Physical Properties and Supermolecular Structure of Perfluorinated Ion-Containing (Nafion) Polymers

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Synopsis

The supermolecular structure and viscoelastic and diffusion properties of a perfluorinated polymer containing sulfonic acid (Nafion) were investigated. The breakdown of time–temperature superposition for the dry salt and and acid in the presence of 0.5 H_2O/SO_3H as well as the results of small-angle x-ray scattering suggest that the ions in this material are clustered. Above 180°C, the reestablishment of the time–temperature superposition in the salt suggests that ions in the clusters become mobile. Dynamic mechanical studies were performed over a temperature range from −190°C to above the glass transition temperatures T_g of the materials. The T_g of the salts is found at ca. 220°C, while in the acid it occurs at 110°C. A β peak in the acid is found at ca. 20°C, while in the salts it occurs between 140°C and 160°C. The β peak shifts to a lower temperature with the addition of water in both the acid and the salts, while the α and γ peaks are unaffected. The latter is located at ca. −110°C at 1 Hz. Dielectric behavior has also been studied as a function of water content for the acid sample and the potassium salt at frequencies of 100 Hz to 10 kHz. Two relaxations with different activation energies were observed. The position of both peaks shifts to a lower temperature as the water content increases. Finally, the diffusion of water in Nafion in the acid form has been determined. The diffusion coefficient can be represented by the equation

$$D = 6.0 \times 10^{-3} \exp(-4.8 \text{ kcal/RT}) \text{ cm}^2/\text{sec}$$

INTRODUCTION

The presence of ions in organic polymers affects a very wide range of properties, not only in solution but also in bulk. A series of recent studies has been devoted to the elucidation of the effect of ions on the viscoelastic properties and structure of ion-containing polymers.[1-23] The bulk of the evidence suggests that at low ion concentration, the ions are present as multiplets, acting as transient crosslinks, while at higher concentrations, more extensive aggregation is encountered, leading to the formation of clusters which contain not only ionic material but also a considerable portion of the organic polymer.[2,4,21,23] These clusters, in turn, act as a reinforcing filler, giving the sample some of the properties of phase-separated systems such as are encountered in some block copolymers or partly crystalline materials. The onset of clustering differs from material to material, occurring, for example, at <1 mole % of ions in polyethylene, at ca. 12–15 mole % in ethyl acrylate-based materials, and not at all in the linear polyphosphates.[20]

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The physical properties of only very few ionic copolymers have been studied in some detail. These are all hydrocarbon-based materials and include polyethylene,[1-9] polystyrene,[10-15] polybutadiene,[16-18] as well as some polar polymers containing low molecular weight salts;[19] the phenomena which arise from the presence of ions are quite similar in all of these.

The organic ionomers that have been studied to date are based on materials which have a narrow range of dielectric constant or cohesive energy density values. It was, therefore, of considerable interest to explore the dependence of ion-related properties in a completely different material, differing from the preceding both in structure and composition. Any similarities in those properties found for all the materials would thus indicate a truly general trend rather than specific interactions. The Nafions represent an excellent choice of such a system, since they not only are based on completely fluorinated polymers, but since the ion is placed at the end of a side chain. Furthermore, while most of the mechanical studies of copolymers were performed on materials containing metal carboxylate ions, the Nafions contain the sulfonic acid group.

The Nafions were developed recently by the du Pont Company as separators in electrochemical applications.[24-28] They are based on the perfluoroethylene backbone, containing a side chain of the structure

$$\mathrm{-\!\!+\!\!O\!\!-\!\!CF_2CF\!\!\xrightarrow{x}\!\!-OCF_2CF_2SO_3H}$$
$$\mathrm{\underset{CF_3}{\overset{|}{}}}$$
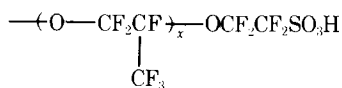
where x is small. Ionization can be performed easily by immersing the polymer sheet in an aqueous solution of an appropriate base. The equivalent weights are in the range of 1000 to 2000. A number of physical properties relevant to the proposed commercial applications were summarized recently,[29,30] and a more detailed report is in press.[31]

It is completely beyond the scope of this introduction to review the literature on the physical properties of ion-containing polymers. Several reviews are already in print in the area,[20,32,33] and a book is in preparation.[34] Only a very brief summary will be given here, and only those properties which have a direct bearing on the present work will be summarized.

For most ion-containing systems, it has been found that the glass transition temperature (as determined, for example, by DSC) increases with increasing ion content. At low concentrations, this increase is linear, but as the concentration increases through the clustering region, the rate of increase also rises. Loss tangent measurements in the glass transition region generally reveal two peaks. At low ion concentrations, this correlates with the DSC value of glass transition; but at high ion contents, deviations may appear. Usually, the lower loss tangent peak is due to the glass transition of the ion-poor material, while the peak at higher temperatures is due to the ionic regions.

Stress relaxation studies of noncrystalline ionomers reveal that for systems which are clustered, time–temperature superposition fails, reflecting the existence of a secondary relaxation mechanism.[35] This secondary mechanism is associated with the clustered ionic regions. If the ions are present in low enough concentrations so that they do not cluster but act as multiplets (or crosslinks), no deviation from the time–temperature superposition is observed.

In all the materials in which clustering of ions is encountered, this clustering also manifests itself by a small-angle x-ray scattering peak. The Bragg distances involved are usually of the order of 50 Å, although smaller distances have been found in some systems.

EXPERIMENTAL

Polymer samples were kindly supplied by Dr. W. Grot of E. I. du Pont de Nemours & Company, in the form of 1.3-mm-thick sheets, of equivalent weight of 1155 or 1365. Unless specified, all measurements were performed on the sample with an equivalent weight of 1365.

Drying and Thermal Stability

A sample (ca. 1 g) which had been stored at ca. 40% relative humidity and which had absorbed ca. 6 wt % water (based on a method of determining the dry weight to be described below) was placed under vacuum at 25°C for several days until there was no further weight loss (<0.1 mg), and its weight was determined. Subsequently, the same sample was replaced in the vacuum system, this time at a higher temperature, again for another few days until another constant weight was reached. The procedure was repeated for temperatures up to 210°C for the acid form and 330°C for the potassium salt. The results are shown in Figure 1 and will be described more fully below.

An inflection point is evident at ca. 170°C for the acid form; this point was taken as the optimum drying temperature since a sample of maximum modulus is obtained at this temperature (see below). It is quite possible that some residual water remains in this sample, but no means were available for determining that amount. Subsequently, samples dried at 170°C for periods of over 24 hr will be referred to as "dry" samples.

For the salt samples, a drying temperature anywhere from 90°C to ca. 240°C yields identical results, and all the salt sample were dried at the glass transition temperature T_g for a period of 24 hr or more.

Water Diffusion

A dry film sample, ca. 1 mm thick, was immersed in water in a constant-temperature bath. After a certain time period, the sample was removed from the water, dried on the surface, and the weight gain M_t was determined. The same sample was then replaced in the bath at the same temperature for a second time period, and the weight was redetermined. The procedure was repeated until there was no further weight gain; the total weight gain is referred to as the equilibrium sorption M_∞. All the weighing procedures were done in less than 10 sec.

Glass Transition Temperatures

The glass transition temperatures were obtained from tan δ maxima at ca. 1 Hz with heating rates of less than 1°C/min. They were compared with those obtained with a Perkin–Elmer differential scanning calorimeter (Model DSC-1),
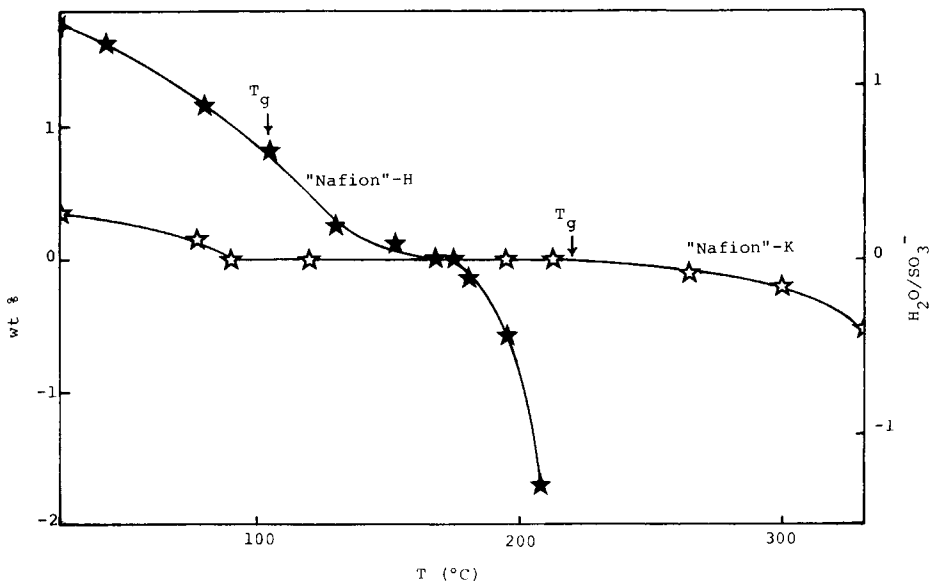
Fig. 1. Drying and thermal stability curves for Nafion-H and Nafion-K.

employing heating rates of 10°C/min, and also with data obtained by measuring the linear expansion coefficient.

Stress Relaxation

Stress relaxation measurements were made under a nitrogen atmosphere using apparatus similar to that described previously.[36] For each sample, the stress at constant strain was measured for periods of time up to 2×10^4 sec for a series of temperatures above and below the glass transition temperature. The temperature variation during any one run was held below ±0.1°C. High modulus measurements were made in the bending mode, while those at lower moduli (below ca. 5×10^8 dyn/cm^2) were done in stretching.

Dynamic Mechanical Tests

Dynamic mechanical studies were mostly undertaken using a torsional pendulum, described elsewhere,[37] for frequencies of ca. 1 Hz. At higher frequencies, a vibrating reed device[38] was used. Heating or cooling rates were less than 1°C/min.

Dielectric Experiments

Dielectric measurements were carried out on a General Radio Precision Capacitance Bridge (Type 1616) using a three-terminal cell of a type previously employed by McCammon and Work.[39] Measurements were made over a temperature range from −190°C to ca. 150°C and at frequencies from 40 Hz to 10 kHz. Heating rates of less than 1°C/min were employed. Three frequencies were measured in one single experiment to assure the same experimental conditions at each frequency.
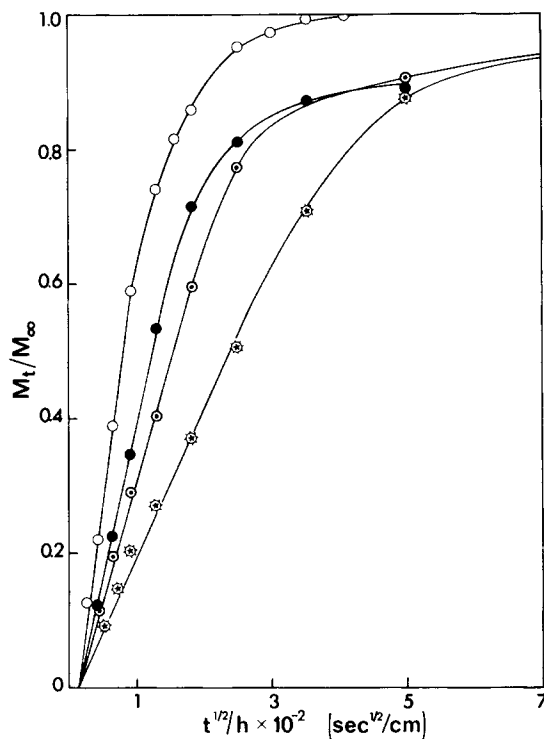
Fig. 2. Water sorption curves of Nafion-H (EW = 1155): (✸) 0°C; (⊙) 28°C; (●) 56°C; (○) 99°C.

X-Ray Diffraction

X-Ray diffraction patterns were obtained at room temperature using a Kiessig vacuum camera with nickel-filtered CuK_α (1.54 Å) radiation (40 kV, 20 mA). The exposure times were of the order of 100 hr. The photographs were micro-densitometered using a Joyce–Loebl double-beam recording microdensitometer.

RESULTS

Desorption of Water and Thermal Stability

Figure 1 shows the desorption of water with increasing temperature presented both as the number of water molecules per sulfonic group (H_2O/SO_3H) and as wt %. For the sake of comparison, the weight loss in the degradation region is also described in the same terms. These plots were discussed above. It is evident that the incorporation of ions into the polymer improves its thermal stability.

Diffusion of Water

For short times, the amount of diffusant M_t taken up by the sheet in time t is given by the following equation:[40]
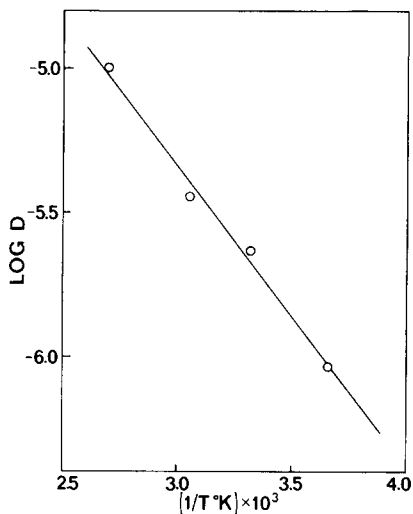
Fig. 3. Log D vs. $1/T$ for Nafion-H (EW = 1155).

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{l^2}\right)^{1/2} \left[\frac{1}{\pi^{1/2}} + 2 \sum_{n=0}^{\infty} (-1)^n \, ierfc \, \frac{nl}{2(Dt)^{1/2}}\right]$$

where D is the diffusion coefficient, l is the thickness of the sheet, n is an integer and $ierfc \, X = (1/\pi^{1/2}) \exp(-X^2) - X \, erfc \, X$, where $erfc \, X$ is $1 - erf \, X$, erf being the error function.

TABLE I
Glass Transition (α) and β Dispersion Determined by Various Techniques

	Dynamic studies (ca. 1 Hz)		Calorimetric studies[a]		Linear expansion by LVDT[b]
	T_α, °C	T_β, °C	T_α, °C	T_β, °C	T_α, °C
PTFE[c]	ca. 127	18 to 53			
Nafion–H					
(OH_2O/SO_3H)	111	23	104 ± 1		122 ± 11[d]
(3 H_2O/SO_3H)[e]	109	−62			
Nafion–CS	211	160	212 ± 15	116	
Nafion–K	225	150	213 ± 20	109 ± 22	
Nafion–Na	235	140	238 ± 25	132 ± 15	
Nafion–Li	217	147	212 ± 18	120 ± 9	

[a] The temperature at which the slope of the lines changed (as determined by the intersection of the extrapolated straight line segments) was taken as the position of the transition or dispersion.

[b] A. Eisenberg and T. Sasada, *Proc. Second Internat. Conf. Physics of Non-Crystalline Solids*, Delft, J. A. Prins, Ed., July 1964, p. 99.

[c] Reference 42.

[d] Expansion coefficients above and below T_g were estimated as 8.2×10^{-3} deg^{-1} and 2.3×10^{-3} deg^{-1}, respectively.

[e] This water content was determined at the end of the experiment.
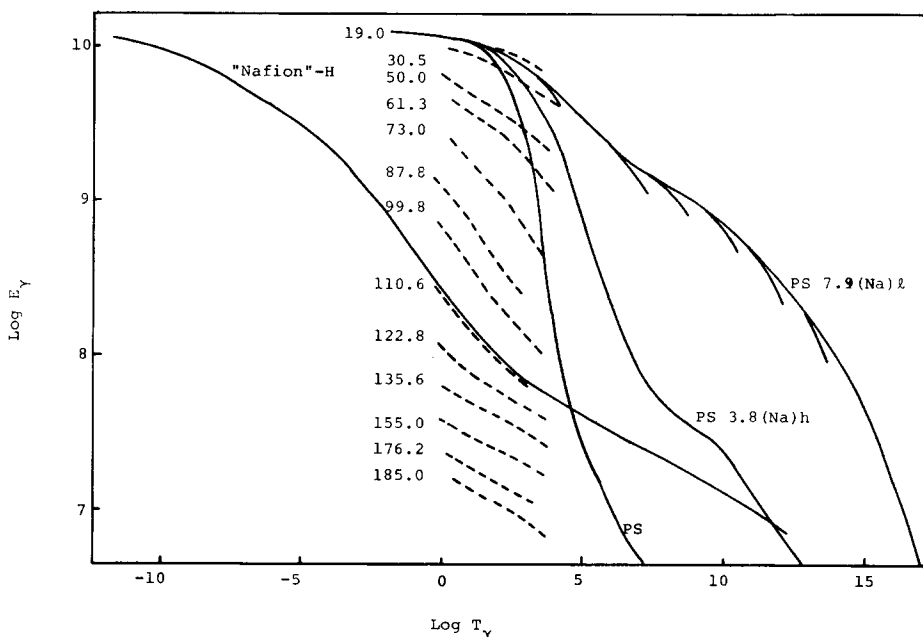
Fig. 4. Original stress relaxation curves and master curve for Nafion-H as well as master curves for polystyrene PS and two styrene ionomers PS 3.8 (Na)h, and PS 7.9 (Na)l. $T_{ref} = T_g$.

Figure 2 shows typical sorption curves at several temperatures. The linearity of the plots below $M_t/M_\infty = 0.5$ suggests that a constant diffusion coefficient is operative. The values of D were calculated from the initial slope of the plots, i.e., by setting the second term in the bracket equal to zero.[41] The induction time is estimated to be 3 sec.

Figure 3 shows a plot of log D versus $1/T$. The behavior is of the Arrhenius type, leading to the expression

$$D = 6.0 \times 10^{-13} \exp(-4.8 \text{ kcal}/RT) \text{cm}^2/\text{sec}$$

Glass Transition

Table I shows the glass transition temperatures of Nafions with different counterions and of poly(tetrafluoroethylene) (PTFE)[42] for comparison. The incorporation of ions into the polymer extends the glassy state to a higher temperature. Except for lithium, the increase in glass transition temperature is inversely proportional to the ionic size. The addition of 3 H_2O/SO_3H has a negligible effect on the glass transition of the acid sample.

Stress Relaxation

Acid and Salts. The results of the stress relaxation runs are shown in Figures 4-6 with $T = T_g$ as the reference temperature and $T_r = t/a_T$, where a_T is the shift factor. Computer programs[43] were used to obtain the master curves along with the shift factors and relaxation spectra from the individual curves of modulus versus time. Figure 4 also shows the stress relaxation master curves for styrene and for two styrene ionomers[13] for the sake of comparison. The latter are labeled
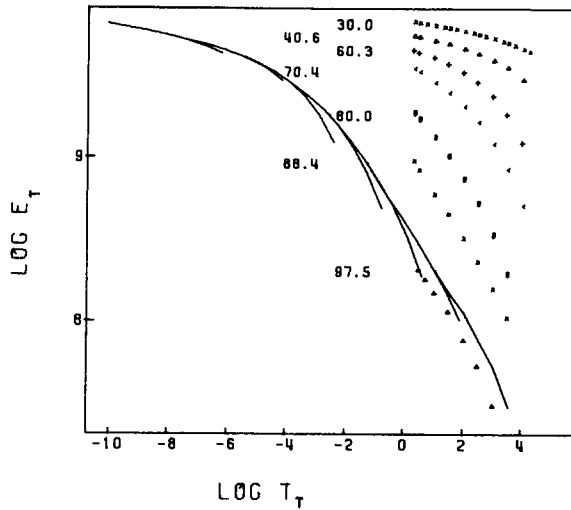
Fig. 5. Original stress relaxation curves and pseudomaster curve for Nafion-H with 0.5 H_2O/SO_3H. $T_{ref} = T_g$.
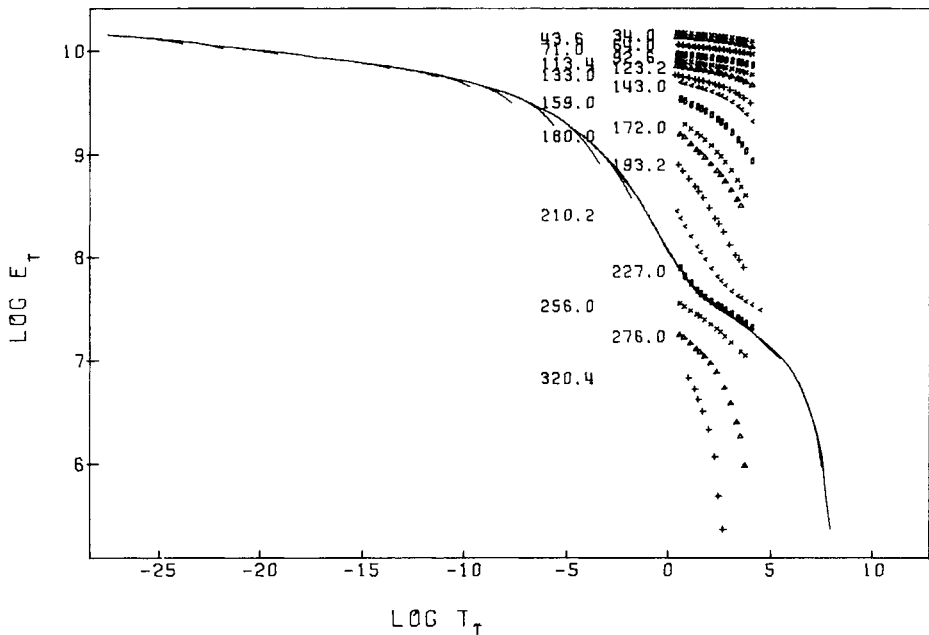

Fig. 6. Original stress relaxation curves and pseudomaster curve for Nafion-K. $T_{ref} = T_g$.

by giving the mole % of methacrylic acid followed by letters in parentheses indicating the counterions, followed by a letter indicating the molecular weight range.

Effect of Water. In contrast with the behavior of the thermorheologically simple dry acid, shown in Figure 4, time–temperature superposition breaks down with the addition of 0.5 H_2O/SO_3H as shown in Figure 5. Since the overlap was
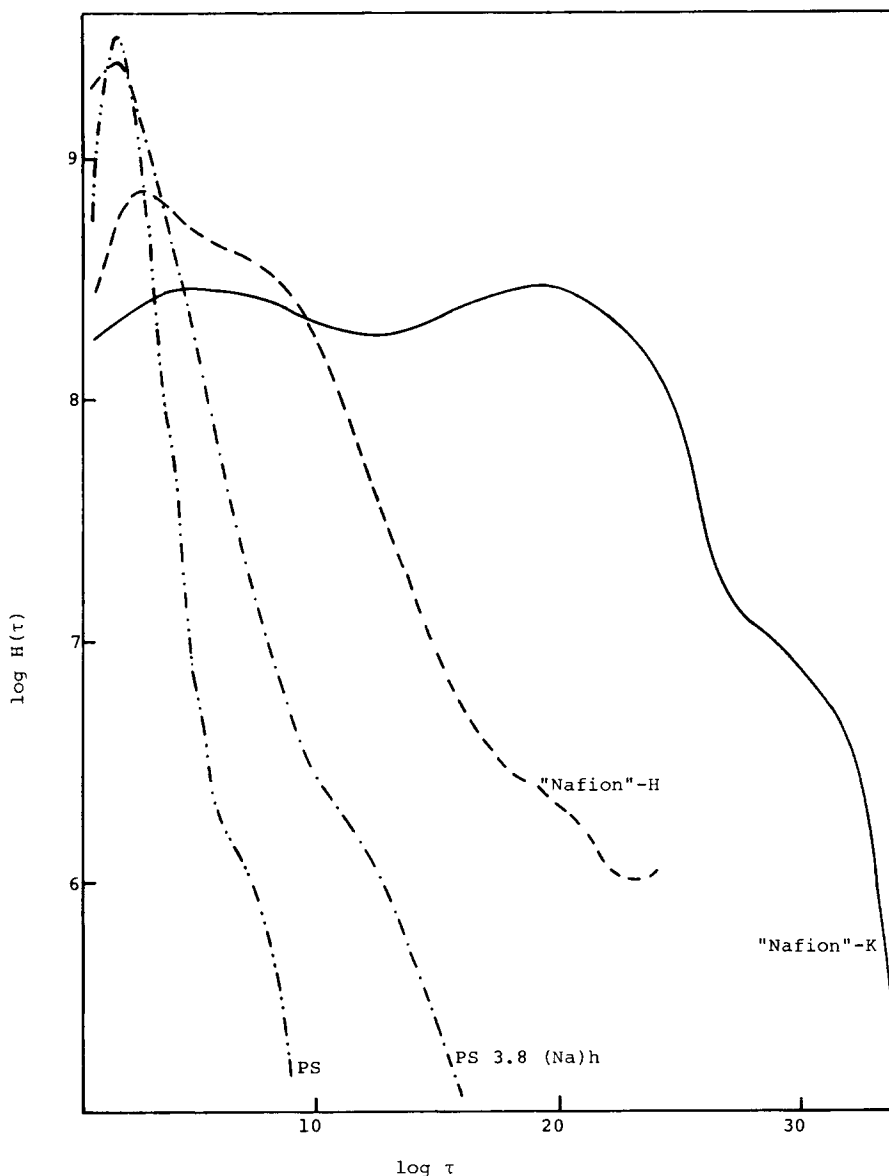
Fig. 7. Distribution of relaxation times for Nafion-H. Nafion-K, PS, and PS 3.8 (Na)h. T_{ref} = 25°C.

maximized in the short time region, pronounced deviations appeared at long times. This shifting procedure results in a pseudomaster curve, rather than a true master curve which was obtained for the dry acid. It can be seen that the rate of stress relaxation is enhanced by the presence of water.

Effect of Neutralization. Figure 6 shows the stress relaxation data of Nafion-K (100% neutralized). It is evident that below 180°C, time–temperature superposition is not applicable, whereas above 180°C it is reestablished. Some other features are noteworthy: The stress relaxation is slowed down by neutralization, so that a broadening in the distribution of relaxation times results,
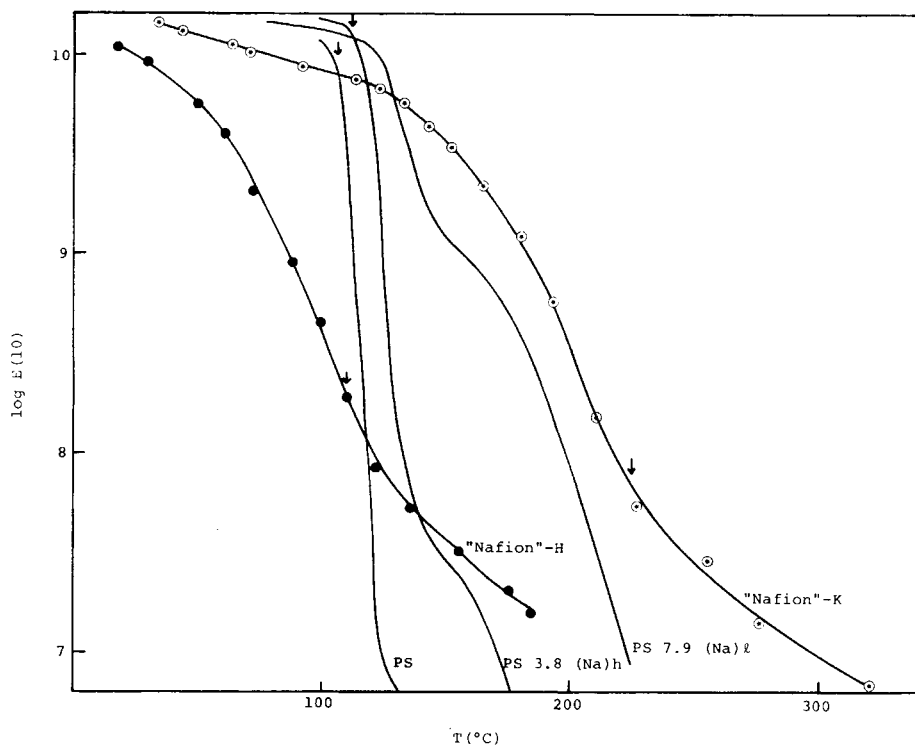
Fig. 8. 10-sec modulus vs. temperature for Nafion-H, Nafion-K, PS, PS 3.8 (Na)h, and PS 7.9 (Na)l.

as shown in Figure 7. Again, data for styrene and a styrene ionomer[13] are shown for comparison. The rubbery region for the Nafion-K is more pronounced than that in Nafion-H. Distinct viscous flow is observed at high temperatures.

Effect on Degradation. A comparative plot (not shown) of the master curves for a degraded (11% wt loss) and an undergraded Nafion-H sample shows that the glassy modulus after degradation decreases, whereas that in the rubbery region increases, revealing a conversion from a plastic-like material to a more rubber-like one as degradation takes place. Possibly, some crosslinking occurs with increasing degradation. Time–temperature superposition remains applicable.

Modulus–Temperature Curves

The simplest way of characterizing the elastic properties of a polymer is to measure its elastic modulus as a function of temperature. The 10-sec modulus is plotted versus temperature in Figure 8 for both the acid and the potassium salt. Curves for styrene and two styrene ionomers[13] are shown for the sake of comparison. Arrows indicate the glass transition for each material.

Dynamic Mechanical Studies

Effect of Water. Figure 9 shows the loss tangent of Nafion-Cs over the temperature range of −150° to +250°C, along with a plot for the material in the acid form for the sake of completeness. Both materials were run on a free vi-
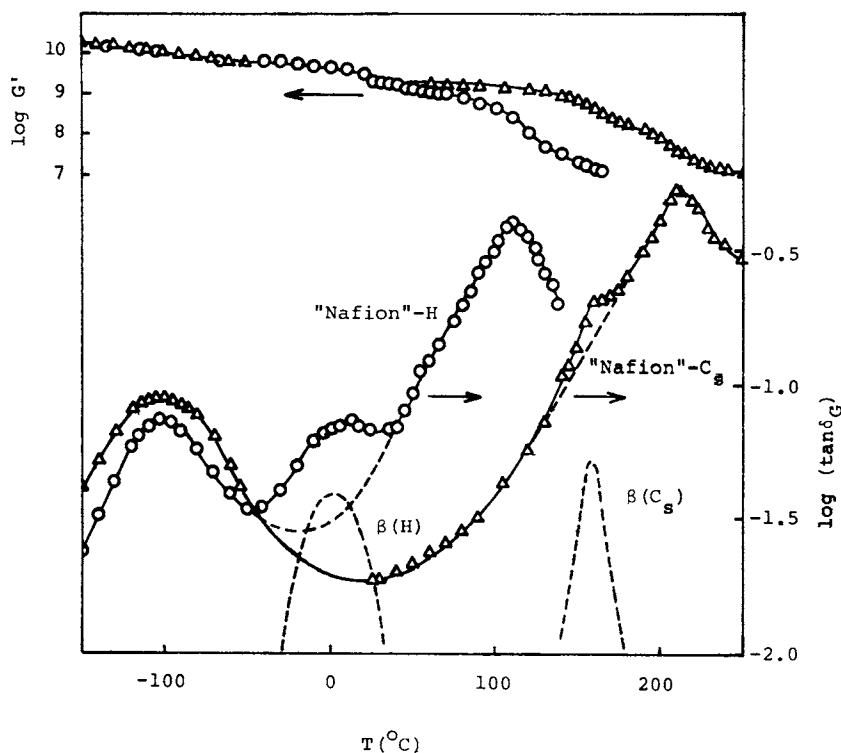
Fig. 9. Mechanical loss tangent vs. temperature for Nafion-H and Nafion-Cs at ca. 1 Hz. Dashed lines represent values for the β peak above background.

bration torsional pendulum at ca. 1 Hz. Three dispersion regions are evident in these plots, as well as in those for the Li, Na, and K salts (not shown); they are the α region, with tan δ values in the range of 0.5 to 0.6, the β region present as a shoulder or a small peak with tan δ values above background of 0.03 to 0.06 (shown also after subtraction from background as a dashed line), and the γ region which occurs at the same temperature as that of pure poly(tetrafluoroethylene).

Figure 10 (bottom) shows the loss tangent (at ca. 1 Hz) for Nafion-H with various water contents as a function of temperature in the β and γ regions; the β peak, as can be seen, shifts to lower temperature with the addition of water. For three of the samples (0, 0.5, and 2.5 H_2O/SO_3H), the shear storage moduli, G', are shown at the top of Figure 10. It can be seen that G' decreases as the water content increases.

Effect of Degradation. In Figure 11, the loss tangent and shear modulus G' of Nafion-H with different degrees of degradation (defined as % weight loss) are plotted as functions of temperature. It is evident that the β peak is not present in the degraded samples.

Figure 12 shows the storage modulus at 0°C and ca. 1 Hz for the samples with various water contents or various degrees of degradation. It can be seen that G' increases with decreasing of water content and a maximum G' value is reached as all the water is removed. Beyond this point, G' decreases again as a result of degradation. The position of this maximum was taken as an indication of dryness.
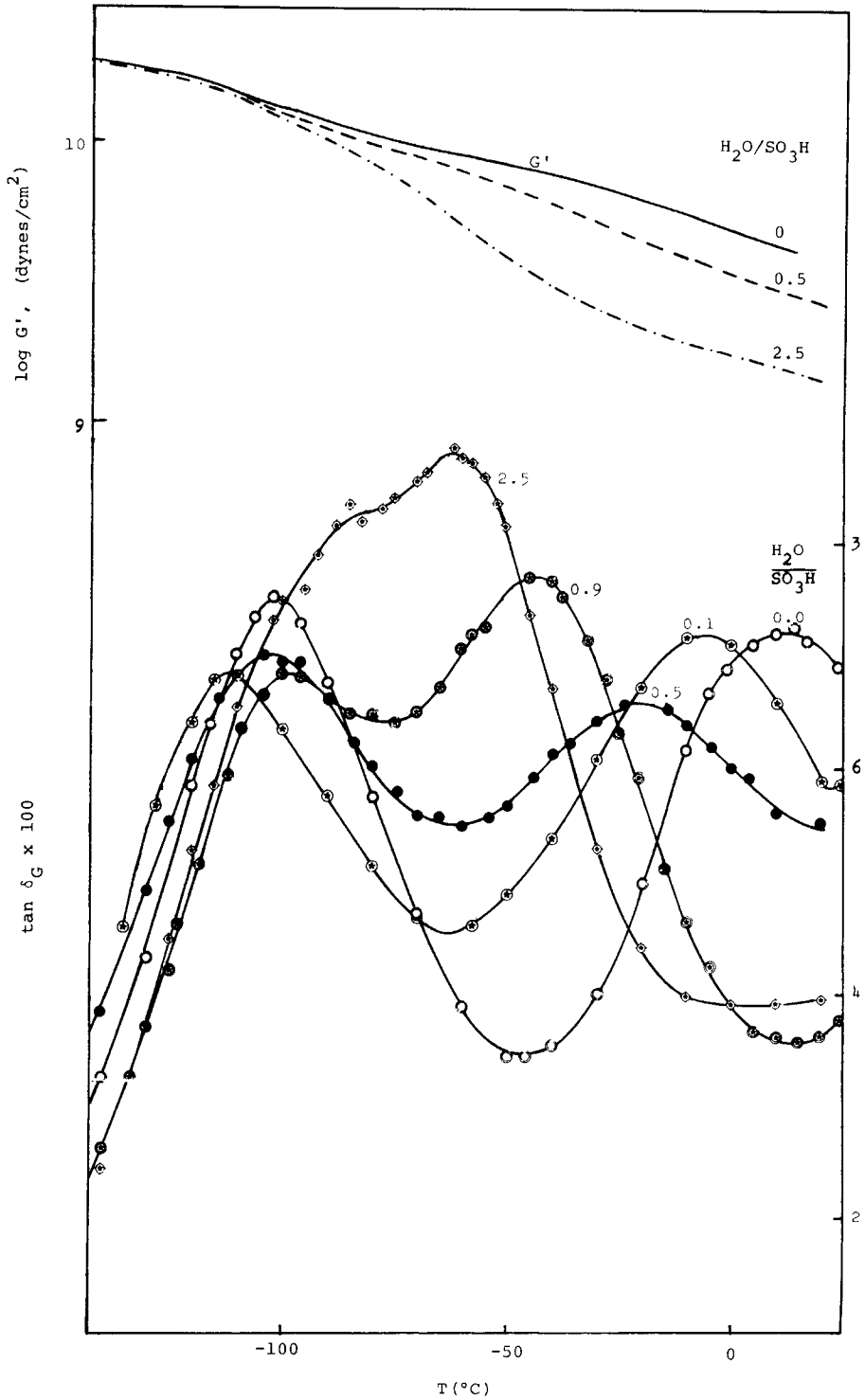
Fig. 10. Mechanical loss tangent and shear storage modulus vs. temperature for Nafion-H samples with varying water content at ca. 1 Hz.
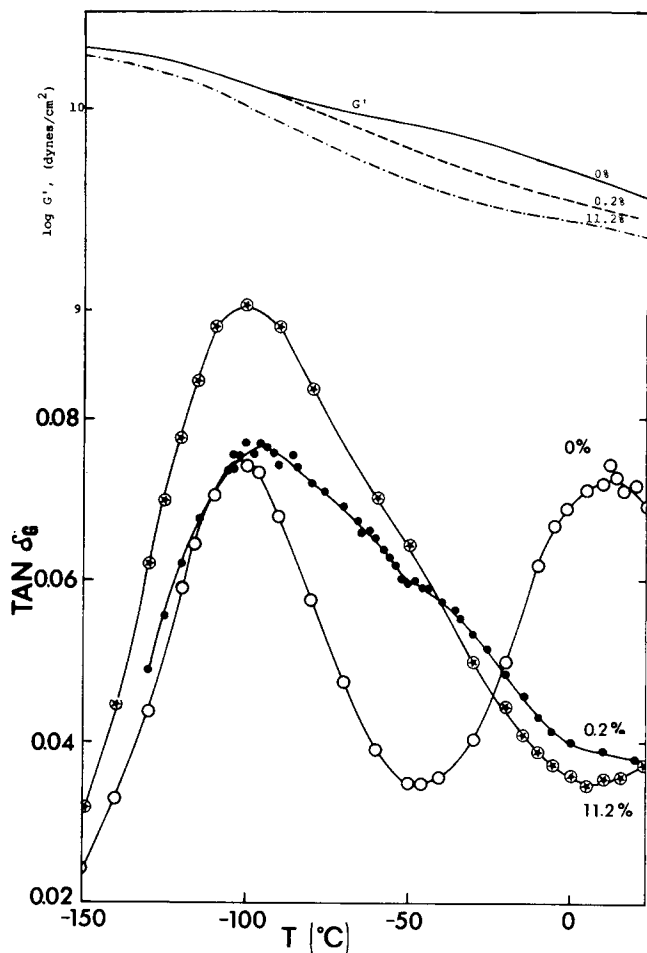
Fig. 11. Mechanical loss tangent and shear storage modulus vs. temperature for Nafion-H samples with varying degree degration (% weight loss) at ca. 1 Hz.

Effect of Counterions.   In the presence of water, the β dispersion which, in the salt is usually present as a shoulder, becomes a peak (tan $\delta \simeq 0.1$) which moves to lower temperatures with increasing water content.   Eventually (at ca. 3 H_2O/SO_3^-), the β peak merges with the γ peak to yield a single dispersion.   This is illustrated in Figure 13 for the Nafion-Li sample.   The positions of the β peaks at ca. 1 Hz for the dry polymers are also listed in Table I.   Figure 14 compares the γ relaxation of the dry Nafion with different counterions.   It is obvious that the peak height is inversely proportional to the cation size, except for the acid. A plot of log ν versus $1/T$ for the γ peak of Nafion-H and PTFE (not shown) reveals that the activation energies are 13 kcal/mole for both materials.   This value of the activation energy agrees with that one found by McCrum for PTFE.[42]

Dielectric Studies

Figure 15 shows the dielectric loss tangent of "Nafion"-H with 4 H_2O/SO_3H at frequencies of 100 Hz, 1 kHz and 10 kHz.   A major peak with minor peak
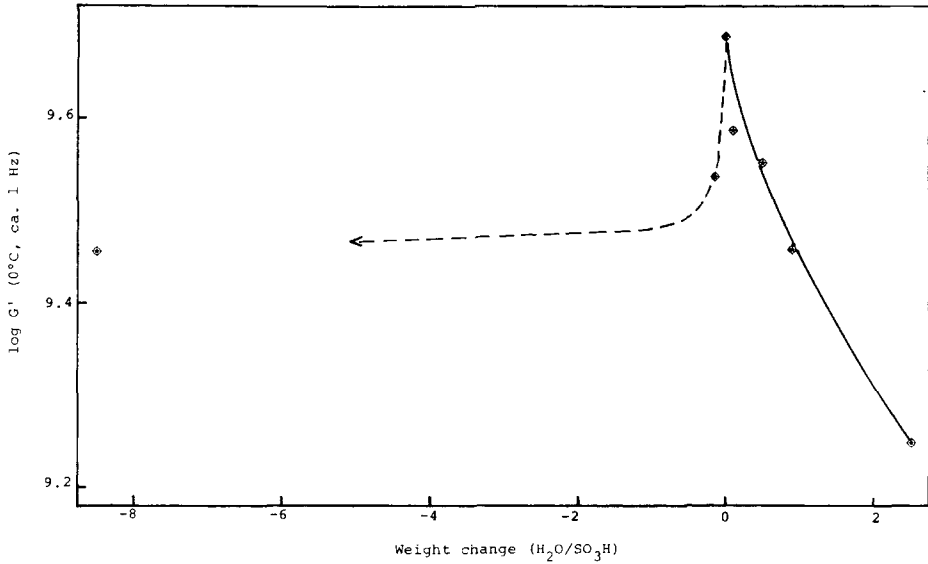
Fig. 12. Shear storage modulus (0°C, ca. 1 Hz) vs. weight loss for Nafion-H.
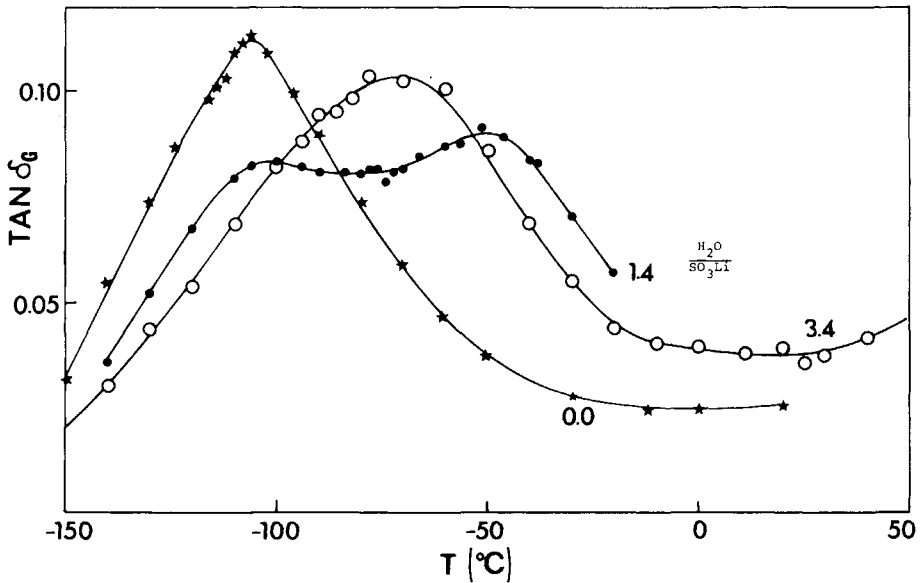

Fig. 13. Mechanical loss tangent vs. temperature for Nafion-Li with varying water content at ca. 1 Hz.

adjacent to it are observed in the β relaxation region, while the γ relaxation is dielectrically inactive, as expected. The α relaxation is difficult to observe due to the fast desorption rate of water above room temperature. The β relaxation region at 100 Hz as a function of water content is shown in Figure 16. It can be seen that the β relaxation shifts to lower temperature as water content increases. For water contents less than 1.7 H_2O/SO_3H, the minor peak appears at temperatures lower than the major peak while above 1.7 H_2O/SO_3H water content, the reverse occurs.
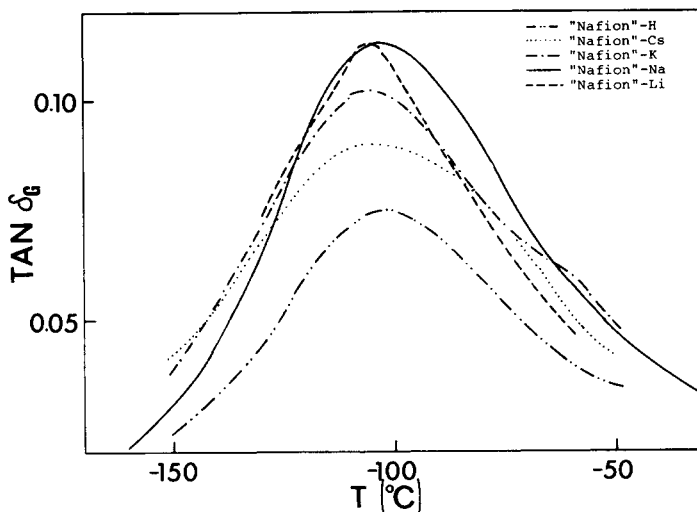
Fig. 14. Mechanical loss tangent vs. temperature for Nafion with various counterions in the γ relaxation region at ca. 1 Hz.
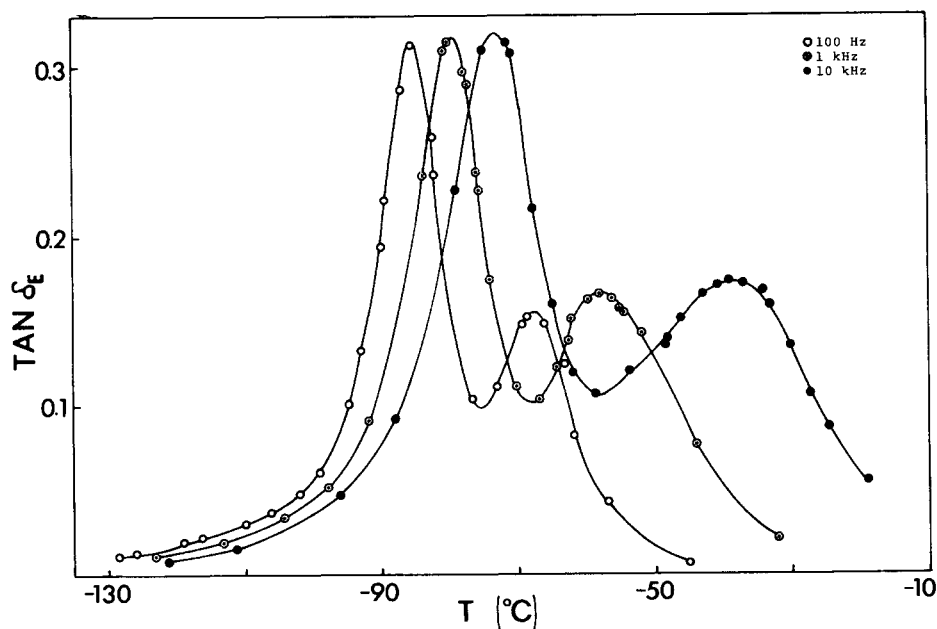
Fig. 15. Dielectric loss tangent vs. temperature for Nafion-H with 4 H_2O/SO_3H at 100 Hz, 1 kHz, and 10 kHz.

The dielectric major peak positions along with the mechanical β peak positions as a function of water content are summarized in Figure 17.

Figure 18 shows the log ν versus $1/T$ plots for the major peaks for varying water contents. The minor peak is not well separated from the major peak in the region of 0.7 to 2.1 H_2O/SO_3H. The activation energies are shown in Table II. The dielectric loss tangent of Nafion-K with various water content is presented in Figure 19.

Fig. 16. Dielectric loss tangent vs. temperature for Nafion-H with varying water content at 100 Hz.

Fig. 17. Mechanical β peak position and dielectric major peak position vs. water content for Nafion-H.
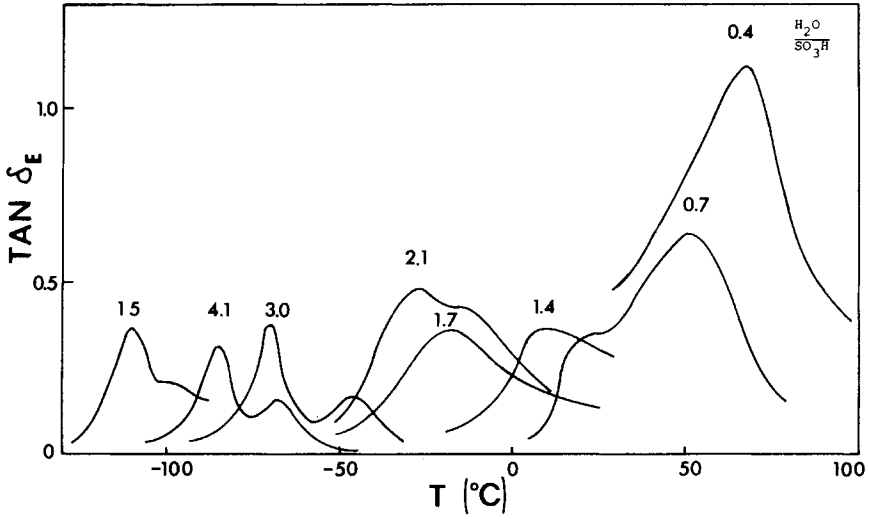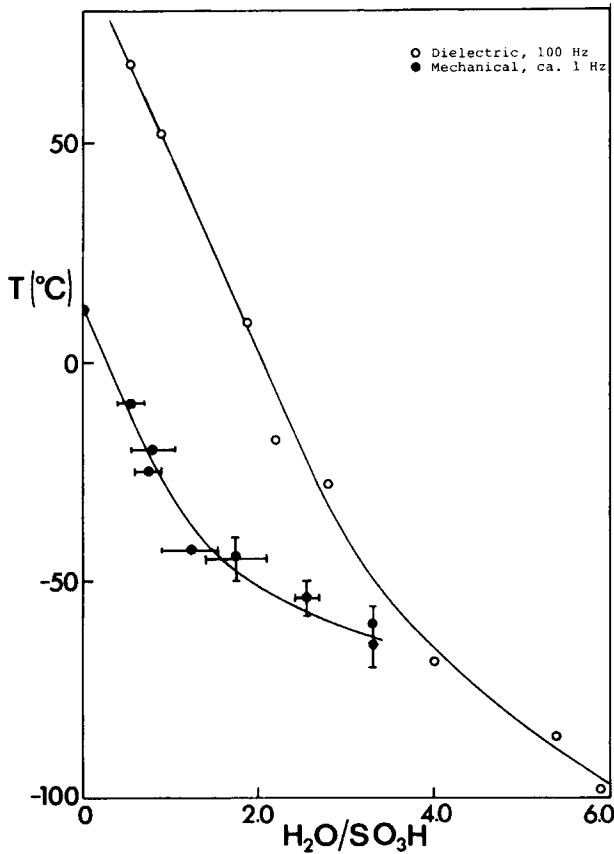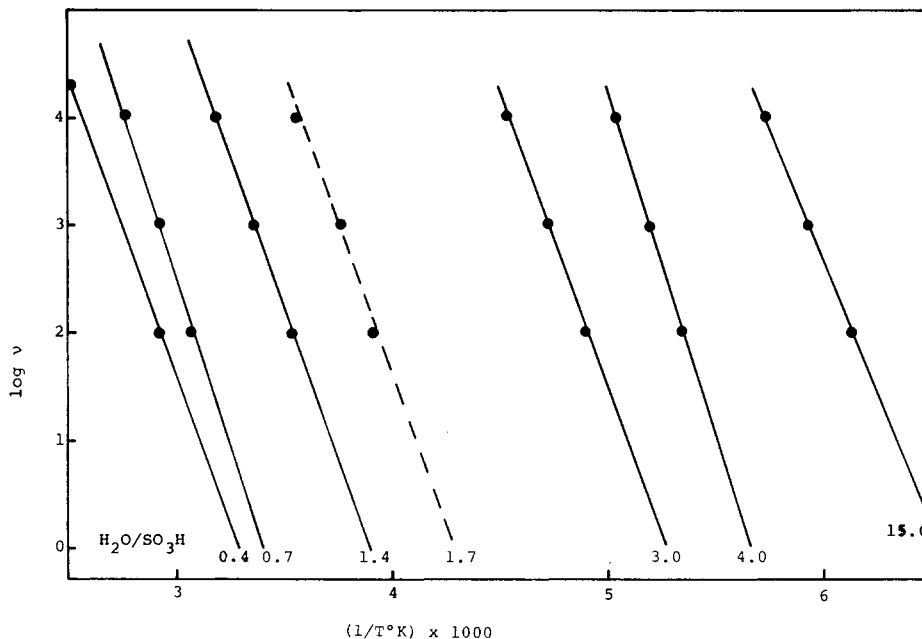
Fig. 18. Log ν vs. $1/T$ for dielectric major peak for Nafion-H.

X-Ray Diffraction

Several diffuse halos were seen in the range $1° < 2\theta < 40°$. The results are listed in Table III, along with those for styrene and several styrene ionomers[15] for comparison. No evidence of crystallinity was found.

DISCUSSION

Glass Transition

While the agreement between DSC and tan δ results for the glass transition of the Nafions is gratifying, the values obtained by the above technique are seemingly inconsistent with the low value of the 10-sec modulus, E_r (10), for the same materials at the glass transition temperature. As can be seen in Figure 8, for the styrene ionomers the E_r (10) value at glass transition temperature is of the order of 10^{10} dynes/cm^2, while for the Nafions the value is two orders of magnitude lower, both for the acid and the salt. Also, an inspection of Figure 4 reveals that in the glassy region the stress relaxation master curve for Nafion-H is placed ca. 10 orders of magnitude of time below that for the styrenes, reflecting the same problem as was found in the isochronal modulus curve.

On the basis of the stress relaxation or modulus temperature curves, it might be tempting to think of the glass transition as being closer to 30°C for the acid and to 100°C for the potassium salt. The acid does show a tan δ peak (ca. 1 Hz) at 23°C; this peak is extremely low (tan δ = 0.07) by comparison to the glass transition peak (tan δ = 0.4). Furthermore, the salt shows no peak or shoulder at 100°C, the β region appearing only 40° to 60° higher. However, here again the peak value of tan δ above the background is only 0.04 to 0.06, which suggests

that it is, most probably, not the glass transition. Thus, in spite of the low value of the modulus, it seems preferable to take the high-temperature tan δ peaks (i.e., ca. 110°C for the acid and ca. 220°C for the salts) as glass transition temperature. Also, the results of studies on wet samples, to be discussed later, support this interpretation.

If this low value of the modulus at the glass transition is correct, then some type of unusual packing is to be expected in these materials. This unusual packing, incidentally, might also correlate with the high water transport that is observed. The densities of the materials are most revealing in this context. The density of the Nafion precursor, i.e., the material in which the —SO$_3$H group is replaced by SO$_2$F is ca. 2.1 for an equivalent weight of 2100.[44] By contrast, the densities of the acid and sodium salt are appreciably lower,[44] suggesting the presence of voids. Clearly, further detailed work is required for an unambiguous determination of the glass transition, since no more detailed explanation can be given at this time for the low value of the modulus at that temperature.

Transient Studies

In spite of the absence of crystallinity, as revealed by x-ray studies, the stress relaxation master curves for the Nafions (Figs. 4–6) are quite broad, resembling those of the styrene ionomers in the clustered region much more than those of styrene or other nonionic and noncrystalline polymers. Furthermore, time–temperature superposition fails for both the dry salt and the acid in the presence of small amounts of water. These facts, coupled with the existence of a small angle scattering peak, suggest that in the Nafions the ions are clustered in the same way as in the polyethylene ionomers or in styrene with ion contents above 6 mole %. It should be recalled, in this context, that clustering is taken to mean not just simply small-scale ion aggregation of the type leading to crosslinking, but large-scale clustering incorporating a large number of ions and also some nonionic material.

The failure of time–temperature superposition is a very strong indication that the ionic regions contribute to the relaxation process. Most probably, this involves a reorganization of the cluster, possibly a hopping of sulfonate-terminated side chains. This would represent a secondary relaxation mechanism and contribute to the total relaxation. The breadth of the distribution of relaxation times (Fig. 7) as well as the breadth of the modulus–temperature curves (Fig. 8) also support the idea that this polymer is phase separated, since it parallels

TABLE II
Activation Energy of Dielectric Relaxation for Nafion–H

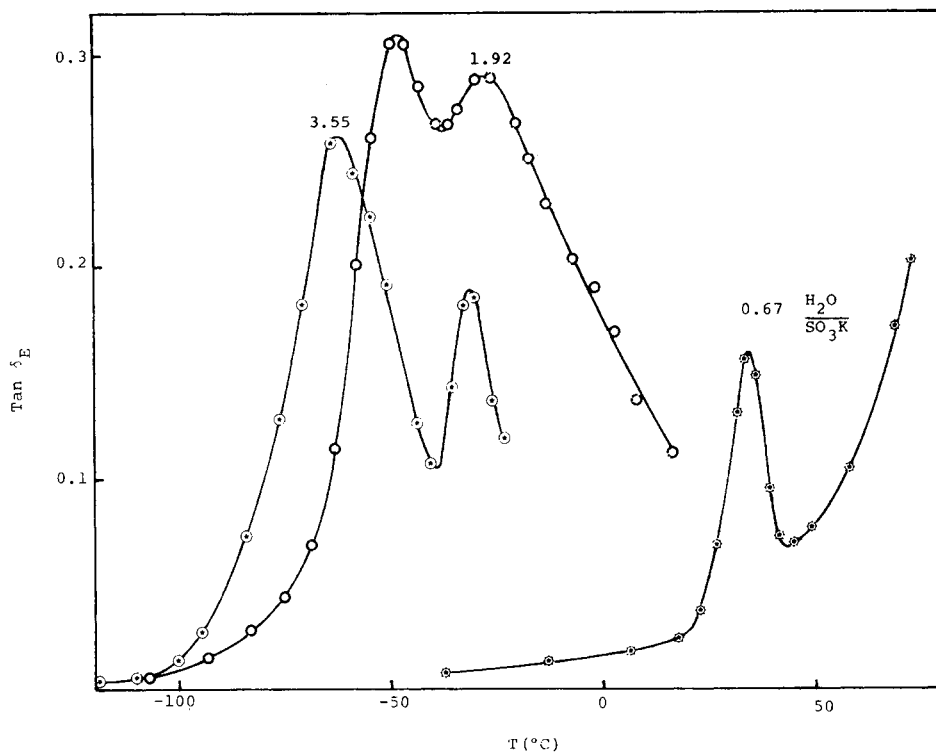| Water content (H$_2$O/SO$_3$H)	E_a, major peak, kcal/mole	E_a, minor peak, kcal/mole
0.4	25.4	
0.7	27.7	ca. 16
1.4	25.0	ca. 16
1.7	ca. 26	
3.0	25.3	16.2
4.1	29.6	14.9
15.0	22.7	

Fig. 19. Dielectric loss tangent vs. temperature for Nafion-K with varying water content at 100 Hz.

the behavior in the styrenes. The fact that superposition applies in the dry acid but fails in the presence of 0.5 H_2O/SO_3H is puzzling, but might indicate that the secondary process, while present, contributes very little to the total relaxation in the dry material. This is consistent with the finding in plasticized poly(sodium acrylate) that water, even in large amounts, decreases the lifetime of the clusters without destroying them.[45]

The reestablishment of time–temperature superposition in the potassium salt is also parallelled by the behavior of a low molecular weight clustered polystyrene ionomer containing 7.9 mole % sodium methacrylate. In contrast to high mo-

TABLE III
X-Ray Diffraction Data for Nafion–H, Nafion–Cs, Polystyrene, and Three Styrene
Ionomers

Samples	Bragg angle (2θ)		
Nafion–Cs	1° 43'	9° 16'	32° 20'
Nafion–H (dried)	3° 9'[a]	9° 26'	
Nafion–H (degraded)		9° 22'	27° 48'
Polystyrene		9° 32'	18° 38'
PS 3.8 (Cs)h	4° 40'	9° 32'	18° 38'
PS 7.9 (Cs)l	1° 28'	9° 32'	18° 38'
PS 9.7 (Cs)h	1° 34'	9° 32'	18° 38'

[a] This value is in close agreement with the one communicated to us privately by Dr. W. Grot of du Pont.

lecular weight styrene ionomers, which remain thermorheologically complex even at the highest temperatures which were studied, in that particular low molecular weight sample, time–temperature superposition is reestablished above ca. 180°C. This suggests that at those high temperatures, the secondary mechanism does not contribute appreciably to the relaxation, possibly because of a breakdown or short lifetime of the clusters.

Dynamic Studies

A dynamic mechanical investigation of the α relaxation in the acid, which has been ascribed to the glass transition, reveals that water (ca. 3 H_2O/SO_3H) has only a minor effect on the magnitude or position of the peak. This tends to reinforce the identification of this peak as due to glass transition of the nonionic phase. Water would not be expected to interact with the PTFE backbone, but would interact strongly with the ionic regions. Therefore, if this peak were due to the ionic regions, then a strong lowering of its position would be expected as the water content is increased.

In the salts, the position of the α peaks for Na^+, K^+, and Cs^+ salts is in qualitative agreement with the q/a effect which has been found operative in many ion-containing polymers.[46] This effect suggests that the glass transition should be proportional to the ratio of the cation charge q to the distance between centers of charge, a. The fact that the Li^+ salt does not fit this relation suggests possibly that the effective average size of the Li^+ ion is larger than anticipated, probably due to the presence of residual water which is associated with that ion. The effect of water on the position of the α peak could not be studied since the salts lose water at a very rapid rate at the glass transition.

The mechanical β peak in the dry acid occurs at 23°C at ca. 1 Hz and moves to lower temperatures with increasing water content. Similar behavior is seen in the salt, a shoulder appearing at ca. 150°C in the dry materials, and again moving to lower temperatures with increasing water content, although now as a small peak. The downward motion of the peak with increasing moisture parallels the behavior found in many other materials, such as polyacrylamide,[47] nylon,[48] and poly (vinyl alcohol).[49] This type of behavior is most probably due either to a change in the nature of the moving group which is responsible for the specific relaxation, or to a change in the barrier which hinders the motion of the group, or to both. In the Nafions, however, a third possibility exists. Since the polar groups probably exist in clusters, it is quite possible that we are dealing with the glass transition of these highly polar regions. This is reinforced by the drastic decrease in peak temperature with water content (Figs. 10 and 13). The drastic effect of water is, incidentally, another bit of evidence against identifying the β peak with the glass transition of the bulk phase, since PTFE would not be expected to interact with H_2O. As can be seen, the α peak, at least in the acid, is insensitive to water and is thus most likely the glass transition. With regard to the β region, on the other hand, the much higher tan δ value in the dielectric experiments than in the mechanical tests leaves no doubt that we are dealing with the polar regions. It is, however, also possible that the β peak is due to a more specific motion within the ionic region or of a polar group, such as the ether oxygen or a water–ether complex.

Only very few experiments were performed on the mechanical β peak in the salts. In so far as it has been studied, its behavior as a function of water content parallels that of the acid, except that the peak is much smaller in the dry salt than in the acid, and it occurs at ca. +150°C. It is reasonable that the salt regions hold together much more tightly than those of the acid, and thus contribute much less to the relaxation.

Due to the identity of both the position and the activation energy of the γ peak in both the acid and salt with that of PTFE, there is little doubt that it is due to the same mechanism. The height of the peak is affected somewhat by the type of ion used, but this effect is not drastic. It is worth recalling that the height of this peak is also affected by the level of crystallinity in PTFE.[42]

The dielectric results are most unusual. Clearly, the major relaxation of the acid involves two peaks (Figs. 15 and 16), the mechanism of the higher peak being probably independent of water content throughout the region. While the position and the height of that peak varies with water content, its activation energy does not. It is conceivable, although by no means certain, that this peak is due to the glass transition of the polar regions. This is supported by the rapid change of the peak position with water content, but not by the constancy of the activation energy. The nature of the minor peak remains unknown.

Small-Angle X-Ray Scattering (SAXS)

The presence of a SAXS peak strongly reinforces the clustering suggestion. Many ion-containing polymers show this behavior, among them the ionomers based on ethylene and styrene. Single peak data are difficult to interpret, but the presence of such a peak, without a doubt, is related to the presence of distinct scattering centers in the polymer.

Diffusion and Drying

The difference in the drying behavior between the acid and the salt is profound. Figure 1 shows clearly that the interaction of water with the acid is much stronger than with the salt; already at 100°C the salt can be obtained in a dry state, while a temperature of over 160°C is necessary for the acid. It is also clear that the salt is much more stable than the acid at high temperatures, the degradation curve for the salt being ca. 130°C higher than for the acid. These results parallel the findings of the du Pont group.[44]

The diffusion coefficient for water in the acid is extremely high, higher than that for any other partly ionic or nonionic polymer for which data are available. It is comparable to that of the ion exchange resins and only one order of magnitude lower than the self-diffusion coefficient of water. Furthermore, the activation energy for diffusion is only 4.8 kcal, close to that for the ion exchangers and for self diffusion of water. Table IV compares the diffusion coefficients and activation energies for diffusion for a wide range of representative polymers, showing that Nafion is, indeed, very permeable and comparable to the completely ionic ion exchangers. This fact reinforces the suggestion of unusual packing of the polymer chains in the Nafions. This low-density packing is undoubtedly due to the presence of the ionic aggregates. It should be noted, however, that

the presence of ions does not always increase the diffusion coefficient for water. In the case of polystyrene, for example, at 9.7 mole % of ions (i.e., in the clustering region), the diffusion coefficient vis-a-vis the nonionic material is decreased[43] by a factor of 500.

CONCLUSIONS

Perhaps the most interesting conclusion of this study concerns the supermolecular structure of the Nafions. It is suggested that the ions in these materials are clustered, i.e., present in large aggregates containing also some fluorocarbon material. This suggestion is based on both the rheological properties of the material and the presence of a halo at a low angle in SAXS.

The glass transition is much higher than would be expected on the basis of rheological data alone. The discrepancy suggests an unusual packing effect, which is also supported by the high value of the diffusion coefficient for water and the low activation energy, as well as by the decrease of density on ionization.

The failure of time–temperature superposition in the materials suggests the presence of two relaxation mechanisms, one due to chain diffusion (as in normal organic polymers) and the other to the presence of ionic clusters (as are also found in the styrene ionomers, among others). The secondary mechanism most probably involves a hopping of ion-terminated chains from one cluster to another. The clusters seem to become mobile above 180°C, as suggested by reestablishment of time–temperature superposition above that temperature in the salts.

The β peak in dynamic studies is probably also related to the ionic regions. Its position is strongly affected by the presence of water and may reflect the glass transition in those regions. Dielectrically, a double peak is observed which is also highly sensitive to water. The γ peak is of the same origin as in PTFE.

The diffusion coefficient for water is extremely high, higher than in any other

TABLE IV
Diffusion Coefficients of Water in Common Polymers and Self-Diffusion Coefficient of Water

	Temperature, °C	D, cm²/sec	E_D, kcal/mole	Reference
Self-diffusion of water	25	3×10^{-5}	4.41	50
Nafion–H				
(EW = 1155)	28	2.3×10^{-6}	4.8	
(EW = 1365)	28	2.6×10^{-6}		this work
Polystyrene-sulfonate				
(4% DVB)	25	9.1×10^{-6}	4.6	51
(16% DVB)	25	2.2×10^{-6}	5.2	
Polystyrene	26	5.5×10^{-7}		43
Polyethylene ($\rho = 0.922$)	25	2.3×10^{-7}	14.2	52
Ethyl cellulose	25	1.8×10^{-7}	6.3	53
Poly(methyl methacrylate)	50	1.3×10^{-7}	11.6	54
Poly(vinyl chloride)	30	1.6×10^{-8}	10	55
Nylon 6	25	9.7×10^{-10}	6.5	56
Styrene ionomer	25	9.0×10^{-10}		43

nonionic or partly ionic polymer for which data are available, and comparable to that of ion exchange resins, although the polymer has a very different structure. The activation energy is comparable to that for self-diffusion in pure water.

It is evident that the Nafions resemble other organic ionomers in a wide range of properties, notably in the presence of ion clustering and the resultant effect on the rheology of the materials. By contrast, the dramatic decrease in the density upon ionization and the accompanying increase in the diffusion coefficient for water are novel features, not encountered in other ionomers. The reason for this difference needs to be elucidated. Finally, the dynamic mechanical studies suggest that, at least in the presence of water, the glass transition of the ionic regions may be lower than that of the matrix. This has also not been encountered in other ionics.

References

1. R. W. Rees and D. J. Vaughan, *Polym. Prep.*, **6**, 296 (1965).
2. T. C. Ward and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **11**, 2403 (1967).
3. E. P. Otocka and T. K. Kwei, *Macromolecules*, **1**, 301 (1968).
4. E. F. Bonotto and E. F. Bonner, *Macromolecules*, **1**, 510 (1968).
5. W. J. MacKnight, L. W. McKenna, and B. E. Reed, *J. Appl. Phys.*, **38**, 4208 (1968).
6. P. J. Phillips and W. J. MacKnight, *J. Polym. Sci. A2*, **8**, 727 (1970).
7. K. Sakamoto, W. J. MacKnight, and R. S. Porter, *J. Polym. Sci. A2*, **8**, 277 (1970).
8. S. R. Rafikov et al., *Vysokomol. Soedin.*, **A15**, 1974 (1973).
9. C. L. Marx and S. L. Cooper, *J. Macromol. Sci.*, **B9**, 19 (1974).
10. W. E. Fitzgerald and L. E. Nielsen, *Proc. Roy. Soc.*, **A282**, 137 (1964).
11. N. Z. Erdi and H. Morawetz, *J. Colloid Sci.*, **19**, 708 (1964).
12. A. Eisenberg and M. Navratil, *J. Polym. Sci.*, **B10**, 537 (1972).
13. A. Eisenberg and M. Navratil, *Macromolecules*, **6**, 604 (1973).
14. M. Navratil and A. Eisenberg, *Macromolecules*, **7**, 84 (1974).
15. A. Eisenberg and M. Navratil, *Macromolecules*, **7**, 90 (1974).
16. E. P. Otocka and F. R. Eirich, *J. Polym. Sci. A2*, **6**, 921 (1968).
17. E. P. Otocka and F. R. Eirich, *J. Polym. Sci. A2*, **6**, 933 (1968).
18. M. Pineri, C. Meyer, A. M. Levelut, and M. Lambert, *J. Polym. Sci. A2*, **12**, 115 (1974).
19. J. Moacanin and E. F. Cuddihy, *J. Polym. Sci.*, **C14**, 313 (1966).
20. A. Eisenberg, *Advan. Polym. Sci.*, **5**, 59 (1967).
21. A. Eisenberg, *Macromolecules*, **3**, 147 (1970).
22. C. L. Marx, D. F. Caulfield, and S. L. Cooper, *Macromolecules*, **6**, 344 (1973).
23. W. J. MacKnight, W. P. Taggart, and R. S. Stein, *J. Polym. Sci.*, **C45**, 113 (1974).
24. F. B. Leitz, M. A. Accomazzo, and S. A. Michalek, paper presented at the 141st Meeting of the Electrochemical Society, Houston, 1972.
25. R. Falvo (Hooker Chemical Corporation) DOS 2,409,193 (Feb. 26, 1974).
26. J. E. Currey, A. T. Emery, C. S. McLarty, paper presented at the Chlorine Bicentennial Symposium, San Francisco, 1974.
27. L. J. Nuttall and W. A. Titterington, paper presented at the Conference on the Electrolytic Production of Hydrogen, London, February 25, 1975.
28. J. E. Harrar and R. J. Sherry, *Anal. Chem.*, **47**, 601 (1975).
29. W. G. F. Grot, G. E. Munn, and P. N. Walmsley, paper presented at the 141st National Meeting, The Electrochemical Society, Houston, May 7–11, 1972.
30. W. G. F. Grot, *Chem. Ing. Tech.*, **44**, 167 (1972).

31. W. G. F. Grot, *Chem. Ing. Tech.*, in press.
32. E. P. Otocka, *J. Macromol. Sci. Rev.*, **C5**, 275 (1971).
33. L. Holliday, Ed., *Ionic Polymers*, Applied Science Publishers, London 1975.
34. A. Eisenberg and M. King, in preparation.
35. A. Eisenberg, M. King, and N. Navratil, *Macromolecules,* **6,** 734 (1973).
36. L. A. Teter, Ph.D. dissertation, Univ. California, Los Angeles, 1966.
37. B. Cayrol, Ph.D. dissertation, McGill University, Montreal, 1972.
38. J. Williams, Ph.D. dissertation, McGill University, Montreal, in preparation.
39. R. D. McCammon and R. N. Work, *Rev. Sci. Instr.,* **36,** 1169 (1965).
40. J. Crank and G. S. Park, *Diffusion in Polymers,* Academic Press, New York, 1968, pp. 16 and 141.
41. G. J. van Amerongen, *Rubber Chem. Technol.,* **37,** 1065 (1964).
42. N. G. McCrum, *J. Polym. Sci.,* **34,** 355 (1959).
43. R. S. C. Yeo, Ph.D. dissertation, McGill University, Montreal, in preparation.
44. W. G. F. Grot, private communications.
45. A. Eisenberg, M. King, and T. Yokoyama, in *Water-Soluble Polymers,* N. Bikales, Ed., Plenum Press, New York, 1973, p. 349.
46. A. Eisenberg, *Macromolecules,* **4,** 125 (1971).
47. J. Kolarik and K. Dusek, *J. Macromol. Sci.,* **B10,** 157 (1974).
48. Y. S. Papir, S. Kapur, C. E. Rogers, and E. Baer, *J. Polym. Sci. A2,* **10,** 1305 (1972).
49. M. Takayanagi, *Mem. Fac. Eng. Kyushu Univ.,* **23,** 1 (1963).
50. J. H. Wang, *J. Amer. Chem. Soc.,* **73,** 4181 (1951).
51. G. E. Boyd and B. A. Soldano, *J. Amer. Chem. Soc.,* **75,** 6091 (1954).
52. D. Jeschke and H. A. Stuart, *Z. Naturfoesch.,* **16a,** 37 (1961).
53. J. D. Wellons and V. Stannett, *J. Polym. Sci. A1,* **4,** 593 (1966).
54. J. A. Barrie and B. Platt, *J. Polym. Sci.,* **4,** 303 (1963).
55. P. M. Doty, W. H. Aiken, and H. Mark, *Ind. Eng. Chem. Ind. (Int.),* **38,** 788 (1946).
56. T. Asada and S. Onogi, *J. Colloid Sci.,* **18,** 784 (1963).