

# Densities and Expansion Coefficients of Nafion Polymers

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## Synopsis

The densities and expansion coefficients of several Nafions in the acid and salt form were measured. For some samples, effects of variations in the equivalent weight, moisture content, and degree of uniaxial orientation were explored. The densities, which show considerable experimental scatter, seem to be independent of the equivalent weight but to be a strong function of the moisture content. Thin films of the as-received, unbacked polymer are strongly uniaxially oriented. After annealing, reproducible values of the expansion coefficient can be obtained. Two distinct breaks in the linear expansion curve are seen; in the salts, the upper one correlates with the glass transition of the material, while the lower one is found in the vicinity of the mechanical  $\beta$ -dispersion of the polymer. The large scatter of the experimental densities is consistent with the hypothesis that the sample is subject either to a microphase separation process which is strongly influenced by the sample history and which affects the density of the material very strongly, or to partial crystallization of the polymer, or both.

## INTRODUCTION

Since their appearance, the Nafions have been the subject of extensive research as a result of their unusual properties. Although several publications<sup>1-4</sup> or presentations at scientific meetings<sup>5-18</sup> have dealt with various aspects of this novel material, only relatively little is known about its properties as a polymer. An introductory study from this laboratory, which was published recently, dealt primarily with the viscoelastic and dielectric properties of this material in an exploratory manner.<sup>19</sup> A subsequent paper described the sorption behavior of the polymer in water and various aqueous solutions.<sup>20</sup>

Among the presentations at the meetings, several dealt with ion clustering<sup>8,9,15</sup> and transport phenomena,<sup>10,16</sup> but most dealt with electrochemical or commercialization aspects. Two report the results of Fourier transform IR<sup>17</sup> and NMR<sup>18</sup> studies on these materials.

In the present paper, the densities and expansion coefficients of the polymer as a function of various parameters will be explored. It is hoped that investigation of such fundamental properties as these, along with the above studies, will contribute to the elucidation of some of the more puzzling aspects of this unusual material.

Since the papers quoted above have appeared very recently, no attempt will be made to review the literature at this point. Only a few of the features most relevant to the present study will be mentioned.

Nafion is a polymer based on the perfluoroethylene backbone with short

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perfluoroether side chains containing an  $\text{SO}_3^-$  endgroup. As a result of the strongly hydrophobic backbone and highly hydrophilic terminal group, it is not surprising that some form of phase separation occurs in the material. Although the nature of this phase separation has been the subject of two model studies<sup>8,9,15</sup> as mentioned above, no unanimity exists as yet on the subject. The material in the acid form exhibits a very high diffusion coefficient for water, as well as a very low activation energy for the diffusion process. Furthermore, the Young's modulus at the glass transition temperature is very low, ca.  $10^8$  dynes/cm<sup>2</sup>, much lower than that of any other polymer studied to date.<sup>19</sup> These are only a few examples which illustrate the uniqueness of this material.

It is also worth noting that a dynamic mechanical study of these polymers<sup>19</sup> reveals the presence of two dispersion regions in the dry polymers. The higher one,  $T_\alpha$ , correlates well with the glass transition, while the lower one,  $T_\beta$ , may be due to a specific molecular mechanism. For the acid form, these two dispersions lie at ca. 100°C and 0°C, while for the salts they lie at >200°C and ca. 100–150°C.

## EXPERIMENTAL

### Materials

Nafion acid form samples (denoted as H-form) were kindly supplied by du Pont de Nemours & Company. Batch designations, thicknesses, and equivalent weights (EW) of the specimens are listed in Table I. The as-received samples are strongly uniaxially oriented and have to be annealed if one wishes to eliminate this effect. Both annealed and unannealed samples were investigated here. For the anisotropic materials, the types of samples utilized in the study are shown schematically in Figure 1. As shown in that figure, three pieces of film (ca. 3 cm × 15 cm) were obtained by cutting in three different directions relative to the direction of stretching: parallel (denoted as A-film), at a 45° angle (B-film), or perpendicular (C-film). For measurements of linear expansion, the films were rolled into cylinders at room temperature and dried under vacuum at about 60°C. The diameter of the cylindrical specimen was ca. 5 mm. Li, Na, K, and Cs salt membranes were prepared by neutralization of the A-films, which had never been exposed to elevated temperatures, in excess 0.1*N* solution of appropriate alkali at 80°C. B-Films and C-films were also transformed to Cs salt membranes by the same procedure. It was observed that all these alkali salt membranes pre-

TABLE I  
The Samples<sup>a</sup>

Specimen no.	Batch no.	EW	Thickness, mm
1	15W 18B-1077	1100	0.25
2	14W 34K-1041	1100	0.12
3	15W 48P-1067	1200	0.26
4	14W 30B-1059	1200	0.13
5	15W 72A-1086	1350	0.12
6	15W 77A-1088	1500	0.13
7		1155	1.26

<sup>a</sup> EW = Equivalent weight.

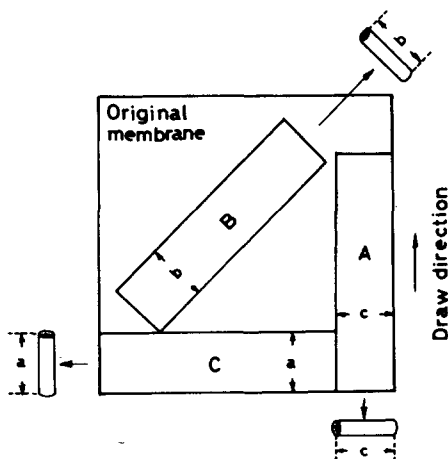


Fig. 1. Schematic representation of films cut from the original membrane: (a) draw direction; (b) 45° direction; (c) transverse direction.

served their uniaxial orientation without any observable changes. These membranes were also rolled into cylinders of ca. 5 mm in diameter and dried under vacuum at room temperature for a long time.

To remove the effect of uniaxial orientation, the H-form membranes were dried at 160°C for 24 hr. Neutralized membranes containing lithium, sodium, potassium, and cesium salts were prepared by reacting these H-form membranes with excess 0.1*N* solution of the appropriate hydroxide at 80°C for several hours. The degrees of neutralization were estimated from the weight change of the original H-form.

### Density Determination

The principle and procedure employed in this experiment are similar to the hydrostatic weighting method.<sup>21</sup> A specimen is weighed at room temperature and suspended from a support wire. A glass vessel filled with distilled water is weighed. The total weight,  $W_0$ , is the sum of  $W_1$  and  $W_2$ , which represent the weight of the glass vessel and water, respectively. Then the specimen is suspended from the wire and hung in midwater without any contact between the specimen and the vessel wall. The total weight of the vessel ( $W$ ) increases by the equivalent volume of the water which is excluded by the insertion of the specimen. Therefore, the density of the specimen,  $d_0$ , is given by the following equation:

$$d_0 = \frac{m}{(W - W_0)/d_w} + d_A \quad (1)$$

where  $m$  is the initial weight of the original specimen,  $d_w$  is the density of ordinary water at 20°C ( $d_w = 0.9982 \text{ g/cm}^3$ ), and  $d_A$  is the density of air ( $d_A = 0.00129 \text{ g/cm}^3$  at 20°C and 76 cm Hg).

Due to the uptake of water by the specimen, weight-versus-time curves were plotted for each run and extrapolated to zero time (the time of immersion). The plots were linear. For the study of the effects of drying temperature on the density, samples were kept under vacuum for 24 hr at the specific temperatures.

The moisture content of the wet samples was determined by drying the specimens for 24 hr at ca. 155°C for the acid and ca. 170°C for the salts.

### Linear Expansion

Glass transition temperatures of the specimens were determined in an automatic device which measured the length of the specimen as a function of temperature.<sup>22,23</sup> The instrument consisted of a quartz tube closed at one end, which contained the cylindrical sample of 0.5 cm in diameter. The other end of the tube was attached to the outer part of a cylindrical linear variable differential transformer (LVDT, Schaevitz, model 100 MLT). One end of a quartz rod rested on top of the sample, while the other supported the core of the LVDT. Another quartz tube contained a thermocouple. Both tubes were placed in a metal block, which was heated by means of nichrome wire and a variable transformer at the heating rate of  $1.00 \pm 0.2^\circ\text{C}/\text{min}$ . With the output of the LVDT amplifier-indicator (Daytronic model 300C, with type 61 plug-in unit) being used as the  $y$ -axis input of an  $x$ - $y$  recorder and the thermocouple output as  $x$ -axis input, plots of length versus temperature (in millivolts) were obtained directly. The thermocouple (iron-constantan) was kept in an environment very similar to that used to house the sample to minimize the effects of the temperature lag due to the finite heating or cooling rate.

The linear thermal expansion coefficient  $\alpha$  was calculated from the relation

$$\alpha = \frac{1}{L_0} \frac{dL}{dT} \quad (2)$$

where  $L_0$  represents an initial length of the specimen and  $dL/dT$  is the rate of change of length with temperature. In several instances, a coefficient of cubical expansion  $\beta$  is quoted,  $\beta$  being  $3\alpha$  for isotropic samples.

### Dimensional Stability

The dimensional changes for the original H-form, of ca. 3 cm  $\times$  4 cm area of A- and B-films, were measured as a function of temperature. The change in length of the membrane was used to determine the shrinkage  $S$  from the relation

$$S = \frac{\text{initial length} - \text{final length}}{\text{initial length}} = \frac{\Delta L}{L_0} \quad (3)$$

## RESULTS

### Densities

The parameters which were explored in their relation to the density of the Nafions are the composition (acid or salt), drying procedure (related to water content), and equivalent weight. The results will be presented separately for the acids and the salts.

**H-Form Membranes.** While appreciable differences were observed between samples of different equivalent weights for any one drying temperature, no

TABLE II  
Densities of H-Form Nafion Membranes, Mean, Probable Error ( $\bar{d}$ ), and Standard Deviation ( $\sigma$ )

Temperature, °C	Storage or drying conditions	Mean density, g/cm <sup>3</sup>	$\bar{d}$ , g/cm <sup>3</sup> (%)	$\sigma$ , g/cm <sup>3</sup> (%)
20	immersed in water	1.858	0.061 (3.3)	0.077 (4.2)
20	stored in air and in ambient R.H.	1.965	0.021 (1.1)	0.028 (1.4)
20	dried under vac 24 hr	1.986	0.040 (2.0)	0.049 (2.5)
50	dried under vac 24 hr	2.012	0.039 (1.9)	0.057 (2.8)
90	dried under vac 24 hr	2.064	0.054 (2.6)	0.066 (3.2)
124	dried under vac 24 hr	2.079	0.038 (1.8)	0.045 (2.2)
152	dried under vac 24 hr	2.039	0.051 (2.5)	0.065 (3.2)
155	dried under vac 24 hr	2.055	0.036 (1.8)	0.046 (2.2)
180	dried under vac 24 hr	2.019	0.038 (1.9)	0.049 (2.5)
224	dried under vac 24 hr	1.984	0.033 (1.7)	0.039 (2.0)

systematic trends could be detected at any temperature; furthermore, the sequence of samples in going from the highest to the lowest density also varied from one temperature to another. Therefore, the data for any one drying process were averaged and reported as averages in Table II, along with the probable errors and the standard deviations. Figure 2 shows a plot of the density as a function of the water content expressed as the ratio  $f$  of the weight of water to the weight of dry polymer. The curve is theoretical, calculated on the assumption of simple additivity of volumes, using the relations given in the Appendix. Clearly, that assumption is only a very rough approximation but seems to reproduce the data at low  $f$  values satisfactorily.

**Salts.** The densities as a function of drying temperature and type of cation are given in Table III for a membrane of equivalent weight 1155 and 1.26 mm thick. The effect of sample thickness and of water content on the densities of the Li and Na salts is shown in Figure 3 for samples 0.26 and 1.26 mm thick and water contents up to 15 wt %.

### Dimensional Changes of Uniaxially Oriented Membranes

Figure 4 shows the results for successive heating runs for an A sample of equivalent weight 1100, measured in the  $c$  direction, while Figure 5 shows the same results for a C-sample measured in the  $a$  direction. It is clear that the low temperature value of  $\alpha$  is quite reproducible but that above ca. 80°C considerable

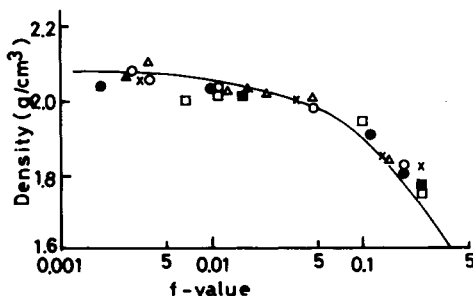


Fig. 2. Water content dependence of the density of the H-form membranes. Curve: calculated, (see Appendix) Points: experimental. EW and thickness (mm): (○) 1200, 0.26; (●) 1350, 0.12; (△) 1155, 1.26; (▲) 1200, 0.13; (□) 1500, 0.13; (■) 1100, 0.12; (×) 1100, 0.25.

TABLE III  
Densities of Alkali Salt Membranes<sup>a</sup>

Temperature, °C	Storage or drying condition	Li salt		Na salt		K salt		Cs salt	
		Water content, %	<i>d</i> , g/cm <sup>3</sup>	Water content, %	<i>d</i> , g/cm <sup>3</sup>	Water content, %	<i>d</i> , g/cm <sup>3</sup>	Water content, %	<i>d</i> , g/cm <sup>3</sup>
20	immersed in water	14.0	1.860	9.4	1.940	1.8	2.056	0.9	2.177
20	stored at R. T. in ambient R.H.	2.9	2.027	1.7	2.065	0.7	2.076	0.4	2.187
105	dried under vac	1.3	2.052	0.7	2.073	0.4	2.071	0.1	2.179
120	dried under vac	0.2	2.054	0.1	2.077	0	2.077	0	2.171
160	dried under vac	0	2.044	0	2.065	0	2.067	0	2.166
190	dried under vac	0	2.047	0	2.074	0	2.072	0	2.178
220	dried under vac	0	2.037	0	2.049	0	2.048	0	2.152

<sup>a</sup> EW = 1155, thickness = 1.26 mm.

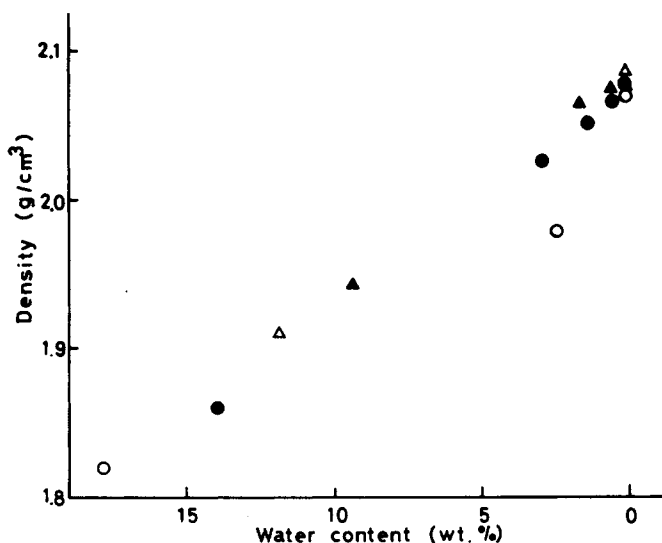


Fig. 3. Density vs. water content for the Li salt and Na salt membranes: (○) Li salt, EW 1100, 0.26 mm thick; (●) Li salt, EW 1155, 1.26 mm; (△) Na salt, EW 1100, 0.26 mm; (▲) Na salt, EW 1155, 1.26 mm.

irreproducibility may occur depending on sample history. In these figures, peak positions or slopes at  $T > 80^{\circ}\text{C}$  should therefore not be taken as describing any fundamental property of the material, merely as indications of the types of phenomena to be expected from oriented samples. Samples cut in the B-mode exhibit still more complicated behavior.

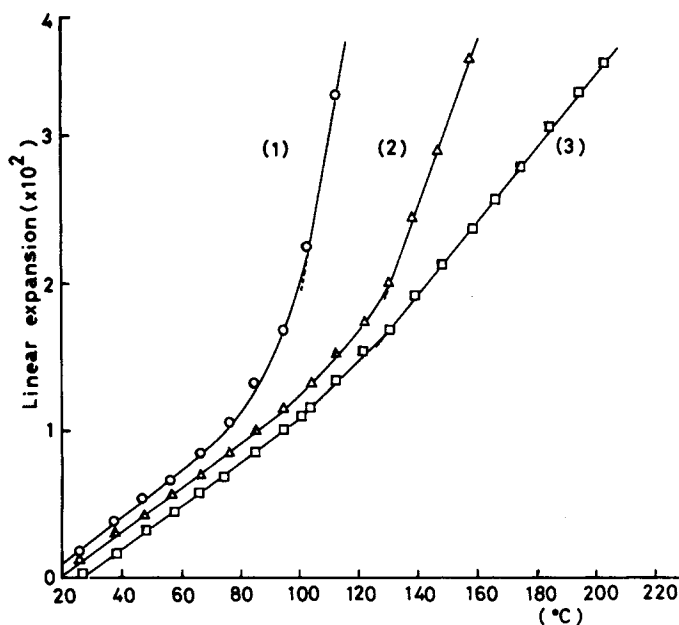


Fig. 4. Linear expansion vs. temperature for the H-form membrane (EW = 1100) in the  $c$  direction: (1) (○) first heating run; (2) (△) second heating run; (3) (□) third heating run.

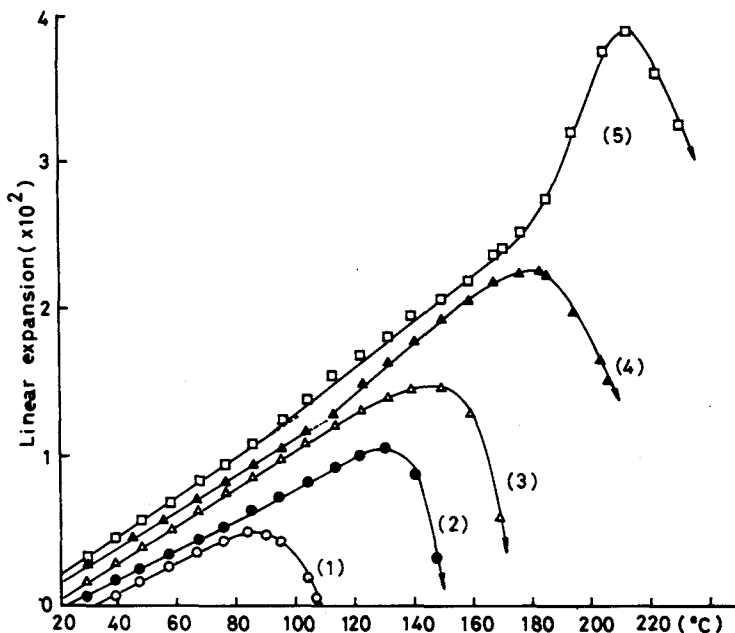


Fig. 5. Linear expansion vs. temperature for the H-form membrane ( $EW = 1100$ ) in the  $a$  direction. (1) (○) first heating run; (2) (●) second heating run; (3) (△) third heating run; (4) (▲) fourth heating run; (5) (□) fifth heating run.

The alkali salt membranes exhibited quite similar behavior, except that the peak positions or inflection points occurred at considerably higher temperatures. The figures for these materials are not presented here, but an idea of the changes observed in two successive heating runs can be obtained from Table IV, which gives the values of the apparent linear expansion coefficient for the Li, Na, and K salts in the  $c$  direction for the first two runs, and from Table V, which gives the data for the Cs salt in the  $a$ ,  $b$ , and  $c$  directions for four heating runs. It is

TABLE IV  
Apparent Linear Expansion Coefficient  $\alpha$  for Various Alkali Salts in the  $c$  Direction<sup>a</sup>

Heating run no.	Li salt $\alpha(\times 10^4)$	Na salt $\alpha(\times 10^4)$	K salt $\alpha(\times 10^4)$
1	(R.T. ~ 140°C) 1.47	(R.T. ~ 130°C) 1.46	(R.T. ~ 60°C) 1.46
			(80 ~ 150°C) 1.5
	(>170°C) 7.4	(160 ~ 190°C) 3.3	(170 ~ 190°C) 3.3
		(>195°C) 18	(>200°C) 9.7
2	(R.T. ~ 140°C) 1.37	(R.T. ~ 70°C) 0.85	(R.T. ~ 100°C) 1.17
		(90 ~ 140°C) 1.34	(130 ~ 220°C) 1.47
	(>170°C) 1.7	(>180°C) 1.7	

<sup>a</sup> R.T. = Room temperature.



TABLE V  
Apparent Linear Expansion Coefficient  $\alpha$  for the Cs-salt in Various Directions

Heating run no.	$\alpha(\times 10^4)$		
	a Direction	b Direction	c Direction
1	(R.T. $\sim 70^\circ\text{C}$ )	R.T. $\sim 60^\circ\text{C}$	(R.T. $\sim 60^\circ\text{C}$ )
	0.83	1.03	0.83
	(80 $\sim 120^\circ\text{C}$ )	(80 $\sim 180^\circ\text{C}$ )	(70 $\sim 100^\circ\text{C}$ )
	0.88	1.20	1.40
			(120 $\sim 160^\circ\text{C}$ )
		2.05	
		(>200 $^\circ\text{C}$ )	
		>10	
2	(R.T. $\sim 70^\circ\text{C}$ )	(R.T. $\sim 80^\circ\text{C}$ )	(R.T. $\sim 70^\circ\text{C}$ )
	0.90	1.00	0.83
	(80 $\sim 100^\circ\text{C}$ )	(90 $\sim 160^\circ\text{C}$ )	(80 $\sim 160^\circ\text{C}$ )
	0.95	1.14	1.18
	(120 $\sim 160^\circ\text{C}$ )		
3	(R.T. $\sim 100^\circ\text{C}$ )	(R.T. $\sim 80^\circ\text{C}$ )	(R.T. $\sim 100^\circ\text{C}$ )
	1.03	1.00	1.03
	(120 $\sim 170^\circ\text{C}$ )	(100 $\sim 160^\circ\text{C}$ )	(100 $\sim 160^\circ\text{C}$ )
	1.22	1.15	1.28
	(>170 $^\circ\text{C}$ )	(>180 $^\circ\text{C}$ )	(>170 $^\circ\text{C}$ )
4	(R.T. $\sim 110^\circ\text{C}$ )		
	1.00		
	(120 $\sim 160^\circ\text{C}$ )		
	1.35		
	(>170 $^\circ\text{C}$ )		
Annealed specimen	(R.T. $\sim 100^\circ\text{C}$ )	$\bar{d}$	$\sigma$
	0.94	0.09	0.14
	(110 $\sim 160^\circ\text{C}$ )		
	1.19	0.13	0.17
	(>200 $^\circ\text{C}$ )		

stressed that no fundamental significance should be attached to these numbers; they are given here for illustrative purposes only.

As a further demonstration of the changes in dimensions with heating temperature (24 hr under vacuum) for the unannealed samples, the dimensions of two initially rectangular samples, one cut so that the draw direction is parallel to one side while in the other it lies at 45° to one side, are reported in Figures 6 and 7. Again, no absolute significance should be attached to these numbers, as the degree of initial orientation may vary from sample to sample.

### Expansion Coefficients of Annealed Membranes

All the runs on dry annealed membranes, whether in the salt or acid form, exhibit three linear segments, examples of which are shown in Figure 8 for the Li and Na salts. The expansion coefficients themselves are summarized in Table VI for both the H-form and the salts.

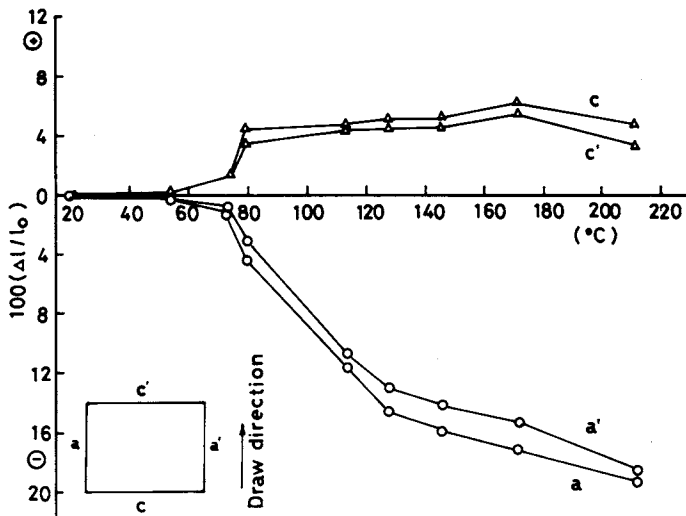


Fig. 6. Dimensional changes of uniaxially oriented H-form membrane (EW = 1100) in the  $a$ - $c$  plane, as a function of annealing temperature.

The intersections of these straight-line segments are also of interest, in that they can be related to the glass transition or the sub- $T_g$  relaxations of the materials. For the H-form, the primary intersection lies at an average value of  $104^\circ\text{C}$  ( $\bar{d} = 2$ ,  $\sigma = 3$ ), in excellent agreement with the glass transition temperature for the material as determined by previous dynamic mechanical and thermal studies.<sup>19</sup> For the salt samples, the results are shown in Table VII along with the relevant comparisons with the previous work.<sup>19</sup>

Finally, in order to explore qualitatively the effect of residual moisture on the expansion coefficient, a rolled and annealed Cs salt membrane was stored in distilled water for 24 hr at room temperature and its expansion coefficient studied without subsequent drying. The results are shown in Figure 9. The apparent

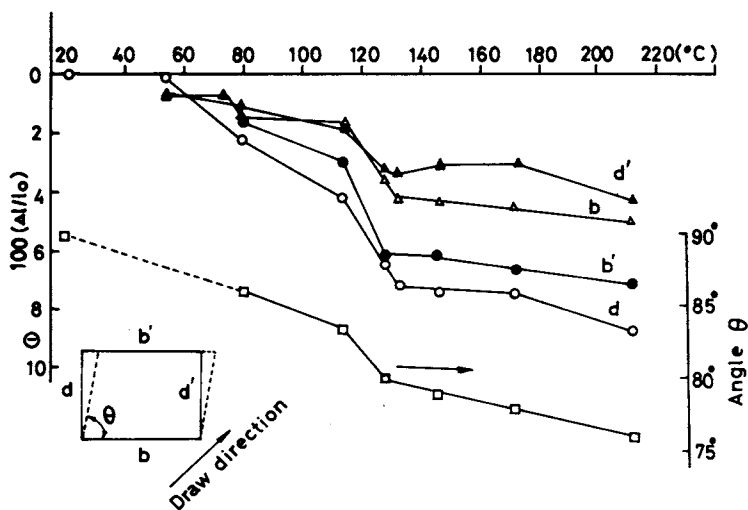


Fig. 7. Dimensional changes of uniaxially oriented H-form membrane (EW = 1100) for the B-film as a function of annealing temperature.

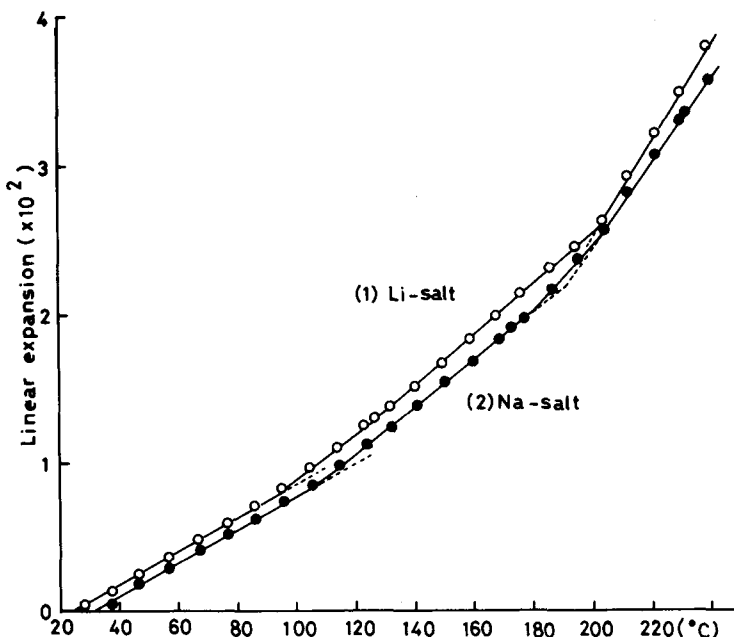


Fig. 8. Linear expansion vs. temperature for the Li salt and the Na salt membranes which had previously been dried under vacuum at 160°C: (1) (O) Li salt; (2) (●) Na salt.

expansion coefficient in the first run exceeds  $8.5 \times 10^{-4}$  for the temperature range of 40–80°C. The H-form membrane exhibits similarly irreproducible results, although the magnitude of the effect is not as large. In subsequent runs, as the sample dries, the values of  $\alpha$  approach those of the annealed samples.

TABLE VI  
Linear Expansion Coefficients of Nafion Polymers  $\alpha(\times 10^4)$  in Various Temperature Ranges

Specimen				
H-form		R.T. ~80°C	>100°C	
	$\bar{\alpha}$	1.47	2.98	
	$\frac{\bar{\alpha}}{d}$	0.03	0.12	
Li salt	$\sigma$	0.04	0.25	
		R.T. ~90°C	120~190°C	>190°C
	$\bar{\alpha}$	1.23	1.98	3.3 <sup>a</sup>
Na salt	$\frac{\bar{\alpha}}{d}$	0.10	0.21	
	$\sigma$	0.13	0.29	
		R.T. ~100°C	120~180°C	>200°C
K salt	$\bar{\alpha}$	0.95	1.40	2.8 <sup>a</sup>
	$\frac{\bar{\alpha}}{d}$	0.10	0.13	
	$\sigma$	0.15	0.21	
Cs salt		R.T. ~120°C	130~190°C	>230°C
	$\bar{\alpha}$	1.23	1.44	2.5 <sup>a</sup>
	$\frac{\bar{\alpha}}{d}$	0.11	0.16	
	$\sigma$	0.16	0.22	
		R.T. ~120°C	130~190°C	>200°C
	$\bar{\alpha}$	0.94	1.20	2.6 <sup>a</sup>
	$d$	0.09	0.13	
	$\sigma$	0.14	0.17	

<sup>a</sup> Only one determination.

TABLE VII  
Transition Temperatures for Alkali Salt Membranes<sup>a</sup>

Specimen		$T_{\alpha}$ , °C	$T_{\beta}$ , °C
Li salt	Dyn.	217	147
	Cal.	218 ± 18	120
	Exp.	200 ± 5	98 ± 9
Na salt	Dyn.	235	140
	Cal.	238 ± 25	132 ± 15
	Exp.	206 ± 12	104 ± 11
K salt	Dyn.	225	150
	Cal.	213 ± 20	109 ± 22
	Exp.	213 ± 14	140 ± 12
Cs salt	Dyn.	211	160
	Cal.	212 ± 15	116
	Exp.	199 ± 4	125 ± 3

<sup>a</sup> Dyn. = Dynamic mechanical<sup>19</sup>; Cal. = calorimetric<sup>19</sup>; Exp. = expansion coefficient, present work.

## DISCUSSION

### Density

As can be seen clearly in Table II, the standard deviations of the density measurements range from 1.4 to 4.2%, very high values considering the limits of the method. For example, in an independent determination of the densities of styrene ionomers<sup>24</sup> as a function of ion concentration, the average deviation of the experimental points from the best smooth line was ca. 0.17%, a more rea-

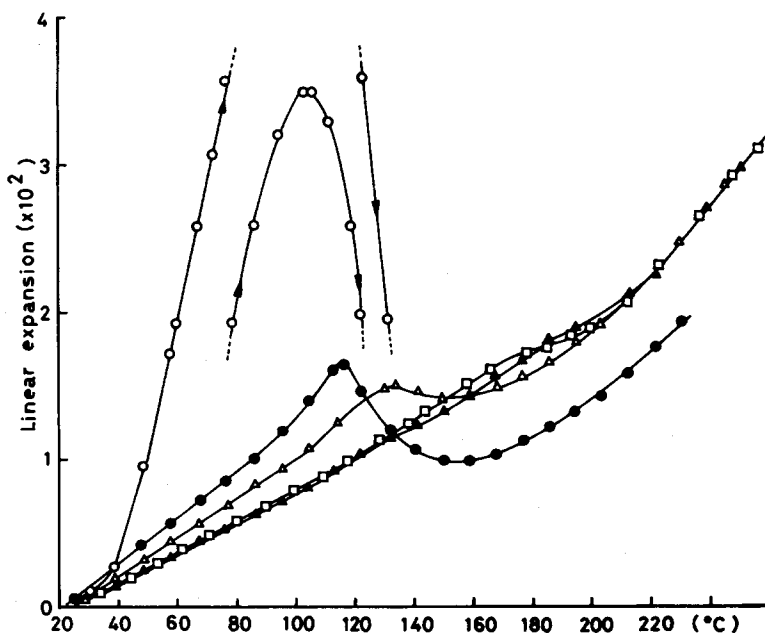


Fig. 9. Linear expansion vs. temperature for the Cs salt which was rolled, annealed at 200°C, and then immersed in distilled water at room temperature for over 24 hr: (○) first heating run; (●) second heating run; (△) third heating run; (▲) fourth heating run; (□) fifth heating run.

sonable estimate of the error. The fact that the material is hygroscopic and thus absorbs water as a function of time cannot be used to explain the high scatter, because the extrapolation procedures were identical for all the samples and because the plots were linear.

For systems involving the interaction of sulfonate groups with water, it seems quite clear that volume additivity is only a rough approximation. Nevertheless, calculations based on this assumption reproduced the density values of the wet systems well, especially at low water contents. This, again, suggests that the other factors which affect the density of the materials introduce irreproducibility to such an extent that the above assumption becomes tenable.

One possibility which could explain this large scatter of the data is based on the suggestion that the materials are phase separated, as has been suggested before, while another is based on the possibility that the polymer crystallizes to varying extents. As a matter of fact, both effects might be contributing to the observed scatter.

Furthermore, the degree of phase separation or crystallinity or the morphology of the ion-rich regions must be, in a very critical way, dependent on the detailed sample history. Such phenomena are not unusual in systems subject to phase separation (i.e., spinodal decomposition, and UCST- or LCST-related micro-phase separation), but such a wide scatter in density data has to our knowledge not been observed yet.

Whatever the structure of the material, the ion-rich regions do not seem to possess an appreciable number of holes of molecular size. If such holes were present, then the introduction of small quantities of water would increase the density since the water would fill the holes first. The applicability of the assumption of volume additivity rules out that possibility.

### Uniaxial Orientation

The types of curves shown in Figures 4 and 5 are exactly of the type one would expect for uniaxially oriented samples. A change in dimensions of 20% (Fig. 6) or in the angles from  $90^\circ$  to  $<80^\circ$  is also not unreasonable but should obviously be taken into account in applications involving the material at elevated temperatures. The occurrence of a peak in Figure 5 is undoubtedly due to the fact that in that temperature region the material has softened sufficiently for strain relief to begin, i.e., for the sample to begin its shrinkage process if the dimension measured is in the direction of uniaxial orientation. It should be stressed that these results have been obtained on relatively dry material, not on membranes stored under water. Under those circumstances, the behavior might be expected to be quite different.

### Expansion Coefficients

The standard deviations for the expansion coefficient measurements, while large, are not unusually so. Again, when one compares the Nafions with the styrene ionomers,<sup>24</sup> the standard deviation for  $\alpha$  for the latter was 13%, while for the Nafions it is of the same order (Table VI). Thus, the experimental scatter in the expansion coefficients of these materials seem to result from the same range of phenomena encountered in other materials.

It is very significant that the salts exhibit two very clear breaks in the region studied, one at the glass transition temperature, and the other in the vicinity of the mechanical  $\beta$  dispersion. The latter phenomenon is not encountered in other polymers to the extent observed here,<sup>19</sup> if at all. Its presence here may indicate that the  $\beta$  relaxation is accompanied by a significant loosening of the structure of the material.

The financial assistance of the Olin Chemicals Group of the Olin Corporation in the course of this work is gratefully acknowledged.

## APPENDIX

The weight of a wet polymer sample is given by the algebraic sum of the completely dried polymer and the weight of water absorbed by the polymer. The density of the wet polymer sample,  $d_0$ , is given by the following equation:

$$d_0 = \frac{M_s + M_w}{V_s + V_w} \quad (1)$$

where  $M_s$  and  $M_w$  are respectively the weight of the dry polymer and of the water and  $V_s$  and  $V_w$  are the volume of the dried polymer and of the water, assuming volume additivity. If one denotes the densities of the dry polymer and of the water by  $d_s$  and  $d_w$ , eq. (1) can be rewritten as

$$d_0 = \frac{M_s + M_w}{\frac{M_s}{d_s} + \frac{M_w}{d_w}} = \frac{d_s d_w (M_s + M_w)}{M_s d_w + M_w d_s} \quad (2)$$

Rearranging, one obtains

$$M_s(d_0 d_w - d_s d_w) = M_w(d_s d_w - d_0 d_s) \quad (3)$$

which leads to

$$\frac{M_w}{M_s} = \frac{d_w(d_0 - d_s)}{d_s(d_w - d_0)} \quad (4)$$

If one defines  $M_w/M_s = f$ , eq. (4) can be rewritten as

$$d_0 = \frac{f d_s d_w + d_w d_s}{d_w + f d_s} = \frac{d_w d_s (1 + f)}{d_w + f d_s} \quad (5)$$

Substitution of  $d_s = 2.078$  g/cm<sup>3</sup> (at 20°C) and  $d_w = 0.9985$  g/cm<sup>3</sup> (at 20°C) into eq. (5) yields the relation between  $d_0$  and  $f$ .

If one wishes to obtain that relation in terms of  $V_0/V_s$ , the ratio of the volumes of the wet polymer, and dry polymer one starts with the relation

$$f = \frac{M_w}{M_s} = \frac{M_0 - M_s}{M_s} \quad (6)$$

which is equivalent to

$$f = \frac{M_0}{M_s} - 1 \quad (7)$$

Substitution of  $M_0 = d_0 V_0$  and  $M_s = d_s V_s$  into eq. (7) yields eqs. (8) and (9):

$$\frac{d_0 V_0}{d_s V_s} = f + 1 \quad (8)$$

$$\frac{V_0}{V_s} = \frac{d_s}{d_0} (1 + f) \quad (9)$$

Therefore, the values of  $V_0/V_s$  can be calculated as a function of  $f$  because one knows the relation between  $f$  and  $d_0$  from eq. (5).

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Received March 26, 1979