termined from the fluorescence data for miscible (toluene cast) blends by using eq 4.

A good fit of the results for the THF-cast blends was obtained with $\phi_L = 0.008$ and $\phi_R = 0.98$. M_L and M_R were taken to be equal to 0.30 and 0.031, respectively, corresponding to $(I_D/I_M)_{\text{isolated PS chains}} = 0.98$ and $(I_D/I_M)_{\phi_{PS}=0.98} = 13.2$. The result of this fit is given in Figure 1, shown by the solid line through the THF-cast data. The results are insensitive to the value of Q_D/Q_M because of the empirical nature of the two-phase model. Regardless of the value of Q_D/Q_M, the same values for the rich- and lean-phase concentrations are obtained at the best fit.

Summary

For sufficiently high polystyrene concentration, a three-dimensional model for singlet energy migration has been found to explain quite well the observed dependence of I_D/I_M on concentration for PS/PVME blends. Although migrating excitons make very few hops before emission in concentrated systems, it would be difficult to explain the fluorescence results without including energy migration in the analysis. This is contrary to the claims of MacCallum.[3,4] Perhaps more important, however, is the result that excimer fluorescence can be used to study phase-separated blends quantitatively. As has been shown, a model describing energy migration it not even required to do so. The only requirement is that fluorescence data be available for a similar system for which the assumption of random mixing is valid.

Acknowledgment. Informative discussions with S. N. Semerak are gratefully acknowledged. This work was supported by the Army Research Office under Contract DAAG-29-78-C-0047.

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Water Relaxation in Perfluorosulfonate Ionomers

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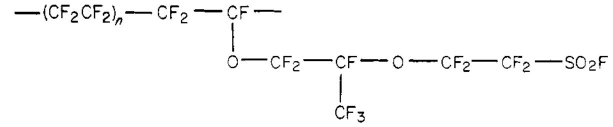
ABSTRACT: The sorption of water by perfluorosulfonate ionomers produces a relaxation near −100 °C in dynamic mechanical experiments. This phenomenon is also seen dielectrically and by proton NMR. When the sulfonic acid groups are neutralized with potassium or sodium, the temperature of the relaxation at low and moderate frequencies is increased and the activation energy is decreased. It is concluded that this relaxation is the glass transition of the aqueous domains in the ionomer.

Perfluorosulfonate ionomers are derived from copolymers of tetrafluoroethylene having the structure



$$-(CF_2CF_2)_n-CF_2-CF(-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_2F)-$$

They are characterized by their equivalent weights (EW), which are given by

$$EW = 100n + 446$$

Samples were prepared in the manner described by Gierke and co-workers.[1,2] Their crystallinity has been described in a recent paper.[3]

Table I
Concentration of Water in Samples Conditioned at Room Temperature

	EW 1504			EW 1108		
	K^+	Na^+	H^+	K^+	Na^+	H^+
total water, %	4.9	8.2	11.9	14.8	21.5	27.8
free water, %	nil	nil	nil	0.4	2.0	2.5
bound water, %	4.9	8.2	11.9	14.4	19.5	25.3
bound water, mol/equiv	4.1	6.9	9.9	8.9	12.0	15.6

The sulfonyl fluoride groups can be hydrolyzed to give sulfonic acid groups or various metal sulfonates. The sulfonyl fluoride is hydrophobic, but the sulfonic acid and sulfonates absorb increasing amounts of water as the equivalent weight is decreased. Samples having equivalent weights of 1504 and 1108 in the form of $^1/_{16}$-in. sheets which had initially been exposed to a laboratory humidity were conditioned over Drierite, saturated salt solutions, or water until the weight no longer changed. The sample of EW 1504 showed no freezable water by DSC, but the sample of EW 1108 showed a small endotherm at 0 °C.

Table II
Effect of Relative Humidity on the Acid Form

	EW 1504		EW 1108	
RH, %	% water (dry basis)	mol of H_2O/EW	% water (dry basis)	mol of H_2O/EW
20	0.05	0.04	0.16	0.1
43	1.87	1.6	2.21	1.4
58	1.95	1.6	3.62	2.2
79	4.25	3.6	7.33	4.5
satd	11.9	9.9	25.3	15.6

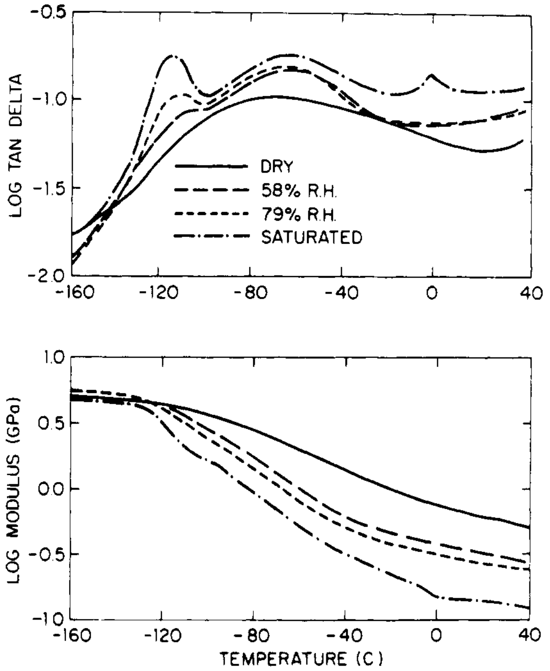


Figure 1. Effect of water on the dynamic mechanical properties of the acid form of EW 1108.

The concentration of free water was calculated by assuming that the heat of fusion was the same as that of pure water. The levels of water as percentages of the dry polymer are shown in Table I. Other specimens were conditioned to lower relative humidities by storing them over appropriate saturated salt solutions. These experiments are covered in Table II. The reported water contents are actually increments over that of samples conditioned to constant weight over Drierite at room temperature and may not include all the water which was present.[4] The relative humidity to which each sample was conditioned is considered to be a more reliable characteristic.

Dynamic Mechanical Properties

Various samples of sheet were tested with a DuPont dynamic mechanical analyzer[5] which had been interfaced with a digital calculator and plotter.[6] This instrument operates in flexure and gives data from which the elements of the complex Young's modulus can be computed. Data for the acid form of EW 1108 conditioned to several humidity levels are shown in Figure 1. Samples conditioned to 20% and 43% relative humidity were in line with those shown. All of the specimens had a broad loss peak near −70 °C which is similar to the γ relaxation in poly(tetrafluoroethylene). In the samples containing moisture there is an additional peak at −114 °C which is more sharply defined on a temperature scale. The height of this peak increases steadily with increasing water content. The modulus of the dry specimen decreased gradually over a wide range of temperature. However, there is a much sharper decrease in modulus associated with the water relaxation. From its mechanical properties, it appears that this water relaxation is the glass transition of the aqueous phase. The frequency of the measurements was about 20 Hz in the region of these peaks.

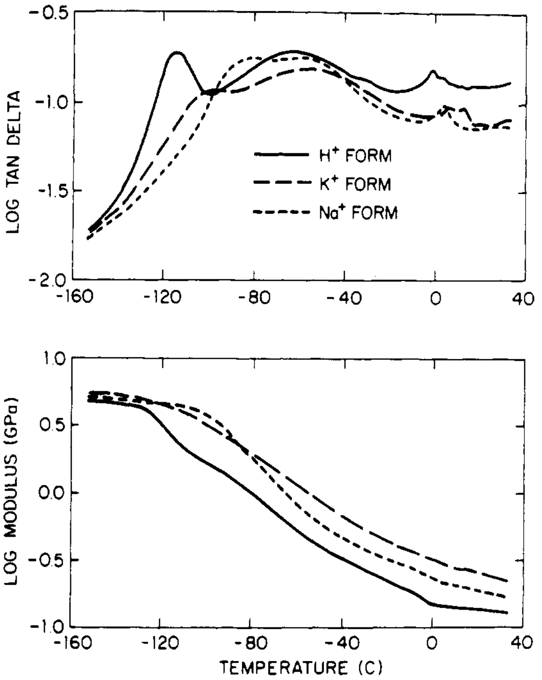


Figure 2. Effect of ionic form on the dynamic mechanical properties of saturated samples of EW 1108.

The saturated sample in Figure 1 shows a small peak at 0 °C. The presence or absence of this peak correlates with an endotherm at the same temperature in DSC scans. It is attributed to the melting of free water.

The temperature of the water relaxation depends on the cation. The acid form is compared with the sodium and potassium salts in Figure 2. The water relaxation which occurs at −114 °C in the acid form is shifted to −97 °C in the K^+ form and −81 °C in the Na^+ form. The water relaxation together with the γ relaxation constitutes the major softening process in the water-saturated polymer. All ionic forms of this equivalent weight exhibited a dynamic mechanical loss peak and a DSC endothermal peak at 0 °C.

Our dynamic mechanical data differ from those of Yeo and Eisenberg[4] for reasons which are not entirely clear. Among the factors which differed were the equivalent weight, the moisture levels, and the frequency of the measurement. They observed a peak which we did not see near 10 °C in a dry sample which disappeared after thermal treatment and shifted to lower temperatures with increasing levels of water.

Dielectric Properties

It is clear that most of the water absorbed in these ionomers is very different from liquid water. It does not freeze at 0 °C but forms a glass at a temperature near −100 °C, depending on the ionic form. Yeo and Eisenberg[4] observed the water relaxation in dielectric measurements on the acid form of EW 1365. Their peaks occurred at −110, −104, and −98 °C in measurements at 10^2, 10^3, and 10^4 Hz, respectively.

We measured the water relaxation dielectrically in the sodium form, for which the temperature was highest in the mechanical experiments. The experimental setup was the same as in an earlier study of water in nylon.[7] The dependence of the loss factor, ϵ'', on frequency at −72 °C is

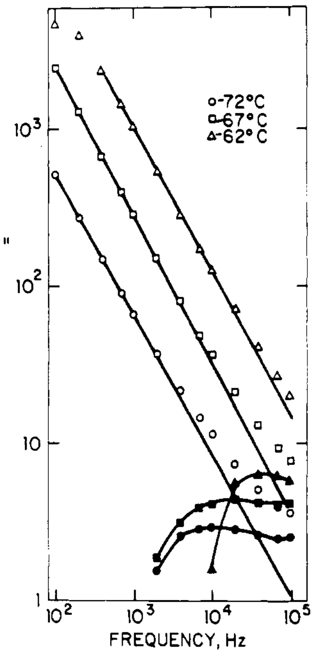


Figure 3. Dielectric loss factor vs. frequency at −72 °C for the sodium form saturated with water: open points, experimental data; filled points, water relaxation after subtracting conduction.

shown in Figure 3. The loss is dominated by conduction, which is reflected in the lower frequency portion where ϵ'' varies as $f^{-0.9}$. According to the "universal" law of Ngai, Jonscher, and White,[8] all loss mechanisms, including conduction and hopping charges, give linear relationships in log–log plots of ϵ'' vs. f in the limit of high frequency. Accordingly, the linear portion of the data in Figure 3 was extended to higher frequenceies. The extrapolated values of ϵ'' were subtracted from the experimental data to reveal a peak with a maximum at 1×10^4 Hz. This treatment is based on the belief that the various contributions to the dielectric loss are additive. The accuracy with which the peak can be determined is limited by the large conductivity. The same procedure at −67 and −62 °C gave peaks at 2×10^4 and 5×10^4 Hz, respectively.

Dielectric loss data on samples conditioned to 79.5% and 58% relative humidity are shown in Figures 4 and 5, respectively. At low frequencies, the loss factor varies as the −0.9 to −1.0 power of the frequency, as expected for a conduction process. At low temperatures and humidities, the negative slope becomes smaller. This may reflect a change from conduction to hopping charges due to the effect of the percolation limit, which has been discussed by Hsu and co-workers.[9] Under these conditions, it becomes difficult to define the separated water relaxation, partly because of the appearance of another process at higher frequencies.

Nuclear Magnetic Resonance

In these ionomers the only protons are in the sulfonic acid groups and the water associated with them. Therefore, proton NMR is an appropriate tool to look selectively at motions in the aqueous phase. An HFX90 Bruker spectrometer was used at a frequency of 90 MHz, and the typical H_1 field was about 3 G. T_1 measurements were generally made with a standard 180–τ–90 inversion–recovery pulse sequence. In some cases, a variation of this sequence, 180_x–τ–90_x–T–180_x–τ–90_y, was used in order to compensate for errors due to nonideality of the 180° pulse. The materials were molded into $^1/_4$-in.-diameter spheres to minimize the effects of bulk susceptibility and to facilitate the removal of surface water.

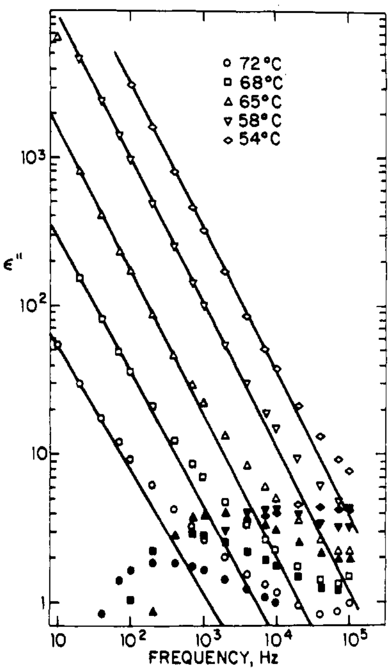


Figure 4. Dielectric loss factor for the sodium form conditioned to 79.5% relative humidity: open points, experimental data; filled points, water relaxation after subtracting conduction.

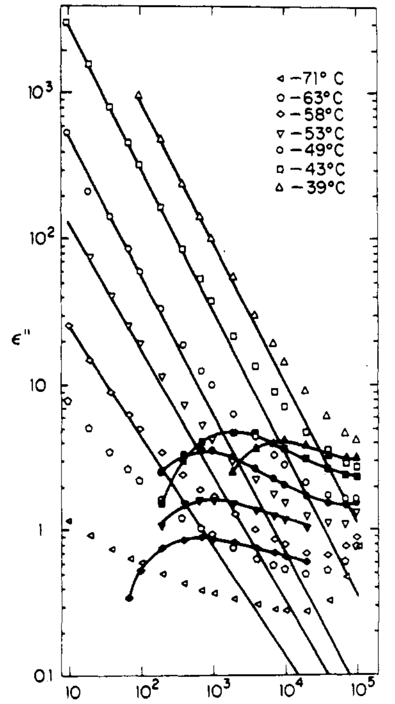


Figure 5. Dielectric loss factor for the sodium form conditioned to 58% relative humidity: open points, experimental data; filled points, water relaxation after subtracting conduction.

Measurements were made on the H^+, Na^+, and K^+ forms of EW 970, 1100, 1200, and 1375 and on the H^+ form of EW 1500. Typical data for T_1 are shown in Figure 6. In each case, there was a minimum in T_1 near −55 °C. The activation energies calculated from the dependence of T_1 on temperature near the minima are 5–6 kcal/mol. Above 10 °C, the slope is smaller and corresponds to an activation energy close to the value of 3.7 kcal/mol for pure water.[10,11] Somewhat different T_1 data have been reported by Duplessix and co-workers[12] for a sample of EW 1200 in the acid form containing various levels of moisture. The

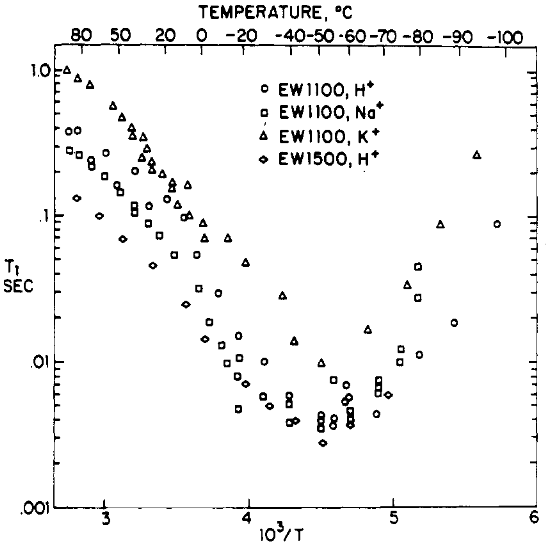


Figure 6. Spin-lattice relaxation times by proton NMR.

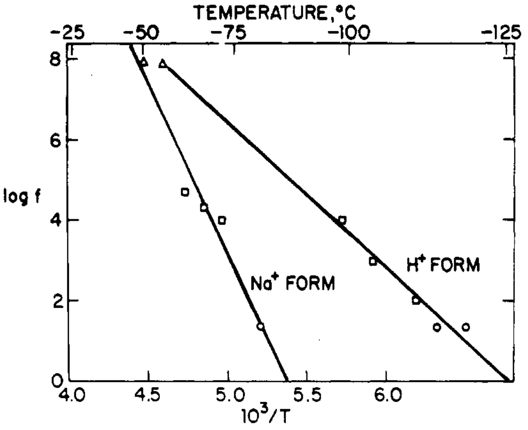


Figure 7. Arrhenius plot for samples saturated with water: (○) mechanical; (□) dielectric; (△) NMR.

reasons for these differences are not known.

Arrhenius Plots

Dynamic mechanical, dielectric, and NMR data for the acid and sodium forms saturated with water are combined in Figure 7. It is clear that all three techniques are reflecting the same process. In the various ionic forms, the water relaxation occurs at about the same temperature at the high frequency of the NMR experiment. As the frequency is decreased through the dielectric and dynamic mechanical experiments, the temperatures diverge. The activation energy is 17 kcal/mol for the acid form and about 40 kcal/mol for the sodium form. From the dynamic mechanical and NMR data, it appears that the activation energy for the potassium form is 25 kcal/mol. Within experimental uncertainty, the plots are linear over 7 decades of frequency.

The effect of humidity on the temperature dependence of the water relaxation in the sodium form is shown in Figure 8. As the moisture level is reduced, the dielectric water relaxation shifts to higher temperatures or lower frequencies. The line for the water-saturated state was copied from Figure 7 and corresponds to an activation energy of about 40 kcal/mol. The solid point is from the dynamic mechanical measurement on this sample. It was shown in Figure 1 that the temperature of this mechanical loss peak does not depend on the humidity. The dielectric data for a sample conditioned to 79.5% relative humidity lie on the line in the Arrhenius plot which points to the mechanical point. The slope of this line corresponds to an activation energy of 21 kcal/mol. The data from the sample conditioned to 58% relative humidity are more scattered, but the apparent activation energy is 12 kcal/mol.

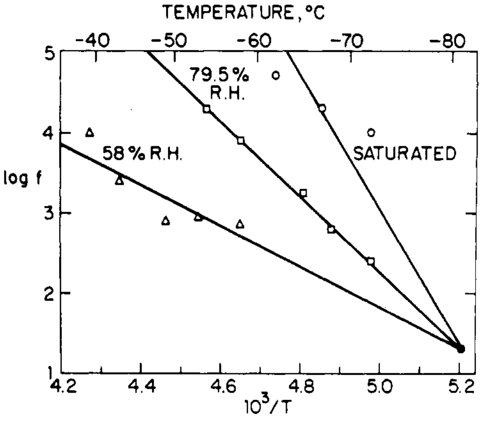


Figure 8. Arrhenius plot showing the effect of humidity for the sodium form.

According to Ngai and White,[13] in a cooperative, many-body relaxation the frequency scale is effectively stretched out. This produces an increase in the apparent activation energy, $\bar{E}_a$, according to the relationship

$$\bar{E}_a = E_a/(1 - n)$$

where E_a is the "true" activation energy, and $n - 1$ is the slope of a log-log plot of ϵ'' vs. f on the high-frequency side of the maximum. In earlier work on the effect of water on the dielectric relaxations in nylon,[7] it was found that E_a for the α and β relaxations was substantially independent of the moisture level, even though $\bar{E}_a$ and n were changing. The "true" activation energy for the water relaxation in the sodium form calculated from the product of the apparent activation energy from Arrhenius plots and the slope of the dielectric plots is about 5 kcal/mol for both the sample saturated with water and that conditioned to 79.5% relative humidity. This is close to the value calculated from the dependence of T_1 on temperature in the proton NMR experiments. This suggests that the NMR experiment is sensitive to the "true" activation energy of the elementary molecular motions without the involvement of cooperative effects. A similar conclusion was reached from studies of the glass transition in several elastomers.[14] The "true" activation energy is also equal to the activation energy for the diffusion of water in these ionomers.[4]

Conclusions

It seems clear that the water relaxation in perfluorosulfonate ionomers is the glass transition of the aqueous domains as has been suggested by Yeo and Eisenberg.[4] This is especially evident from the magnitude of the change of modulus and from the NMR T_1 data. It should be noted that the data follow the Arrhenius rather than the WLF form. This is more commonly characteristic of secondary relaxations. It is of interest to compare this phenomenon with relaxations in other aqueous systems.[15] In liquid water, there is a dielectric relaxation in the microwave (GHz) region. That process is slightly broader than a Debye relaxation and has an activation energy of about 4.5 kcal/mol. In ice at −11 °C, there is a relaxation in the kilohertz region which has an activation energy of about 13 kcal/mol. Johnson and co-workers[16] reported that clustered water in 2-μm domains in several polymers has a relaxation at −100 °C and 10^3 Hz with an activation energy of 7 kcal/mol. In the ionomers discussed here, the water is less mobile than in liquid water. The relatively large activation energies indicate that there is more cooperative character to the motion. A somewhat similar relaxation has been observed for water adsorbed on silica gel.[15]

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Effects of Annealing and Prior History on Enthalpy Relaxation in Glassy Polymers. 1. Experimental Study on Poly(vinyl chloride)

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Received August 24, 1981

ABSTRACT: Endothermal peaks below T_g have been observed by differential scanning calorimetry (DSC) in samples of poly(vinyl chloride) (PVC) which were given a variety of thermal, mechanical, and vapor treatments and subsequently aged for varied times (t_e) at several temperatures (T_e). The peaks increase in magnitude and shift to higher temperature with increased t_e and T_e and appear as the well-known "T_g overshoot" as T_e approaches T_g. The magnitude, but not the position, of the peaks is strongly dependent upon the treatment given the sample before aging. The peaks are enhanced by an increased rate of thermal quenching, by tensile or compressive mechanical stressing, and by prior exposure to a swelling vapor (e.g., methyl chloride). Development of the peaks upon aging is suppressed by the presence of a soluble vapor (CH_3Cl or CO_2) during aging. The DSC observations may be qualitatively explained as a consequence of the slow approach toward equilibrium of a system with a broad distribution of relaxation times.

Introduction

Differential scanning calorimetry (DSC) has revealed enthalpy relaxations occurring near or below T_g in glassy polymers aged after a wide variety of thermal, mechanical, and solvent or vapor treatments. Illers[1] and Gray and Gilbert[2] observed sub-T_g endothermic peaks in annealed PVC samples which had been rapidly quenched and found that the magnitude and temperature of the peaks increased with increasing annealing time and/or temperature between the quench and the DSC scan. Foltz and McKinney[3] and Petrie[4] demonstrated that the magnitude of the DSC endothermic peak at T_g ("T_g overshoot") provided a quantitative measure of the enthalpy relaxation which had occurred during prior annealing at temperatures somewhat below T_g. In a recent study of aging in ABS and SAN, Wysgoski[5] found no endothermic peaks in samples scanned immediately after a rapid quench, whereas aging at room temperature led to a slow development of small, broad endotherms well below T_g; with increasing aging temperature, the endotherms became more pronounced and occurred at higher temperatures, appearing as the familiar T_g overshoot for aging temperatures within about 20 °C of T_g.

DSC endotherms showing similar dependences upon annealing time and temperature have been observed by Weitz and Wunderlich[6] and others[7–9] in polymers vitrified by cooling through T_g under high hydrostatic pressure. Application of mechanical stress to polymers in the glassy state, through either compression[10] or tensile drawing,[11] also results in endothermic maxima below or near T_g. Matsuoka[12] has suggested that dilation under tensile stress increases the enthalpy of the glass, reducing the relaxation time and therefore increasing the rate of enthalpy relaxation during annealing.

Compared with these studies of enthalpy relaxations induced by thermal and mechanical treatments, reports dealing with vapor or solvent effects on glassy state relaxations are less extensive or explicit but nonetheless suggestive of closely related effects. Chan and Paul[13] found that exposure of annealed polycarbonate to high CO_2 pressure reduced the magnitude of the DSC endotherm and suggested that sorption of CO_2 dilated the polymer, increasing its enthalpy relative to the annealed state. Shultz and Young,[14] in studying polystyrene and PMMA samples freeze-dried from naphthalene solutions, observed sub-T_g endothermal maxima which intensified and moved to higher temperature with increasing annealing time or temperature. Their observations were attributed to a broad distribution of relaxation times in the very "open" glass structure produced by the rapid quench and matrix sublimation. Berens and Hopfenberg[15,16] found that prior exposure to a swelling vapor enhances the sorptive capacity of glassy PVC and polystyrene and suggested this effect may be due to an increase of frozen-in free volume; although DSC data were not included in their study, it seemed likely, in view of the other calorimetric findings, that the vapor-swelling process might also produce an enhancement of enthalpy relaxation effects.

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