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Effect of Pressure on the Dielectric γ-Relaxation in Poly(tetrafluoroethylene) and FEP

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ABSTRACT: Dielectric measurements have been made on PTFE at temperatures from 188 to 237 K and pressures up to 3000 atm. With increasing pressure, internal motions are restricted due to decreases in volume, and the γ-relaxation shifts to higher temperatures and lower frequencies with an increasing Arrhenius activation energy. The activation volume decreases with increasing temperature but is larger than for the analogous relaxation in polyethylene. The distribution of Helmholtz activation free energies is independent of pressure. In FEP, the copolymer of tetrafluoroethylene and hexafluoropropylene, the loss peak is thought to be a composite of the γ- and β-relaxations.

Introduction

In early work on the dielectric properties of poly(tetrafluoroethylene) (PTFE),[1-3] it was reported that all three of the dynamic mechanical relaxations, α, β, and γ, were dielectrically active. However, in later studies,[4-6] it was found that only the low-temperature γ-relaxation is dielectrically active. Probably, the polymer used in the earlier work was decorated with dipoles which are not essential to PTFE.

In an earlier paper,[6] we studied the dielectric γ-relaxation over a range of frequencies for several polymers and copolymers of tetrafluoroethylene. We have now extended this study to elevated pressures for PTFE and FEP, the copolymer of tetrafluoroethylene with about 7 mol % hexafluoropropylene. This enables one to gain increased understanding of internal motions from the effect of pressure on the temperatures and activation energies of the relaxations under study as well as the activation volume as a function of temperature.

Experimental Section

The materials and electrodes are the same as described elsewhere[6] for vacuum measurements. For the present set of experiments, the samples were placed in a pressure vessel, the details of which are given in another paper.[7] Pressures to about 3000 bars were generated using an Enerpac 11-400 pump. A 50/50 mixture of pentane and 2-methylbutane was used as the pressure-transmitting fluid. The pressure vessel was placed in a temperature bath of Freon-11 which was cooled using a mechanical refrigerator down to −40 °C and liquid nitrogen flowing through coils for the lowest temperatures. The temperature bath was heated using a "red rod" heater, and on–off temperature control was achieved using an Apple IIe computer. The temperature was measured and controlled using a platinum resistance thermometer in conjunction with a Keithley 195A digital multimeter. Finally, as in previous experiments,[6] the equivalent parallel capacitance and resistance of the sample was then measured using a CGA-85 microprocessor-controlled bridge which operates at 17 frequencies between 10 and 10^5 Hz.

It is known that the sorption of hydrocarbons by PTFE or FEP is very low.[8] Moreover, the specimens were protected by electrodes evaporated directly onto the sample so that only the edges were exposed. Since a three-electrode, guard ring configuration was used, the portions of the samples near the edges were outside of the measuring field. Finally, in order to minimize any effect of the pressure-transmitting fluid, the samples were cooled rapidly to −40 °C, and data were taken in the order of increasing temperature.

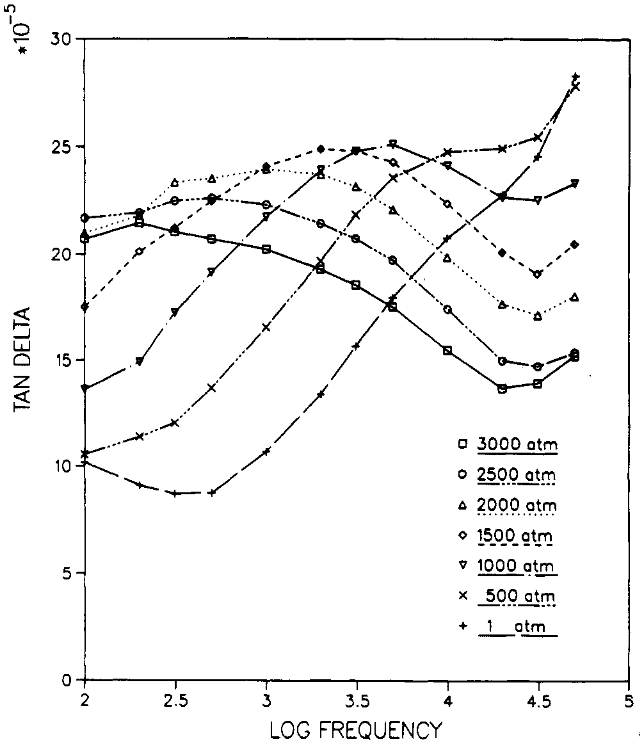

Figure 1. PTFE isobaric frequency scans at 212 K.

Poly(tetrafluoroethylene)

The dielectric properties of PTFE were measured at 13 frequencies from 10^2 to 10^5 Hz, nine temperatures from 188 to 237 K and seven pressures from 1 to 3000 atm. The location of the relaxation was determined by plotting tan δ against pressure, temperature, or the logarithm of frequency while the other two variables were held constant. All three procedures gave substantially equivalent locations for the maxima. Isobaric curves of tan δ vs log frequency at 212 K are shown in Figure 1, and isothermal curves of tan δ vs pressure at a frequency of 1 kHz are shown in Figure 2.

Figure 3 is an Arrhenius plot of log frequency vs the reciprocal of the absolute temperature, showing data for

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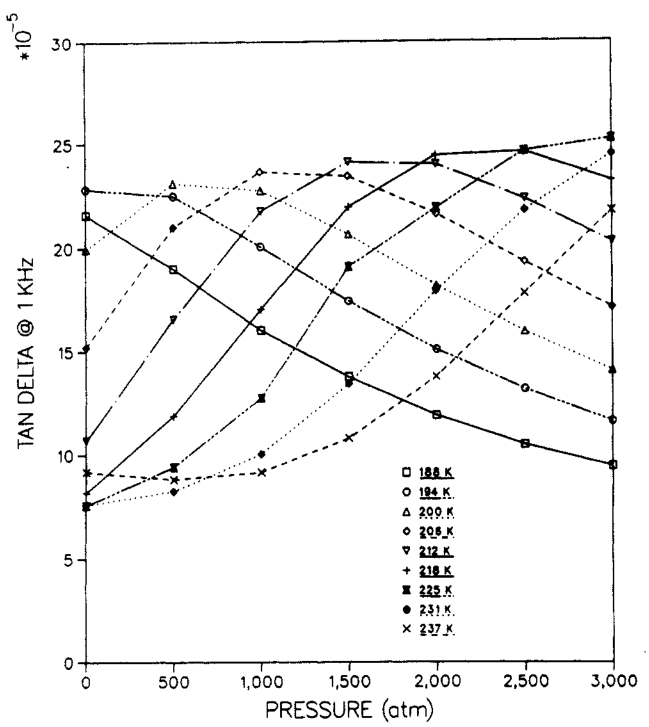

Figure 2. PTFE isothermal pressure scans at 1 kHz.

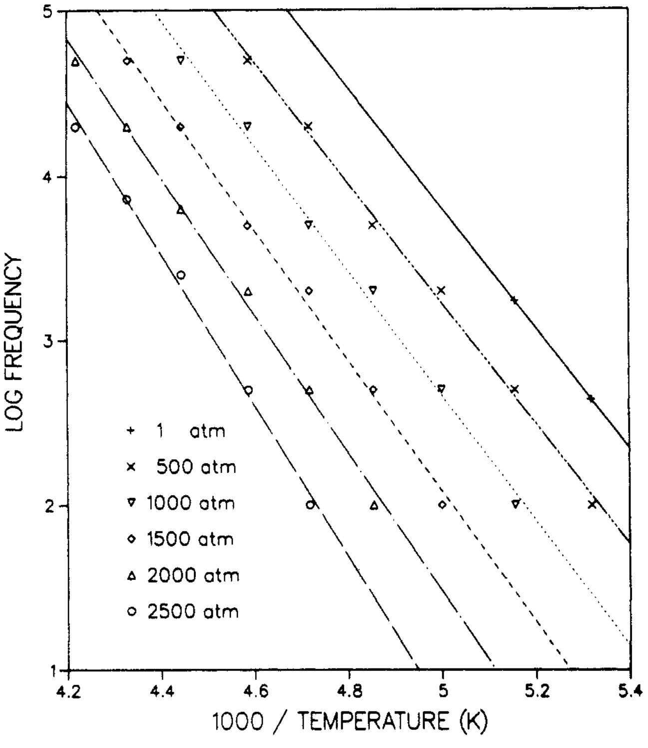

Figure 3. Arrhenius plot of isobaric data from PTFE.

six pressures. The activation energies which are listed in Table I increased from 16.4 kcal/mol at atmospheric pressure to 21.1 kcal/mol at 2500 atm. This reflects the restrictions which a reduction in volume places on the internal motions. A similar increase has been reported for polyethylene.[9]

The Eyring expression for the relationship between $f_{\max}$, the frequency at maximum loss in Hertz, and the temperature, T, in Kelvin is given by the following equation.[10]

$$f_{\max} = \frac{kT}{2\pi h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \qquad (1)$$

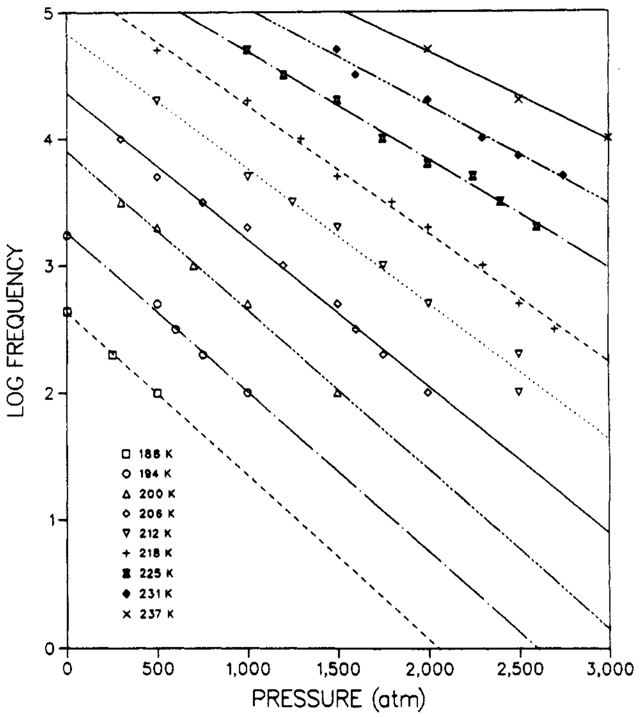

Figure 4. Plot for the determination of activation volumes for PTFE.

Table I
Effect of Pressure on the Activation Energy

pressure (atm)	E_a (kcal/mol) PTFE	E_a (kcal/mol) FEP
1	16.4	13.5
500	16.7	14.3
1000	17.4	14.2
1500	18.2	14.1
2000	19.2	14.2
2500	21.1	13.9
av		14.0
σ		0.3

where k is Boltzmann's constant, h is Planck's constant, R is the gas constant, $\Delta H^{\ddagger}$ is the activation enthalpy ($=E_a - RT$), and $\Delta S^{\ddagger}$ is the activation entropy. (E_a is the Arrhenius activation energy $= -R[\mathrm{d} \ln f_{\max}/\mathrm{d}(1/T)]$.) The activation free energy may be written

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} = \Delta E^{\ddagger} + P\Delta V^{\ddagger} - T\Delta S^{\ddagger} = RT[\ln(k/2\pi h) + \ln T - \ln f_{\max}] \qquad (2)$$

From this it follows that the activation volume, $\Delta V^{\ddagger}$, is

$$\Delta V^{\ddagger} = -RT(\partial \ln f_{\max}/\partial P)_T \qquad (3)$$

The dependence of the peak frequency on the pressure for each temperature is shown in Figure 4. From the slopes, it was determined that the activation volume decreased with increasing temperature from 0.0455 L/mol at 188 K to 0.0313 L/mol at 237 K (Table II). For the corresponding relaxation in polyethylene, $\Delta V^{\ddagger}$ decreased from 0.014 L/mol at 175 K to 0.011 L/mol at 208 K.[9]

The activation volume is the incremental volume needed for an internal motion to occur. For the γ-relaxation, $\Delta V^{\ddagger}$ is a little less than the volume of a CH_2 unit in polyethylene and between 1 and 2 times the volume of a CF_2 unit in PTFE. The temperature of the relaxation is also higher in PTFE.

Table II
Effect of Temperature on the Activation Volume

temp (K)	$\Delta V^{\ddagger}$ (L/mol) PTFE	$\Delta V^{\ddagger}$ (L/mol) FEP
188	0.0455	
194	0.0460	
200	0.0472	
206	0.0449	
212	0.0426	
213		0.0225
218	0.0414	
219		0.0272
225	0.0.362	0.0255
231	0.0337	0.0262
237	0.0313	0.0228
243		0.0220
249		0.0222
av		0.0241
σ		0.0022

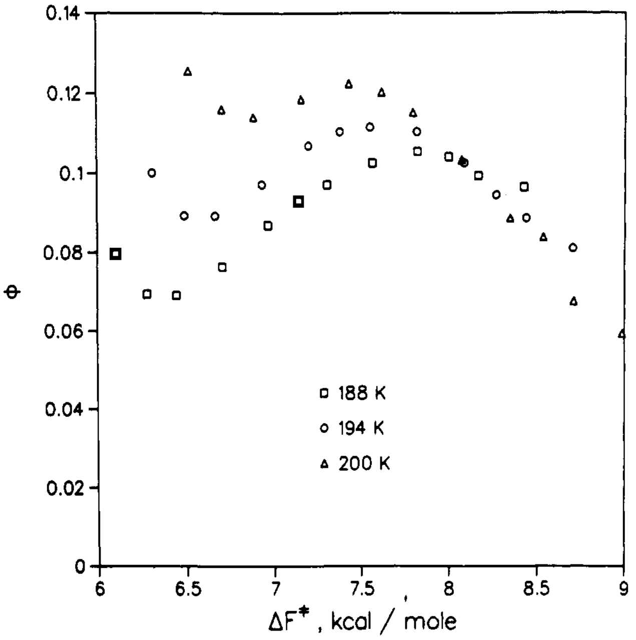

Figure 5. Distribution of activation free energies in PTFE at 1 atm.

The distribution function for the relaxation times or the activation parameters can be approximated by

$$\Phi = \frac{2}{\pi}\frac{\epsilon''}{\epsilon_r - \epsilon_u} \tag{4}$$

where the relaxed and unrelaxed permittivities, ϵ_r and ϵ_u, are defined by the intersections of a Cole–Cole plot of ϵ'' vs ϵ' with the ϵ' axis.[1] If a plot of Φ vs $\Delta F^{\ddagger}$ is independent of temperature, $\Delta S^{\ddagger}$ is close to zero, $\Delta F^{\ddagger} \cong \Delta H^{\ddagger}$, and the relaxation involves local, noncooperative motions.[10,11] A comparison of Figure 5 (1 atm) and Figure 6 (2000 atm) shows that this condition is more nearly met at elevated pressures and temperatures. Perhaps pressure suppressed a low-temperature, high-frequency motion which clouds the main peak.

At a constant temperature (206 K), increasing the pressure shifts the distribution to larger values of $\Delta F^{\ddagger}$ (Figure 7). However, when the distribution is expressed in terms of the activation Helmholtz free energy, $\Delta A^{\ddagger} = \Delta F^{\ddagger} - P\delta V^{\ddagger}$, it is nearly independent of pressure (Figure 8).

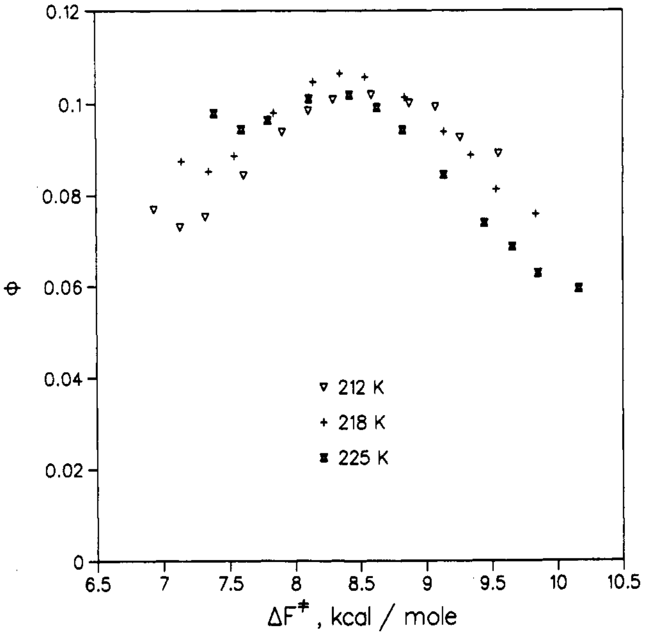

Figure 6. Distribution of activation free energies in PTFE at 2000 atm.

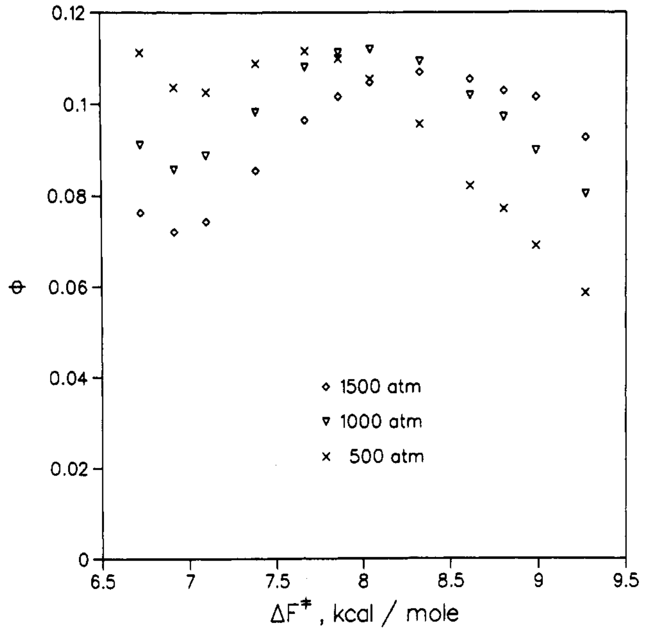

Figure 7. Distribution of activation Gibbs free energies in PTFE at 206 K.

FEP

There are a number of differences between the dielectric γ-relaxations in FEP and PTFE. At atmospheric pressure and a frequency of 1 kHz, the maximum in tan δ occurs at 194 K in PTFE and 220 K in FEP. The peak height is larger in FEP, but the values are similar on the low-temperature side of the peak. It was suggested that this may reflect an overlapping β-relaxation in FEP.[6] In the present study, the experimental approach was the same for the two polymers except that the range of temperatures for FEP was from 207 to 255 K.

We are dealing with a four-dimensional situation: tan δ, frequency, temperature, and pressure. As stated above, when tan δ for PTFE is plotted against frequency, temperature, or pressure (the other two parameters being held constant), one obtains essentially the same coordinates for the maxima. This is not the case with FEP.

In Figure 9, tan δ is plotted against the logarithm of frequency for seven pressures at a temperature of 225 K. Unlike Figure 1, the analogous plot for PTFE, the maximum value of tan δ decreases markedly with increas-

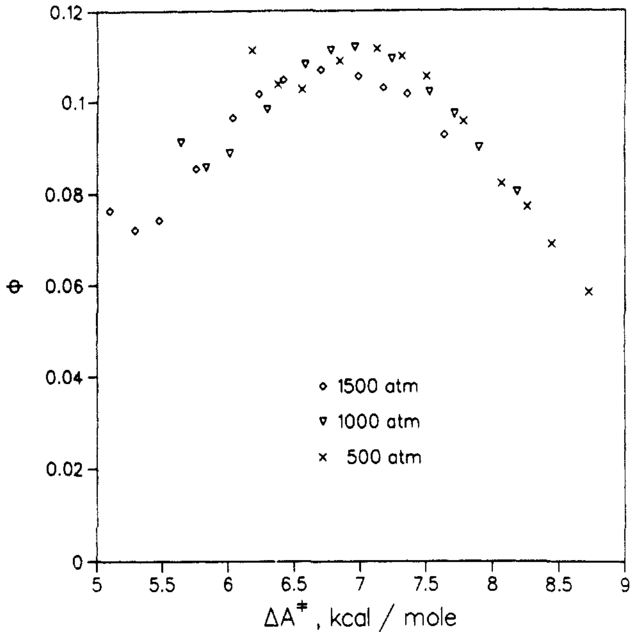

Figure 8. Distribution of activation Helmholtz free energies in PTFE at 206 K.

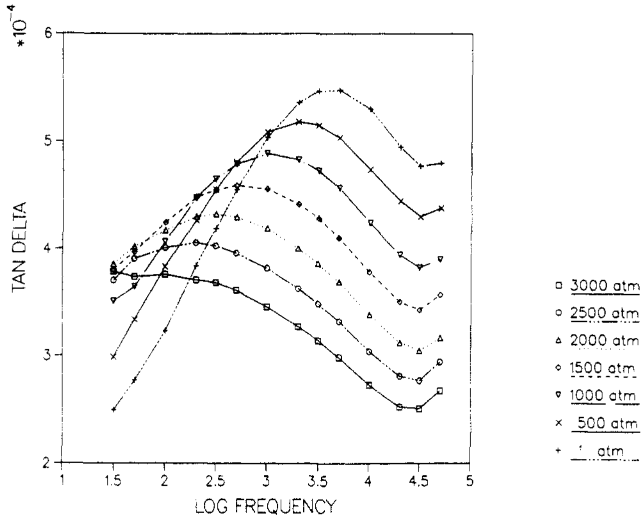

Figure 9. Isobaric frequency scans for FEP at 225 K.

ing pressure. Figure 10 is a plot of tan δ at 1 kHz vs pressure for nine temperatures, and Figure 11 is a plot of tan δ at 1 kHz vs temperature at seven pressures. In both of these figures, the maximum value of tan δ is nearly constant.

In spite of their complexity, we consider that the frequency scans at constant temperature and pressure (and thus at a defined volume) have the greatest scientific significance, and those maxima will be used in the analysis. Changing the temperature or the pressure changes the volume and produces a different state. The strength of the relaxation, the difference between the relaxed and unrelaxed permittivities, is independent of temperature but increases with increasing pressure. The width of the distribution of relaxation times increases with increasing volume whether caused by an increase in temperature or a decrease in pressure.

Unlike PTFE, the frequency scans in FEP give an Arrhenius activation energy of 14.0 kcal/mol, almost independent of pressure (Table I). The activation volume of 0.024 ± 0.002 L/mol is also smaller than that in PTFE and varies randomly between 213 and 249 K (Table II). The Gibbs and Helmholtz free energies of activation, $\Delta F^‡$ and $\Delta A^‡$, are compared in Table III. The values are higher for FEP, reflecting the higher temperature of the relaxation. For both polymers the activation free energy decreases with increasing temperature, indicating that the activation entropy is positive. The calculated activation entropies are 42 cal deg^{-1} mol^{-1} for PTFE and 14 cal deg^{-1} mol^{-1} for FEP.

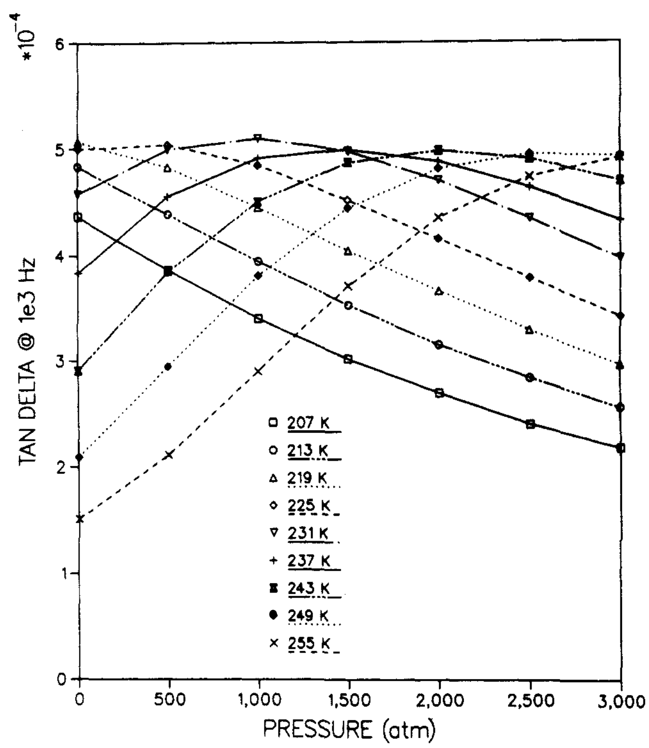

Figure 10. Isothermal pressure scans at 1 kHz for FEP.

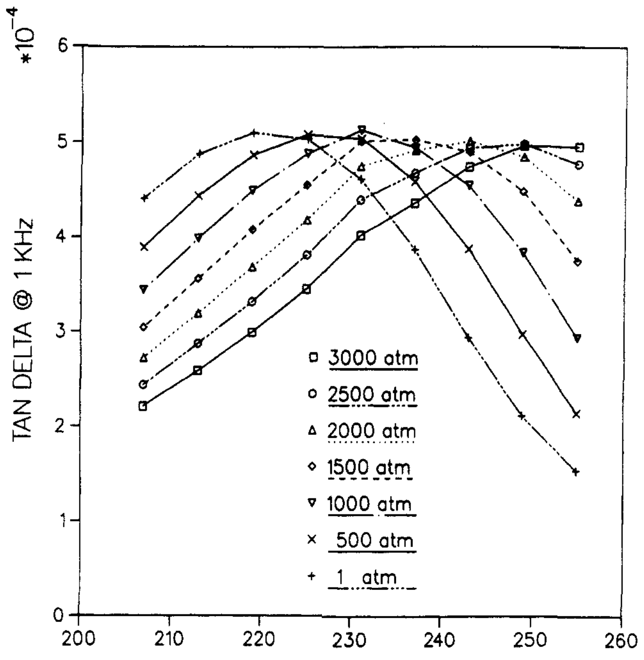

Figure 11. Isobaric temperature scans at 1 kHz for FEP.

Conclusions

There are close similarities in the way that the γ-relaxations in PTFE and polyethylene change with pressure. In both cases, the activation energy increases with increasing pressure, and the activation volume decreases with increasing temperature. On the other hand, the so-called γ-relaxation in FEP differs from these processes in

Table III
Values of Maxima in the Distributions of Activation Free Energies

temp (K)	ΔF^* (kcal/mol) 1 atm	500 atm	1000 atm	1500 atm	2000 atm	2500 atm	3000 atm	ΔA^*
				PTFE				
188	7.8							
194	7.5	8.1						7.5
200	7.6	8.1						7.25
206		7.6	8.0	8.3				7.0
212			7.6	8.2	8.5			6.7
218				8.1	8.4	8.7	8.7	6.5
225					8.4	8.5	8.7	6.35
231						8.5	8.7	6.3
				FEP				
207	8.8	9.2						8.8
213	8.6	9.1	9.25					8.75
219	8.55	8.8	9.25	9.5				8.55
225	8.5	8.8	9.0	9.4	9.6			8.5
231		8.7	9.0	9.3	9.6			8.4
237			8.9	9.2	9.45	9.6	10.0	8.4
243					9.3	9.5	9.9	8.25
249						9.5	9.7	8.1

several ways. Not only does the peak occur at a higher temperature or a lower frequency, but the height of the peak in frequency scans increases with increasing temperature and decreases with increasing pressure. There is almost no dependence of the activation energy on pressure or of the activation volume on temperature.

These observations support the suggestion that the peak in FEP is actually a composite of the γ- and β-relaxations. In a study of dynamic mechanical properties, McCrum found that the β-relaxation in PTFE shifted to lower temperatures in copolymers with increasing amounts of hexafluoropropylene and eventually merged with the γ-relaxation.[12,13] He also observed that the peak height for the γ-relaxation was smaller in the copolymers but that this was obscured by the overlap of the β-relaxation.

The β-relaxation in PTFE is a property of the crystalline phase and is associated with the crystalline transitions which occur near room temperature. Weeks and coworkers found that the transition temperature was lower in copolymers with hexafluoropropylene, eventually falling below 240 K.[14] There is a discontinuity in the viscoelastic properties at the crystalline transition, and the associated loss maximum may occur at a different temperature.[15]

We conclude that the dielectric loss maximum in FEP is a composite, that the properties of the peak are dominated by the β-relaxation, and that the underlying γ-relaxation is the low-temperature, high-frequency component. This is illustrated in Figure 12 in which data for the two polymers at 2000 atm and 1 kHz are plotted against temperature and Figure 13 in which data at 225 K and 2000 atm are plotted against the logarithm of frequency.

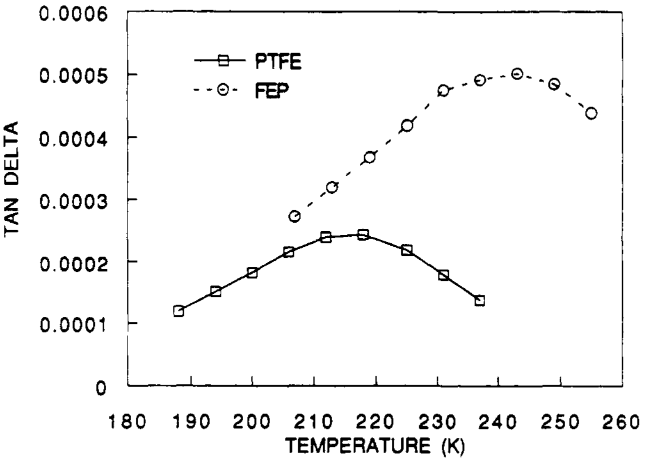

Figure 12. Comparison of PTFE and FEP: temperature scans at 2000 atm and 1 kHz.

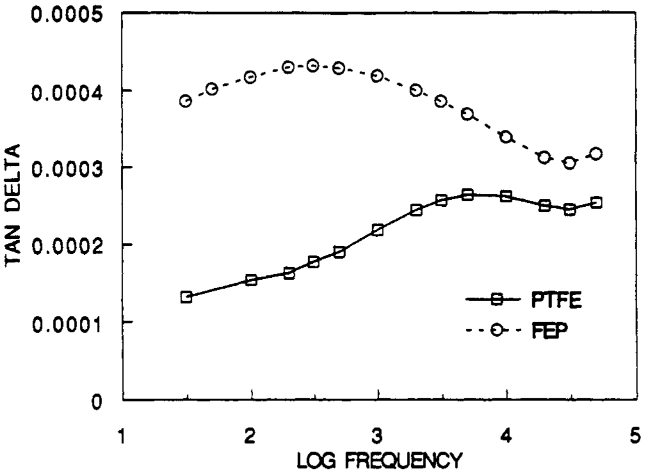

Figure 13. Comparison of PTFE and FEP: frequency scans at 225 K and 2000 atm.

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