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

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Introduction

In a recent paper,[1] we described the effects of absorbed chemicals on the dielectric properties of poly(tetrafluoroethylene) (PTFE). The "guest" molecules used in that study were chloroform and fluorocarbon-113 (1,1,2-trichloro-1,2,2-trifluoroethane). As chlorofluorocarbons are phased out, they are frequently replaced by hydrofluorocarbons. It was of interest to determine to what extent these compounds would be absorbed by PTFE and how they would effect the dielectric properties. It is known that the presence of hydrogen in organic molecules tends to greatly reduce absorption by fluoropolymers, even when the solubility parameters are similar.[2]

Three compounds were selected for this study. Two are partially fluorinated toluenes, trifluorophenylmethane ($C_6H_5CF_3$) and pentafluoromethylbenzene ($C_6F_5CH_3$). The third compound was a fluorinated normal hexane with a single hydrogen at one end (n-$C_6F_{13}H$). Some properties of these compounds are shown in Table 1. As expected, the amount absorbed by PTFE decreased as the number of hydrogens on the molecules was increased.

The experimental procedures were the same as in the earlier study.[1]

Results

The dielectric tan δ at a frequency of 1 kHz for the three saturated samples is plotted against temperature in Figure 1. In each case, there is a loss peak near 190 K where the γ-relaxation is observed in a PTFE control.[3] Its properties are summarized in Table 2. The temperatures for the control and the three saturated samples are similar, but the activation energy is reduced for the samples saturated with $C_6F_5CH_3$ and n-$C_6F_{13}H$. The height of the loss peak, tan δ_{max}, is greatly increased in the saturated samples. This effect is largest for $C_6H_5CF_3$ and smallest for n-$C_6F_{13}H$. This is opposite the order of the weights absorbed but the same order as the number of hydrogens. Some, but not all, of these differences may be attributed to overlapping with the lower temperature relaxation discussed below.

The γ-relaxation in PTFE is attributed to the motion of short-chain segments in the amorphous regions.[4] This relaxation is stronger in the present samples than in pure PTFE. One possible explanation is that the polar guest molecules move sympathetically with the chain segments without changing the underlying character of the γ-relaxation. Another possibility is that the number of mobile short segments is increased.

Each of the saturated samples exhibits a prominent relaxation at a temperature below the γ-relaxation. These phenomena, which we will designate δ-relaxations, occurred in samples saturated with chloroform or fluorocarbon-113 but not in a PTFE control or in a sample saturated with CCl_4.[1] The properties of the δ-relaxations in the present samples are summarized in Table 3 based on isothermal frequency scans.

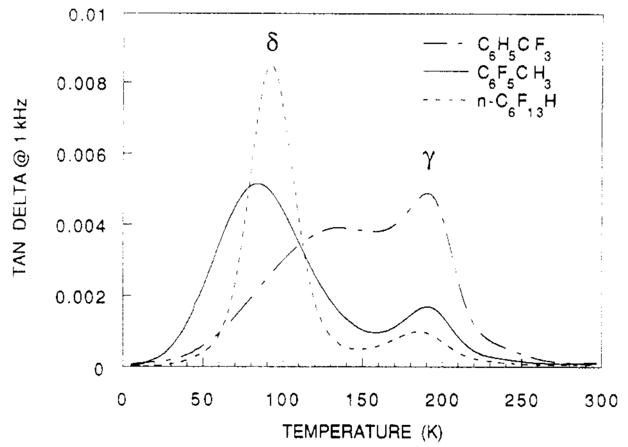

Figure 1. Plot of the dielectric tan δ at 1 kHz versus temperature for PTFE saturated with $C_6H_5CH_3$, $C_6F_5CH_3$, and n-$C_6F_{13}H$.

Table 1. Properties of Hydrofluorocarbons

	$C_6H_5CF_3$	$C_6F_5CH_3$	n-$C_6F_{13}H$
mol wt	146	182	320
melting point, °C	−29	−29	−81
wt absorbed in PTFE, %	2.13	3.1	5.6

Table 2. Properties of the γ-Relaxation

additive	temp (K) at 1 kHz	tan δ_{max} × 10^3	E_a, kcal/mol
none	194	0.22	16.3
$C_6H_5CF_3$	187	4.81	16.5
$C_6F_5CH_3$	193	1.69	13.5
n-$C_6F_{13}H$	190	0.96	15.1

Table 3. Properties of the Low-Temperature δ-Relaxation

	$C_6H_5CF_3$	$C_6F_5CH_3$	n-$C_6F_{13}H$
temp (K) at 1 kHz	108	74	88
E_a, kcal/mol	4.34	2.87	3.76
$\Delta F^\ddagger$, kcal/mol	4.22 ± 0.03	2.84 ± 0.02	3.52 ± 0.01
N, molecules/cm^3	1.89×10^{20}	2.21×10^{20}	2.27×10^{20}
ϵ_r	2.155	2.352	2.315
ϵ_u	2.025	2.216	2.203
$\epsilon_u - \epsilon_r$	0.130	0.136	0.112
g	0.455	0.286	0.246
U, cal/mol	410	418	475

In each case, the activation free energy, $\Delta F^\ddagger$, as defined by eq 1 is independent of temperatures within 1%.

$$\Delta F^\ddagger = RT[\ln(k/2\pi h) + \ln(T/f)] \qquad (1)$$

This means that the activation entropy, $\Delta S^\ddagger$, is close to zero, and the internal motions reflected in the δ-relaxations are noncooperative.[5–7]

It is of interest to note that while the weight absorbed varies significantly, N, the number of molecules per cubic centimeter, remains in a fairly narrow range.

The unrelaxed and relaxed permittivities, ϵ_u and ϵ_r, were determined from Cole–Cole complex plane plots of ϵ'' vs ϵ'. The strength of the relaxation is indicated by their difference ($\epsilon_r - \epsilon_u$).

For each of the additives, the vector sum of the C–H and C–F dipoles can be approximated by an organic molecule having a hydrogen at one end and a fluorine at the other. It is expected that all such molecules will have similar dipole moments. We assumed a value for the dipole moments, μ, of 1.73 D units, which is the average of the values for the following compounds:[8] $CHCF_3$ (1.62), CH_3F (1.81), C_2H_5F (1.92), and C_6H_5F (1.58).

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The Kirkwood g-factor was calculated from[4]

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

and the results are listed in Table 3.

The fact that the values of g are less than 1 suggests three possibilities: (1) not all of the dipoles are able to reorient; (2) the reorientation is restrictd to an angle, θ, less than 180°; (3) the reoriented state has a higher energy, U. Ashcraft and Boyd have given the following relationship.[9]

$$g = 2(1 - \cos\theta)\frac{e^{-U/RT}}{(1 + e^{-U/RT})^2} \qquad (3)$$

Assuming that all of the absorbed molecules are free to reorient by 180°, this leads to the following expression for the energy, U.[1]

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

As given in Table 3, the values of U for the three compounds of the present study range from 410 to 475 cal/mol. These may be compared with the values from the earlier study[1] of 290 cal/mol for chloroform and 462 cal/mol for fluorocarbon-113. This shows that the data can be explained by reorientation of the dipoles between nonequivalent sites, the reoriented state being higher in energy by U.

Conclusions

Three low molecular weight hydrofluorocarbons were absorbed by PTFE to the extent of 2.12–5.6%, the amount decreasing as the number of hydrogen atoms in the compounds increased. The effects on the low-temperature dielectric properties of PTFE are qualitatively similar to those caused by chloroform or fluorocarbon-113.[1] The relationships between temperature and frequency for the γ-relaxation are similar to that for a PTFE control, but the height of the loss peak is greatly increased. Each of the five dipolar additives which have been studied produces a δ-relaxation at a lower temperature. These processes are attributed to the noncooperative reorientation of the absorbed molecules to states having slightly higher energies.

References and Notes

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