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Low-Temperature Dielectric Behavior of Polymers and Copolymers of Tetrafluoroethylene

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ABSTRACT: Dielectric measurements were made on a series of polymers containing tetrafluoroethylene at temperatures from 10 to 300 K and frequencies from 10 to 10^5 Hz. In all cases, the local-mode γ-relaxation was observed. In FEP and PFA, which contain CF_3 and n-C_3F_7O branches, respectively, there is also a lower temperature relaxation for which the activation entropy is close to zero. In Teflon AF, an amorphous copolymer containing a large number of dioxole rings, four relaxations were observed including the glass transition near 200 °C.

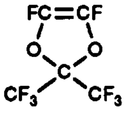
Introduction

In poly(tetrafluoroethylene) (PTFE), three viscoelastic relaxations are seen below the melting point in dynamic mechanical experiments.[1-3] These are designated α, β, and γ in the order of decreasing temperature. In early work,[3-5] all of these processes were reported to be dielectrically active. However, subsequent studies, which we have confirmed, have found that only the low-temperature γ-relaxation exhibits a significant dielectric loss peak.[6,7] It is thought that the α- and β-relaxations are seen dielectrically only in samples that are decorated with dipolar groups and are not characteristic of the basic structure of PTFE.

FEP and PFA resins are copolymers of tetrafluoroethylene with hexafluoropropylene and perfluoropropyl vinyl ether, respectively. Thus, they contain CF_3 and n-C_3F_7O side groups. In Sacher's data[7] for these polymers, tan δ rises at the lowest temperature reported, suggesting that there is an additional loss peak below the temperature of liquid nitrogen. Such a relaxation has been reported for FEP resin by Eby and Wilson.[6] In the case of FEP resin and possibly PFA as well, there is a small loss peak associated with the high-temperature α-relaxation.[7]

ETFE fluoropolymer is a largely alternating copolymer of ethylene and tetrafluoroethylene. The probability that a given monomer unit is followed by one of the other kind is approximately 90%. This copolymer is equivalent to a head-to-head polymer of vinylidene fluoride. When ETFE is in a planar zigzag conformation, there is a center of symmetry every two carbon atoms. Compared to the isomeric polymer, poly(vinylidene fluoride), the melting point is more than 100 °C higher, and the dielectric loss is much lower.[8] Nevertheless, dielectric loss peaks have been observed for both the γ- and α-relaxations.[7,8]

Teflon AF is a family of amorphous copolymers of tetrafluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole.[9]



Teflon AF 1600 contains 66 mol % dioxole and has a glass transition temperature of 160 °C.

In the present study, we undertook to measure the dielectric properties of these polymers between 10 and 300 K.

Experimental Section

The materials were in the form of 1-in.-diameter disks, which were between 0.005 and 0.050 in. thick. Aluminum electrodes were vacuum evaporated onto the faces in a standard three-terminal configuration. The gap between the low electrode and the guard electrode was approximately 0.005 in. wide. The samples were placed in a holder, which holds eight samples simultaneously and which is attached to the cold finger of a Precision Cryogenics CT-14 dewar (temperature range 4-300 K). For higher temperatures (to 525 K) we used a custom-made variable-temperature dielectric cell, which employed electrical resistive heaters and liquid-nitrogen coolant. The temperature was controlled to within 0.005 K with a Lake Shore Cryotronics DRC 82C temperature controller. Measurements of the equivalent parallel conductance, G, and capacitance, C, of the sample were carried out at 17 frequencies between 10 and 10^5 Hz on an Andeen-Hagerling, Inc., impedance bridge (Model CGA-85) and an Apple IIe microcomputer.

The data were then transformed to the complex dielectric constant, $\epsilon^* = \epsilon' - i\epsilon''$. The procedure was to set the 1000 Hz, 295 K value of ϵ', 2. The remaining values of the real part of the dielectric constant were calculated assuming that the relative change in dielectric constant equals the relative change in capacitance. Finally, the values of the imaginary part of the dielectric constant were calculated from

$$\epsilon'' = \epsilon' G / \omega C$$

Results

The dependence of tan δ at 10^3 Hz on temperature for the first four polymers is shown in Figure 1. A logarithmic scale is used to show peaks of different magnitudes clearly. For three out of four materials, the limiting value at low temperatures is less than 10^{-5}.

The γ-relaxation, which is attributed to the motion of short-chain segments, is seen for all four polymers. At this frequency the peak occurs at 194 K for PTFE, 220 K for FEP, 198 K for PFA, and 186 K for ETFE. The higher temperature for FEP may reflect an overlapping β-re-

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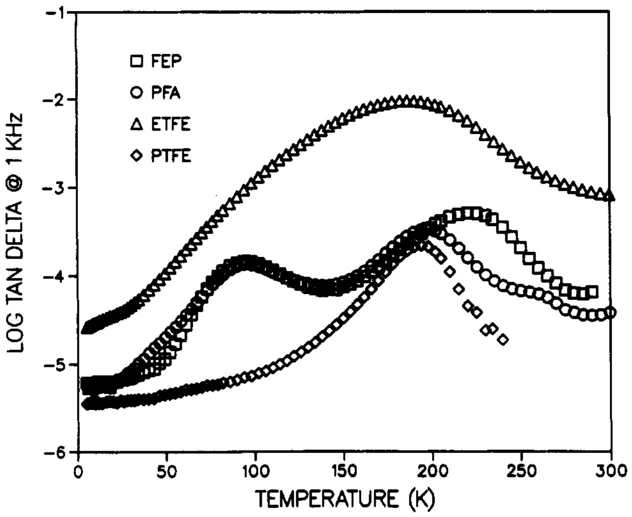

Figure 1. Dissipation factors at 10^3 Hz.

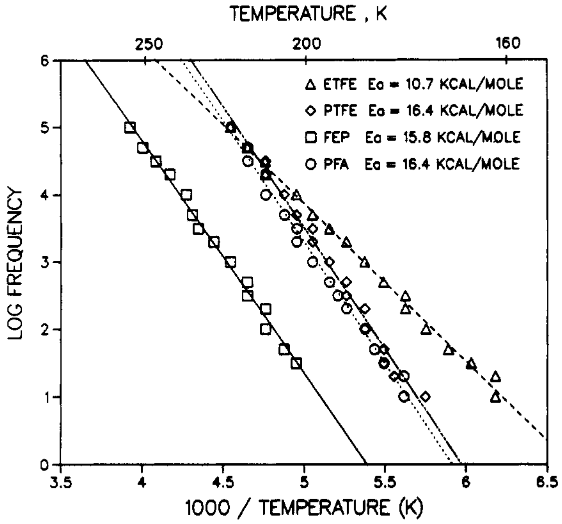

Figure 2. Arrhenius plot of the γ-relaxation.

laxation.[3] For ETFE, the maximum value of tan δ is 20–40 times as large as that in the other polymers.

Both FEP and PFA exhibit an additional loss peak at 94 K. This relaxation has previously been reported by Eby and Wilson.[6] We attribute it to the motion of side groups that are not present in PTFE and ETFE.

The dependence of the frequency of the γ-relaxations on temperature is shown in Figure 2 as an Arrhenius plot. The activation energies are close to 16 kcal/mol for PTFE, FEP, and PFA. This is slightly lower than the value of 18 kcal/mol in early reports.[2,3] In a review of data from many sources, McCall[10] gave values of 16 kcal/mol for PTFE and 18 kcal/mol for FEP. At all frequencies, the temperature of the γ-relaxation is higher in FEP than in PTFE or PFA even though the activation energies are similar. For the γ-relaxation in ETFE, the activation energy is 10.7 kcal/mol. This agrees well with an earlier value of 10.6 kcal/mol based on a combination of dynamic mechanical, dielectric, and NMR data.[8]

An Arrhenius plot for the low-temperature relaxations in FEP and PFA is shown in Figure 3. The frequency–temperature relationships are essentially identical with an activation energy of 3.7 kcal/mol in agreement with the previously reported value of 4 kcal/mol.[6,10]

These low-temperature relaxations belong to the category that has been called simple, noncooperative relaxations for which the activation entropy is close to zero.[11,12]

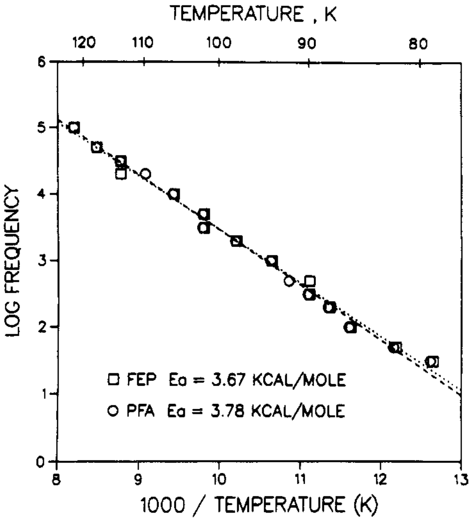

Figure 3. Arrhenius plot of the low-temperature relaxations in FEP and PFA.

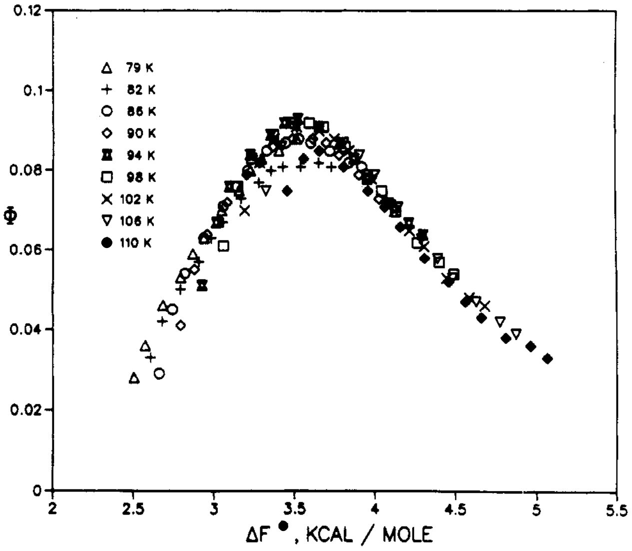

Figure 4. Distribution of activation free energies for the low-temperature relaxation in FEP.

This can be tested by rearranging the Eyring relationship between the frequency and temperature of the relaxation to give the following expression for the activation free energy.

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

When this calculation is done for the combinations of temperature and frequency for the maxima in tan δ for the low-temperature relaxations, it is found that $\Delta F^{\ddagger}$ is 3.68 ± 0.05 kcal/mol for FEP and 3.69 ± 0.04 kcal/mol for PFA. Since $\Delta F^{\ddagger}$ is independent of temperature, the activation entropy, $\Delta S^{\ddagger}$, is essentially zero. This situation is taken to mean that the groups responsible for these relaxations move independently of each other.

It has been found that, for this kind of relaxation, the distribution of activation enthalpies is also independent of temperature.[13] The first step in this analysis is to prepare a complex plane plot of ϵ'' vs ϵ' for each temperature in the region of the relaxation and fit the data to least-squares circular arcs. This corresponds to the Cole–Cole model, which fits the data very well for these relaxations. The intercepts with the ϵ' axis are the unrelaxed and relaxed permittivities, ϵ_u and ϵ_r. The distri-

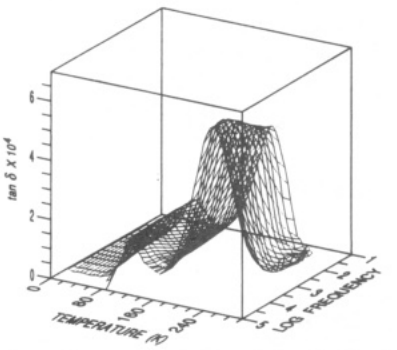

Figure 5. Three-dimensional plot of the dissipation factor of FEP.

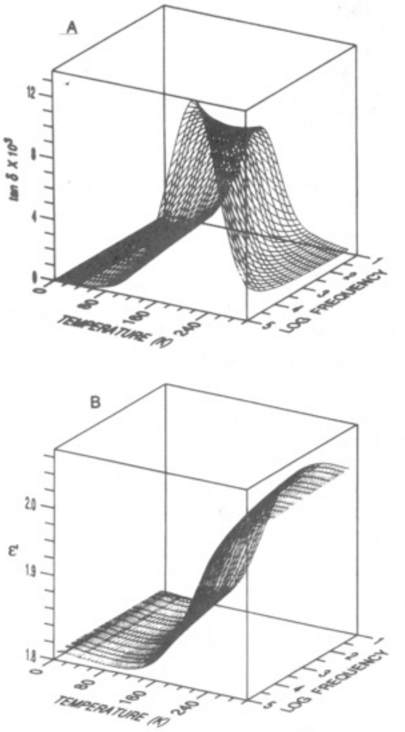

Figure 6. Three-dimensional plots of the dissipation factor and permittivity of ETFE.

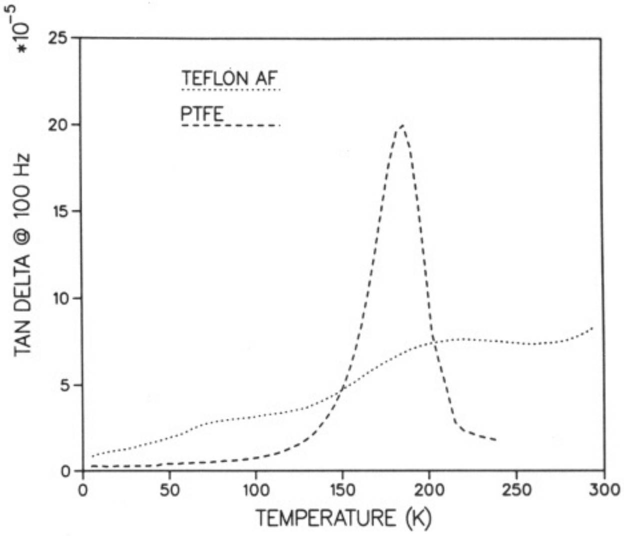

Figure 7. Dissipation factors at 100 Hz for Teflon AF and PTFE.

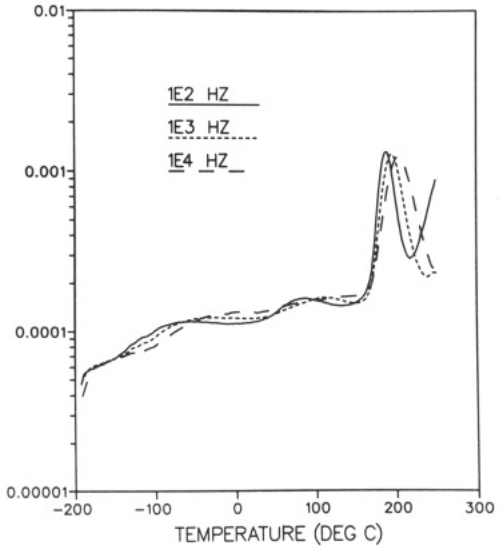

Figure 8. Higher temperature dissipation factor data for Teflon AF.

bution of relaxation times, Φ, can be approximated by

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

One then plots Φ against $\Delta F^{\ddagger}$ from eq 1 to give a distribution of activation free energies. If the data from different temperatures form a common relationship, one again concludes that $\Delta S^{\ddagger}$ is close to zero. In Figure 4, this is shown to be the case for the low-temperature relaxation in FEP. The width of the distribution at half-maximum is 1.9 kcal/mol, considerably smaller than the values of 5–6 kcal/mol, which have been found for many relaxations.[13] This may reflect the low cohesive energy of fluoropolymers.

A three-dimensional plot of the dissipation factor for FEP is shown in Figure 5. The lines in the net are parallel to the temperature or frequency axes, and each intersection represents a measurement at a particular combination of temperature and frequency. The maxima corresponding to the two low-temperature relaxations are clearly shown.

Similar three-dimensional plots of the dissipation factor, tan δ, and the permittivity, ε′, of ETFE are shown in Figure 6. In this polymer, only the γ-relaxation occurs in this temperature range. The strength of this relaxation, $(\epsilon_r - \epsilon_u)$, is about 0.195 for ETFE, much larger than the values of 0.0027 for PTFE and 0.0075 for FEP. Since the strength of the relaxation is independent of the temperature between 160 and 220 K, the increase in the peak height with increasing temperature is attributed to a narrowing of the distribution of relaxation times.

The γ-relaxation in polymers is attributed to local motions of aliphatic segments involving at least four chain atoms.[3] Since Teflon AF contains only 34 mol % tetrafluoroethylene, the concentration of active sequences of two or more TFE units is quite low, especially assuming random copolymerization with the dioxole. In Figure 7, the dissipation factors of Teflon AF and PTFE are compared at a frequency of 100 Hz. Teflon AF exhibits a broad maximum at 220 K, which is much lower than the relatively sharp maximum in PTFE at 186 K. The strength of the relaxation $(\epsilon_r - \epsilon_u)$ is 9×10^{-4}, which is one-third the value for PTFE. The peak heights differ by about the same ratio. The activation free energy, $\Delta F^{\ddagger}$, is about 10 kcal/mol, independent of temperature, indicating that the activation entropy is close to zero and that the internal motion is noncooperative.[11,12] This supports the conclusion that the size of the moving unit is more narrowly defined than in the other polymers of TFE.

Teflon AF also exhibits a very weak, low-temperature relaxation, which appears as a shoulder near 70 K in Figure

7. We suspect that this reflects motion of the CF_3 groups of the dioxole units. The low-temperature relaxations in FEP and PFA occur at 86 K at this frequency.

Data on Teflon AF extending to higher temperatures are shown in Figure 8. The large relaxation corresponding to the glass transition occurs at temperatures ranging from 188 °C at 10^2 Hz to 215 °C at 10^5 Hz. The apparent activation energy is 115 kcal/mol. The β-relaxation is observed at 88 and 111 °C for frequencies of 10^2 and 10^3 Hz, respectively. These data correspond to an Arrhenius activation energy of 27 kcal/mol or an Eyring activation free energy of about 16 kcal/mol. We tentatively attribute the β-relaxation to a local motion of the dioxole units, the γ-relaxation to a local motion of sequences (mostly dimers) of TFE units, and the low-temperature δ-relaxation to motions of CF_3 groups on dioxole units.

Conclusions

The dielectric characterization of the γ-relaxations in fluoropolymers is consistent with earlier reports. In ETFE, the maximum in tan δ is larger and the activation energy is smaller than in the perfluoropolymers, PTFE, FEP, and PFA. In the branched copolymers, FEP and PFA, there is an additional relaxation, which appears at 94 K at 10^3 Hz. This process has an activation entropy close to zero, an indication that the active units move noncooperatively.

In Teflon AF, an amorphous fluoropolymer containing a large number of dioxole rings, the γ-relaxation is weaker and broader and at a higher temperature. In this polymer, the glass transition, a β-relaxation, and a very weak low-temperature relaxation were also observed.

References and Notes

(1) McCrum, N. G. *J. Polym. Sci.* **1959**, *34*, 355.
(2) Sperati, C. A.; Starkweather, H. W. *Adv. Polym. Sci.* **1961**, *2*, 465.
(3) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: New York, 1967.
(4) Kabin, S. P. *Sov. Phys.-Tech. Polys.* **1956**, *1*, 2542.
(5) Krum, F.; Muller, F. H. *Kolloid Z.* **1959**, *164*, 8.
(6) Eby, R. K.; Wilson, F. C. *J. Appl. Phys.* **1962**, *33*, 2951.
(7) Sacher, E. *J. Macromol. Sci., Phys.* **1981**, *B19*, 109.
(8) Starkweather, H. W. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 587.
(9) Resnick, P. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (1), 312.
(10) McCall, D. W. In *Molecular Dynamics and Structure of Solids*; Carter, R. S., Rush, J. J., Eds.; National Bureau of Standards Special Publication No. 301; *National Bureau of Standards*: Washington, DC, 1969; p 475.
(11) Starkweather, H. W. *Macromolecules* **1981**, *14*, 1277.
(12) Starkweather, H. W. *Macromolecules* **1988**, *21*, 1798.
(13) Starkweather, H. W. *Macromolecules* **1990**, *23*, 328.

Registry No. PTFE (homopolymer), 9002-84-0; FEP (copolymer), 25067-11-2; PFA (copolymer), 26655-00-5; ETFE (copolymer), 25038-71-5; $(F_2C{=}CF_2)$(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole) (copolymer), 37626-13-4.