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Effect of Absorbed Chemicals on the Low-Temperature Dielectric Properties of Poly(tetrafluoroethylene)

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ABSTRACT: Dielectric measurements were made from 5 to 300 K on poly(tetrafluoroethylene) which had been saturated with chloroform, fluorocarbon-113 (1,1,2-trichloro-1,2,2-trifluoroethane), or carbon tetrachloride. The peak height for the γ-relaxation was increased by the polar additives. In the case of fluorocarbon-113 at frequencies below 1 kHz, it was shifted to lower temperatures with a lower activation energy. In the presence of either of the polar additives, a new relaxation appeared with a maximum in tan δ at 1 kHz of 49 K for chloroform and 61 K for fluorocarbon-113 in isothermal frequency scans. These relaxations had activation energies of 2–3 kcal/mol and activation entropies close to zero. They are assigned to the reorientation of the absorbed molecules moving independently of each other. In separate measurements on chloroform and fluorocarbon-113, a relaxation was observed at temperatures below their melting points which became weaker after purification.

Introduction

Although poly(tetrafluoroethylene) (PTFE) is resistant to many chemicals, it can absorb limited amounts of compounds which contain little or no hydrogen.[1] The effect of several of these compounds on the dynamic mechanical properties has been studied.[2] The peaks in the loss modulus associated with the γ- and β-relaxations were unchanged, but the α-relaxation was shifted to lower temperatures, and a new loss peak appeared near −30 °C. Three liquids from the mechanical study, carbon tetrachloride, chloroform, and fluorocarbon-113 ($CCl_2F\ CClF_2$), were selected for dielectric measurements to study the differences between polar and nonpolar additives. In addition to samples of PTFE saturated with the additives and a PTFE control, dielectric measurements were made on the low molecular weight additives themselves.

Experimental Section

The techniques for the measurement of the solid samples were the same as those in a recent study of PTFE and copolymers of TFE[3] except that the values of the real part of the permittivity, ϵ', were based on an absolute measurement at room temperature. Specifically, the value of the capacitance, C, at 1000 Hz and the area, A, and separation, d, of the electrodes at room temperature were used to calculate the corresponding value of ϵ' via

$$\epsilon' = Cd/A\epsilon_0 \qquad (1)$$

where ϵ_0 is the permittivity of free space. The values of ϵ' at all other frequencies and temperatures were calculated using the approximation that the relative change in dielectric constant is equal to the relative change in capacitance.

In an attempt to minimize the loss of absorbed liquid from the samples, all procedures were carried out as rapidly as possible. The evaporation technique used for the electrode deposition required that the samples be in vacuum for about 10 min for each of two sides. In addition, the sample holder for the low-temperature measurements also required that the samples be in vacuum. In that case, the samples were cooled below 200 K within about 15 min. By monitoring the weight of the samples, it was found that those procedures resulted in very little loss of the liquid from the samples.

For the measurement of the materials which are liquid at room temperature a new cell was constructed. A cross section of the cell is shown in Figure 1. The "high" electrode was constructed using 0.04-mm-thick brass and is thus flexible, allowing for thermal expansion of the material and ensuring that the sample remains in contact with the electrodes. The "low" electrode is solid brass. The diameter of the "low" electrode is approximately 12 mm and is separated from the "high" electrode by about 1.5 mm. However, the geometry was not sufficiently well-defined to allow accurate absolute determination of the dielectric constant at room temperature. Instead, the room temperature value was set equal to 4.8 for chloroform[4] and 2.41 for fluorocarbon-113.[5] Because of the design of the sample cell, the change in the capacitance includes the change in thickness of the material and the area of the brass "low" electrode in addition to the change in dielectric constant of the material. However, in determining the values of the dielectric constant, those corrections were not carried out. As noted above, the approximation was made that the relative change in dielectric constant is equal to the relative change in capacitance.

Results

Low Molecular Weight Compounds. Chloroform. As shown in Figure 2 for a frequency of 1 kHz, laboratory-grade (EM Science) chloroform exhibits a maximum tan δ at 127 K. This relaxation has an activation energy, E_a, of 14.5 kcal/mol. Since chloroform melts at 209.6 K, this represents a relaxation in the solid state. According to the label, the laboratory-grade solvent contains 0.75% ethanol, which is added to react with any phosgene which may be formed through oxidation. Consequently, ethanol represents a likely source of the relaxation.

To check this possibility, the ethanol was partially removed by shaking three times with equal volumes of water followed by drying over calcium chloride and storage over a mixture of equal parts of anhydrous potassium carbonate and calcium chloride in a dark bottle.[6] The results of the dielectric measurements on the dried material are also shown in Figure 2. It is found that the maximum value of tan δ is reduced by a factor of about 9 after purification by the method described above. Consequently, the concentration of ethanol and the strength of the relaxation peak appear to be correlated.

To check this possibility further, a Cole–Cole complex plane plot for the laboratory-grade chloroform was made

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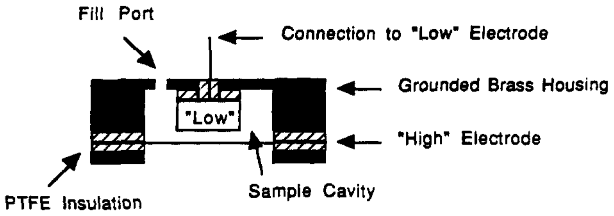

Figure 1. Cell for dielectric measurements on liquids.

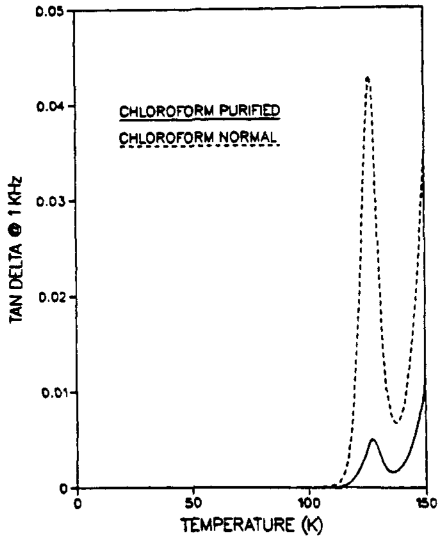

Figure 2. Dielectric tan δ of chloroform at low temperatures.

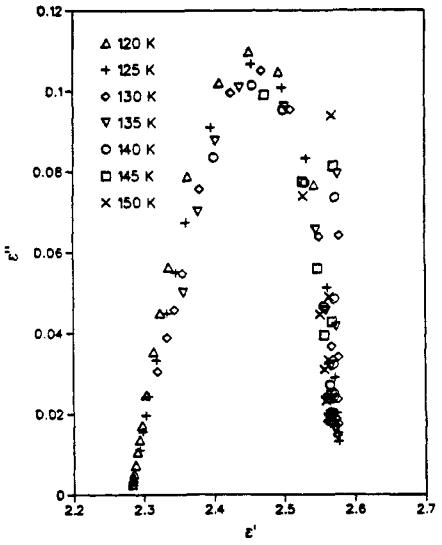

Figure 3. Cole–Cole plot for the low-temperature dielectric relaxation in laboratory-grade chloroform (nominally containing 0.75% ethanol).

and is shown in Figure 3. The difference between the relaxed and unrelaxed permittivities, $\epsilon_r - \epsilon_u$, is approximately 0.297. According to Onsager,[7] the strength of a relaxation is given by the following equation, where N is the number of reorientable dipoles per cubic centimeter, μ is their dipole moment, and g is a factor related to angular or energetic restrictions.

$$\epsilon_r - \epsilon_u = \frac{3\epsilon_r}{2\epsilon_r + \epsilon_u}\left(\frac{4\pi N}{3kT}\right)\left(\frac{\epsilon_u + 2}{3}\right)^2 g\mu^2 \qquad (2)$$

The dipole moment of ethanol is 1.7 D,[8] and $N = 1.465 \times 10^{20}$ for 0.75% ethanol in chloroform. Solving eq 2 for g gives a value of 1.39. Its value would be 1 if the concentration of ethanol were 1.04%. In view of the assumptions which have been made, the data agree quite well with our model, i.e., molecules of ethanol reorienting within a crystal of chloroform. For the purified chloroform $\epsilon_r - \epsilon_u = 0.034$, and one obtains an apparent concentration of ethanol of 0.12%.

Fluorocarbon-113. Fluorocarbon-113 (1,1,2-trichloro-1,2,2-trifluoroethane) melts at 236.7 K with a heat of fusion by DSC of 14.8 J/g. A high-quality grade supplied by the Du Pont Co. known as PCA (precision cleaning agent) has a purity of at least 99.90%. There is a dielectric loss peak with a maximum at 82 K at a frequency of 1 kHz and an activation energy of 11.0 kcal/mol. As shown in Figure 4, this relaxation is about twice as strong in normal F-113 as in the PCA grade. We believe that this strength is proportional to the concentration of impurities.

As shown in Figure 5 for the PCA grade, the Cole–Cole plot for the relaxation in F-113 is well fitted by the Davidson–Cole equation.[9]

$$\frac{\epsilon^*(\omega) - \epsilon_u}{\epsilon_r - \epsilon_u} = \frac{1}{(1 + i\omega\tau_1)^\gamma} \qquad (3)$$

where γ is a constant between zero and 1. The real and imaginary components of the complex permittivity are

$$\frac{\epsilon'(\omega) - \epsilon_u}{\epsilon_r - \epsilon_u} = (\cos\varphi)^\gamma \cos\gamma\varphi \qquad (4)$$

and

$$\frac{\epsilon''(\omega)}{\epsilon_r - \epsilon_u} = (\cos\varphi)^\gamma \sin\gamma\varphi \qquad (5)$$

where

$$\tan\varphi = \omega\tau_1 \qquad (6)$$

At high ϵ' and low frequencies, the curve is similar to that for a Debye relaxation, a circular arc with its origin on the ϵ' axis. At low ϵ' and high frequencies, the curve becomes a straight line with a slope of $\gamma\pi/2$. The Davidson–Cole parameters for the two grades of F-113 are given in Table I. In both cases, the parameter γ is about 0.28.

The distribution of relaxation times for the Davidson–Cole equation involves a sharp cut-off at a maximum time, τ_1, or a minimum frequency, $f_1 = (2\pi\tau_1)^{-1}$.[2]

$$\Phi(\ln(\tau/\tau)_1) = \frac{\sin\gamma\pi}{\pi}\left(\frac{\tau}{\tau_1 - \tau}\right)^\gamma = \frac{\sin\gamma\pi}{\pi}\left(\frac{f_1}{f - f_1}\right)^\gamma \qquad \tau \le \tau_1, f \ge f_1$$

$$= 0 \qquad \tau > \tau_1, f < f_1 \qquad (7)$$

The dependence of f_1 on temperature is also shown in Table I. This relationship corresponds to an activation energy of 13 kcal/mol whereas the loss maxima give 11 kcal/mol.

Polymer Samples. Samples of PTFE were immersed in carbon tetrachloride and the higher purity grades of chloroform or F-113 until the weight no longer increased. Substantially the same results were obtained with the standard-grade additives. The increases in weight were 2.4% for carbon tetrachloride, 1.4% for chloroform, and 5.6% for F-113. The dependence of the dissipation factor (tan δ) at 1 kHz on temperature is shown in Figure 6 for the samples containing chloroform and F-113 and a PTFE control. Both additives increase the maximum for the γ-relaxation and introduce a new, large loss peak at lower temperatures. For the sample containing F-113, the γ-relaxation has also been shifted to a lower temperature.

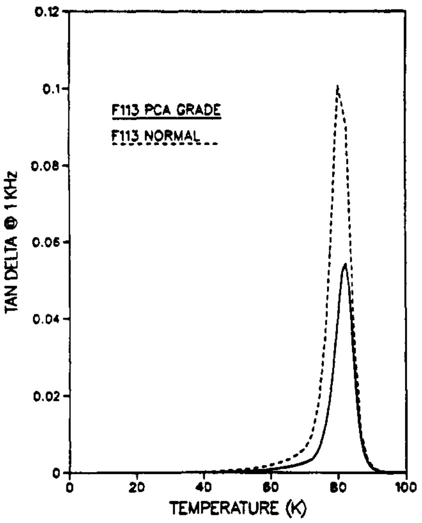

Figure 4. Dielectric tan δ for fluorocarbon-113 at low temperatures.

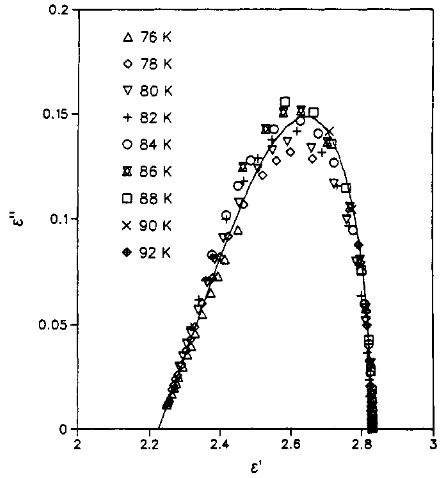

Figure 5. Cole–Cole plot for the low-temperature dielectric relaxation in PCA-grade fluorocarbon-113 fitted to the Davidson–Cole equation.

Table I
Davidson–Cole Parameters for F-113

	normal F-113	PCA grade
ϵ_u	2.170	2.225
ϵ_r	3.447	2.828
$\epsilon_r - \epsilon_u$	1.277	0.603
ϵ''_{max}	0.309	0.149
$\epsilon''_{max}/(\epsilon_r - \epsilon_u)$	0.242	0.247
γ	0.2886	0.2779
f_l (Hz) at temp		
76 K	1.88 ± 0.03	0.594 ± 0.083
78 K	18.1 ± 1.1	7.41 ± 0.15
80 K	132.9 ± 12.3	64.5 ± 4.4
82 K	1127 ± 68	432.6 ± 29.9
84 K		2485 ± 31
E_a (kcal/mol) from f_l	13.11	13.18

The sample containing carbon tetrachloride exhibited the γ-relaxation at the same temperature as the control and is not shown. Plots of tan δ vs temperature at several frequencies are shown in Figures 7 and 8 for PTFE saturated with chloroform and F-113, respectively.

γ-Relaxation. Figure 9 is an Arrhenius plot of the γ-relaxations of the three samples. The points correspond to the maxima in tan δ for isothermal frequency scans. The relationships for the control and the sample saturated with chloroform are very similar with an activation energy of 14 kcal/mol based on isothermal frequency scans and 16 kcal/mol based on isochronal temperature scans. In the sample saturated with F-113, the γ-relaxation occurs at lower temperatures, and the Arrhenius plot exhibits a "dog-leg". For frequencies up to 1 kHz, the activation energy is only 9 kcal/mol. At higher frequencies, it is 15

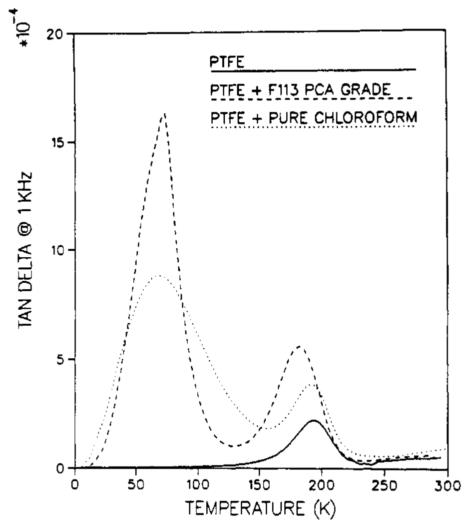

Figure 6. Effect of chloroform and F-113 on the dependence of tan δ of PTFE at 1 kHz on temperature.

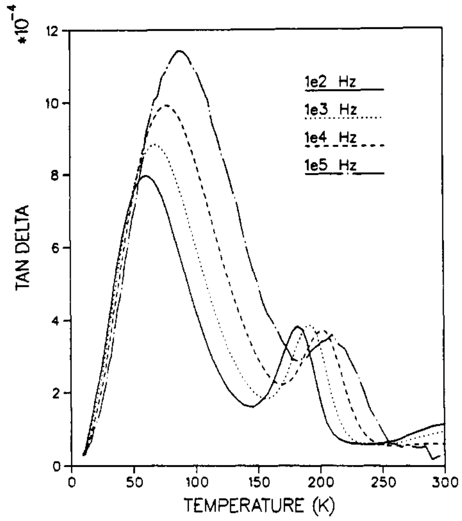

Figure 7. tan δ vs temperature for PTFE saturated with chloroform.

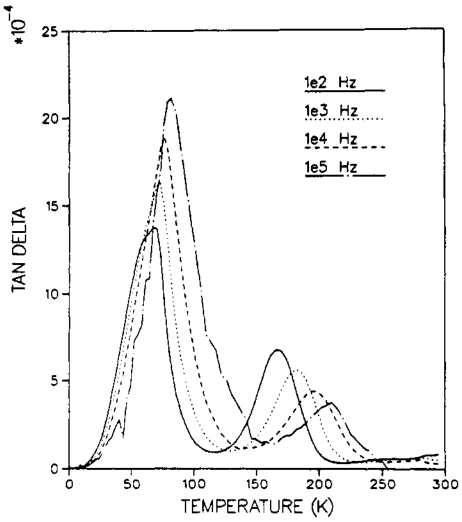

Figure 8. tan δ vs temperature for PTFE saturated with F-113.

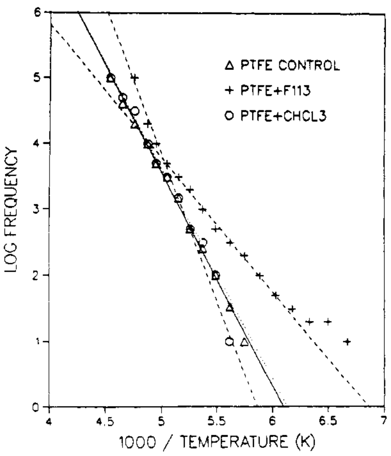

Figure 9. Arrhenius plot for the γ-relaxations.

kcal/mol, and the data are closer to those for the other samples.

The Eyring free energy of activation, ΔF^*, is defined by the following equation:[10]

$$\Delta F^* = \Delta H^* - T\Delta S^* = RT[\ln(k/2\pi h) + \ln(T/f)] \quad (8)$$

For the γ-relaxation in PTFE saturated with F-113 at frequencies up to 1 kHz, $\Delta F^* = 7.56 \pm 0.05$ kcal/mol independent of temperature. This means that the activation entropy, ΔS^*, is essentially zero. We consider this to be a characteristic of a simple, noncooperative relaxation.[11,12] At higher frequencies and in the other samples, ΔS^* is positive. Another distinctive property of this relaxation is the decrease in peak height with increasing temperature and frequency. The data indicate that this is due to a decrease of the strength of the relaxation partially balanced by some narrowing of the distribution of relaxation times.

Low-Temperature Relaxation. The low-temperature relaxations in Figures 6–8 for PTFE saturated with chloroform or F-113 are clearly distinguishable from the crystal impurity relaxations in Figures 2 and 4. The former occur at lower temperatures and have much smaller activation energies.

A striking feature is the increase in peak height with increasing frequency in the isochronal temperature scans. The curves for different frequencies intersect only on the low-temperature side of the peak. Maxima in isothermal frequency scans depend on these intersections. Therefore, in this situation, the relaxation will appear at a lower temperature in frequency scans than in temperature scans. This effect is largely due to increases in the strength of the relaxation with increasing temperature, primarily due to increases in the relaxed permittivity. We believe that data from isothermal frequency scans have the greatest scientific significance. Figure 10 is an Arrhenius plot of these data. Data from both temperature and frequency scans are included in Table II.

The activation energies are 2–3 kcal/mol except for the temperature scans of the sample saturated with F-113. The activation free energies are independent of temperature, indicating activation entropies close to zero, a characteristic of noncooperative internal motions. Thus, we conclude that the absorbed molecules are able to move independently of each other.

Equation 2 can be rearranged to solve for g:

$$g = (\epsilon_r - \epsilon_u)\left(\frac{2\epsilon_r + \epsilon_u}{3\epsilon_r}\right)\left(\frac{3}{\epsilon_u + 2}\right)^2\left(\frac{3kT}{4\pi}\right)\left(\frac{1}{\mu^2 N}\right) \quad (9)$$

The parameter g will be less than one if not all of the dipoles are able to reorient, if reorientation is restricted to an angle, θ, less than 180° or if the reoriented state has a higher energy, U.

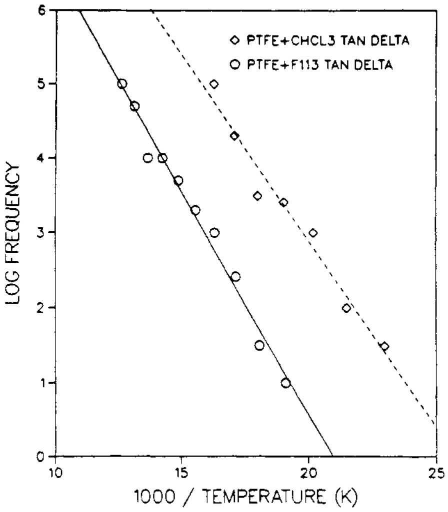

Figure 10. Arrhenius plot for the low-temperature relaxations (data from isothermal frequency scans).

Table II
Low-Temperature Relaxations

	chloroform additive		F-113 additive	
	temp scan	freq scan	temp scan	freq scan
temp (K) at 1 kHz	67	49	73	61
E_a, kcal/mol	2.87	2.25	5.62	2.73
ΔF^*, kcal/mol	2.58 ± 0.04	1.89 ± 0.05		2.37 ± 0.06

Table III
Analysis of the Low-Temperature Relaxations

	additive	
	chloroform	F-113
temp (K) at 1 kHz	49	61
μ, D	1.01	1.26
N, molecules/cm^3	1.60×10^{20}	3.29×10^{20}
ϵ_u	2.006	2.006
ϵ_r	2.039	2.045
g	0.183	0.0846
U, cal/mol	290	462

According to the formalism of Ashcraft and Boyd[11]

$$g = 2(1 - \cos\theta)\frac{e^{-U/RT}}{(1 + e^{-U/RT})^2} \quad (10)$$

In the case of the low-temperature relaxations discussed here, it is appropriate to assume that all of the absorbed molecules are free to reorient by an angle of 180°. In that case

$$U = -RT\ln\left[\frac{2}{g} - 1 - \left(\frac{4}{g^2} - \frac{4}{g}\right)^{1/2}\right] \quad (11)$$

These quantities are listed in Table III for the temperatures corresponding to maxima in tan δ at a frequency of 1 kHz as determined from isothermal frequency scans. Values for the dipole moments were recommended by R. H. Boyd (personal communication). Values for ϵ_r and ϵ_u were determined by fitting data in Cole–Cole plots to least-squares circular arcs. Using these assumptions, it was calculated that U, the difference in energy between orientation states, is 290 cal/mol for chloroform and 462 cal/mol for F-113.

Conclusions

The dielectric and dynamic mechanical relaxations in PTFE saturated with low molecular weight compounds differ in a number of interesting ways. The α- and β-relaxations, which are important features of the mechanical behavior, are dielectrically inactive.[3]

The γ-relaxation, which is assigned to motions of short chain segments in the amorphous regions, is revealed by both techniques. The temperature and peak height for the loss modulus were unaffected by additives, including chloroform and F-113.[2] In contrast with this, the dielectric peak heights were increased by the additives. The relationship between temperature and frequency was unchanged by chloroform. With F-113, on the other hand, the temperature and the activation energy at low frequencies were reduced, and the activation entropy was close to zero. Apparently, the presence of F-113 reduces the cooperative character for this relaxation, and the internal motion is concentrated in the shortest possible segments, probably four CF_2 units. At frequencies above 1 kHz, all three samples were similar.

The presence of absorbed chloroform or F-113 (but not carbon tetrachloride) produced an additional low-temperature dielectric relaxation having a low activation energy and an activation entropy close to zero. This can be interpreted as arising from the reorientation of the absorbed molecules. This process is not found in the pure chemicals. However, in that case, a different relaxation was observed which was assigned to the reorientation of impurity molecules.

Finally, we found no manifestation of the dynamic mechanical relaxation near −30 °C[2] in the dielectric data on the samples containing the additives.

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