chain, assisted by the difference in cohesive energy density between the side chain and backbone. Such aggregation may be reflected in the small-angle x-ray scattering pattern, in which a peak occurs at a Bragg distance of 18 Å and a shoulder at 33 Å. Although these data are consistent with

side chain phase separation, they may also reflect the partly crystalline nature of the material. Further work is needed to clarify this point.

The β Relaxation. Because of its high mechanical intensity and low dielectric strength, this relaxation must be associated either with the fluorocarbon backbone, or the fluorinated ether side chain, or both. For reasons which are discussed below, it is almost certain that both contribute to this relaxation.

The β relaxation in this material and the γ relaxation in polytetrafluoroethylene (PTFE) have comparable activation energies (ca. 12–13 kcal mol⁻¹) and occur at approximately the same temperature at comparable frequencies.^{15–17} Specifically, the PTFE γ relaxation occurs at -96.5 °C at 6×10^{-1} Hz,¹⁵ compared with -96 °C at 2.6×10^{-1} Hz for the precursor β relaxation (Figure 3). In PTFE, the γ relaxation has been unequivocally assigned to the amorphous region of the material,^{15,16} since it has been shown that the intensity is directly related to the amorphous content of this partly crystalline material. Since the precursor is slightly crystalline and since it is possible that side chain aggregation may also be occurring, it is very difficult to compare quantitatively the intensities of the peaks in those two quite different materials. However, it appears that the weight percent of (CF₂)_n in the precursor is very roughly 50%, so that a qualitative comparison can be made with the γ relaxation for 50% crystalline PTFE. Such a comparison reveals the two as having comparable magnitudes ($\tan \delta \sim 10^{-1}$). However, a significant difference is found in the half-widths, ca. 90 °C for the precursor peak compared with only ca. 30 °C for the PTFE peak.

The water-independent mechanical relaxations found in Nafion-H and its alkali salts,⁸ referred to in the introductory section, are also characterized by parameters which are very similar to the precursor β relaxation. In particular, their half-widths are about the same. However, no comparable dielectric peak is found in the Nafions because the precursor relaxation is weak dielectrically ($\epsilon''_{\max} \sim 10^{-3}$) and would be hidden by the relatively intense, water-dependent peaks found on the Nafions ($\epsilon''_{\max} \sim 10^{-1}$).⁸

Inspection of Figure 4 reveals that the plot of G'' vs. $1/T$ has a well-developed shoulder at ca. -95 °C, with a maximum at ca. -125 °C. The corresponding plot of $\tan \delta_G$, also shown in Figure 4, shows a maximum at ca. -88 °C and a shoulder at ca. -110 °C. It is apparent from these spectra that two relaxations are present, which are barely resolvable even at these low frequencies (ca. 10^{-1} Hz). Because of the increase in storage modulus with decreasing temperature, the two peak heights are weighted differently by G'' and $\tan \delta_G$. Thus $\tan \delta_G$ suppresses the low-temperature losses and exhibits its maximum (-88 °C) at essentially the same position at which the G'' spectrum exhibits the shoulder (-95 °C). The agreement of these temperatures constitutes good evidence for two relaxations in the β -relaxation region. The low- and high-temperature components will be referred to as the β' and β'' relaxations, respectively.

The reason for the apparent discrepancies in the Arrhenius plot for the β relaxation (Figure 5), between the positions of the dielectric loss and mechanical loss tangent on the one hand and the mechanical loss modulus on the other, is now clear. The former primarily reflects the β'' component, whereas the latter primarily reflects the β' component. It should be noted that the position of the dielectric loss β peak is not affected by the choice of dielectric loss function, since the dispersion in dielectric constant is very small.

Because the dielectric spectrum appears to reflect primarily the high-temperature β'' component, it is likely that this originates from motions of the ether side chain and that the β' component arises from -CF₂- backbone motions. This assignment is also consistent with the shape of the G'' spectrum

in Figure 4, which indicates that the low-temperature β' component is more active mechanically. It might be expected that, on the basis of this assignment, the PTFE γ and precursor β' relaxations would coincide. This is not the case, the PTFE γ relaxation lying closer to the precursor β'' relaxation (see Figure 5). However, since the (amorphous) CF_2 backbones have markedly different structural environments in the two materials, exact agreement would not be expected.

The width of the precursor mechanical β relaxation decreases with increasing frequency, from ca. 90° at 3×10^{-1} Hz (torsion pendulum) to ca. 40° at 240 Hz (vibrating reed). This is consistent with the β' and β'' components merging together at higher frequencies.

The γ Relaxation. Of the three labeled relaxations observed in this study, the γ relaxation is by far the most intense dielectrically. No comparable dielectric relaxation is observed in Nafion-H or its salts, although it is probable that, if present, it would be masked by the much more intense water-dependent peaks. The relaxation is mechanically very weak compared with the α and β relaxations and has a low activation energy, 4.1 kcal mol $^{-1}$. The relaxation is broad, with a half-width of about 6 decades, as assessed from plots of ϵ'' vs. $1/T$ (at 3.6×10^4 Hz) (not shown). The relaxation is identified with single SO_2F groups. Two reasons may be cited for this assignment. (1) The SO_2F group is by far the most polar entity in this material and would be expected to contribute the most to the dielectric spectrum. (2) The group occurs at the end of a side chain at a low concentration (ca. 5 wt % for $x = 3$) and would thus not be expected to contribute much to mechanical losses. The relaxation could be due either to rotation about the C–S bond or to some type of wagging motion of the SO_2F group itself. It is not possible to determine from the present data which of these occurs, although broadline NMR spectroscopy would probably enable a definite assignment to be made.

However, it is worth noting that the observed activation energy of 4.1 kcal is comparable with rotational energy barriers for several SO_2F molecules. For example, the barrier for methyl rotation in $\text{CH}_3\text{—SO}_2\text{F}$ has been measured as 2.52 ± 0.35 kcal mol $^{-1}$,¹³ and replacement of the methyl group by CF_3 would be expected to increase this somewhat.

General Observations. The relaxation behavior of the precursor material, in the glass transition region, is remarkably similar to Nafion-K. Both the stress relaxation master curves (Figure 6) and the 10-s modulus curves (Figure 7) indicate that the precursor and Nafion-K transitions are very broad compared with typical nonionic polymers such as polystyrene. These data, together with the x-ray evidence, indicate that the Nafion precursor is a phase-separated system, the two-phase behavior being due either to separation between the nonpolar backbone and the polar side chains or to crystallites embedded in an amorphous matrix. The conclusions regarding the mechanisms of the sub- T_g relaxations are unaffected by the above ambiguity.

Summary and Conclusions

The relaxation properties of the Nafion precursor may be summarized as follows:

1. There are four distinguishable relaxations in the region -196 to -70°C . Of these, two can be resolved only at very low frequencies, ca. 0.1 Hz.
 2. A low-temperature γ relaxation at ca. -190°C has an average activation energy of 4.1 kcal as determined dielectrically. It is mechanically very weak ($E''_{\text{max}} \sim 5 \times 10^8$, $\tan \delta \sim 10^{-2}$), but it is dielectrically the most intense ($\epsilon'' = 10^{-2}$). It is identified with the SO_2F group and is probably due either to rotation about the C–S bond or to a localized wagging motion.
 3. A β relaxation occurs in the temperature range -100 to -20°C . At low frequencies, ca. 3×10^{-1} Hz, it can be resolved into two components at ca. -130 and -95°C (β' and β'' , respectively). The activation energy for the combined relaxation is 11 kcal mol $^{-1}$. The β' and β'' relaxations are assigned respectively to backbone $-(\text{CF}_2)_n-$ and ether side chain motions, on the basis of their relative mechanical and dielectric activity.
 4. The glass transition has an apparent activation energy of ca. 75 kcal mol $^{-1}$. As determined by stress relaxation, the transition is broad, comparable with that of the Nafion ionomers. While the crystallinity may contribute to the breadth of the transition, it is possible that some type of side chain aggregation may also be occurring aided, presumably, by the polarity of the terminal SO_2 group and that both of these factors confer on the precursor stress relaxation properties similar to those of the Nafion salts, although displaced to lower temperatures because of a lower glass transition temperature.
- Acknowledgments.** We are indebted to Dr. D. D. Lawson of the Propulsion Laboratories of the California Institute of Technology for supplying us with a sample of the material. It is also a pleasure to thank Professor R. H. Marchessault and Dr. R. St. J. Manley for the x-ray photographs and to acknowledge the financial support of the National Research Council of Canada.
- ## References and Notes
- (1) Nafion is a registered trademark of E. I. du Pont de Nemours and Company, Inc. for its perfluoro sulfonic acid products.
 - (2) (a) A. Eisenberg and M. King, "Ion Containing Polymers, Physical Properties and Structure", Academic Press, New York, N.Y., 1977; (b) S. Bonotto and E. F. Bonner, *Macromolecules*, **1**, 510 (1968).
 - (3) W. J. MacKnight, L. W. McKenna, and B. E. Read, *J. Appl. Phys.*, **38**, 4208 (1967).
 - (4) R. W. Rees and D. J. Vaughan, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **6**, 287 (1965).
 - (5) E. P. Otocka and T. K. Kwei, *Macromolecules*, **1**, 244, 401 (1968).
 - (6) M. Navratil and A. Eisenberg, *Macromolecules*, **7**, 84 (1974).
 - (7) E. Shohamy and A. Eisenberg, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1211 (1976).
 - (8) S. C. Yeo and A. Eisenberg, *J. Appl. Polym. Sci.*, **21**, 875 (1977).
 - (9) A. Eisenberg and M. Navratil, *Macromolecules*, **6**, 604 (1976).
 - (10) R. D. McCammon and R. N. Work, *Rev. Sci. Instrum.*, **36**, 1169 (1965).
 - (11) B. Cayrol, Ph.D. Thesis, McGill University, 1972.
 - (12) S. Reich and A. Eisenberg, *Rev. Sci. Instrum.*, **41**, 1904 (1970).
 - (13) J. E. Jacobs and D. R. Lido, *J. Chem. Phys.*, **54**, 4591 (1971).
 - (14) A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963.
 - (15) N. G. McCrum, *J. Polym. Sci.*, **27**, 555 (1958).
 - (16) N. G. McCrum, *J. Polym. Sci.*, **36**, 355 (1959).
 - (17) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York, N.Y., 1967.