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Dielectric Relaxations in Poly(perfluoropropylene oxide)

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Introduction

Polymers and copolymers of tetrafluoroethylene (TFE) exhibit a dielectric relaxation at 1 kHz and temperatures near 200 K. In addition, FEP, the copolymer of TFE with hexafluoropropylene, and PFA, the copolymer of TFE with perfluoropropyl vinyl ether, which contain CF_3 and n-C_3F_7O branches, respectively, have an additional relaxation at 94 K.[1] We have now extended this study to the closely related polymer poly(perfluoropropylene oxide). This material is compared, in turn, with its protonated analog, poly(propylene oxide) (PPO).

Krytox fluorinated oils are low molecular weight polymers of hexafluoropropylene epoxide which are used in lubrication and related applications. The chemical structure is $F(CF(CF_3)CF_2O)_nCF_2CF_3$.

For Krytox 143 AZ, AB, and AD, the molecular weights are reported to be 1850, 3700, and 8250,[2] respectively, corresponding to values of n of about 10, 21, and 49.

Results

Dielectric measurements were made on Krytox 143 AZ and AD at 17 frequencies from 10 to 10^5 Hz and temperatures from 5 to 295 K using a cell which has previously been described.[3]

In scans by differential scanning calorimetry at 10 °C/min, glass transitions were observed at 195 and 219 K (−78 and −54 °C). A plot of the dielectric dissipation factor at 1 kHz vs temperature for these materials is shown in Figure 1. At this frequency, the α-relaxation, which corresponds to the glass transition, was observed at 213 and 252 K for the lower and higher molecular weight oils, respectively.

For both materials, there is a secondary β-relaxation near 100 K. This is about 7 K higher than the δ-relaxations, which are associated with motions of the side groups in FEP and PFA fluorocarbon resins.[1] It is noteworthy that while the peak heights are similar for the α-relaxation, that for the β-relaxation is about twice as large for the lower molecular weight sample. This is probably related to the fact that it contains more end groups, which, like the side groups, are perfluoromethyls.

As shown in Figure 2,the Arrhenius plot for the β-relaxation based on the peaks in temperature scans at constant frequency, like most secondary relaxations, is linear[4] and is not significantly sensitive to the molecular weight. The activation energy is 4.4 kcal/mol, slightly higher than the value of 3.7 kcal/mol for the δ-relaxations in FEP and PFA.[1]

The Eyring activation free energy can be calculated from the following equation: For the β-relaxation in Krytox,

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

ΔF^* = 4.0 kcal/mol, independent of temperature. This means that the activation entropy is close to zero, a characteristic of noncooperative relaxations.[5,6] For the δ-relaxations in FEP and PFA, ΔF^* = 3.7 kcal/mol. We conclude that all three relaxations are due to noncooperative motions of fluorinated side groups.

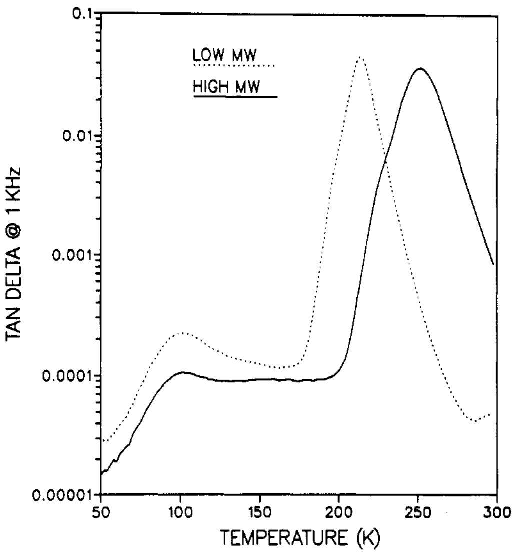

Figure 1. Dissipation factor at 1 kHz vs temperature for Krytox 143 AZ ($\bar{M}_n$ = 1850) and AD ($\bar{M}_n$ = 8250).

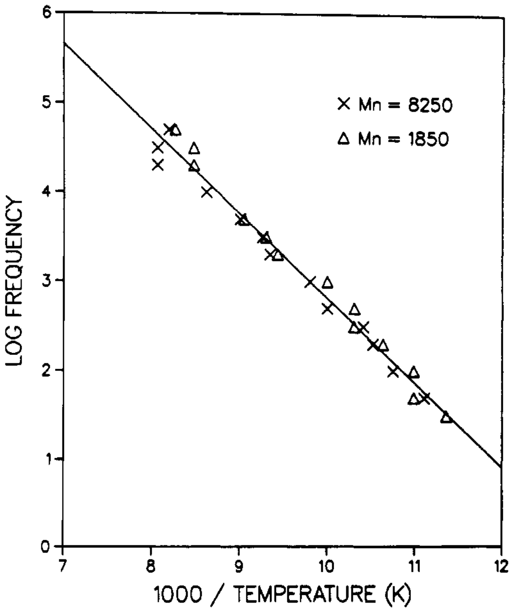

Figure 2. Arrhenius plot for the β-relaxation.

Figure 3 is an Arrhenius plot for the α-relaxation or glass transition. The data of Alper and co-workers[7] for Krytox 143 AB, which has a molecular weight between those of the two materials we studied, have been included. In this range the glass transition is quite sensitive to molecular weight. The data follow curved relationships and were fitted to the WLF equation

$$\log \frac{f(T)}{f(T_0)} = \frac{C_1(T - T_0)}{C_2 + (T - T_0)}$$

with C_1 = 10.5 and C_2 = 66. With these constants fixed, the values for the reference temperatures, T_0, were 196, 209, and 218 K in order of increasing molecular weight. We attribute the dependence of the glass temperature on the molecular weight to the corresponding variations in the density and, presumably, the free volume. At 20 °C,

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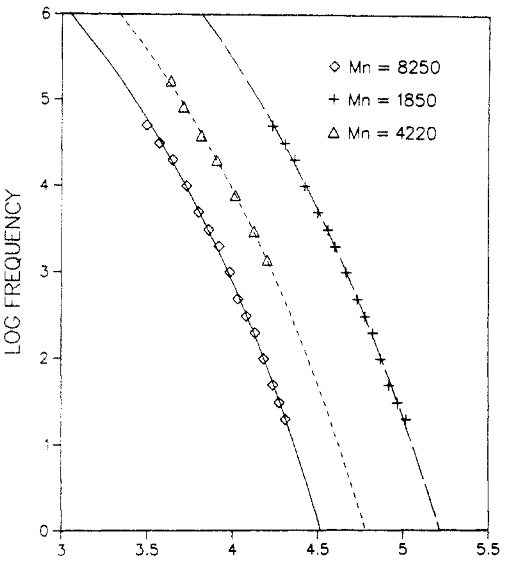

Figure 3. Arrhenius plot for the α-relaxation (data for $\bar{M}_n$ = 4220 from ref 7).

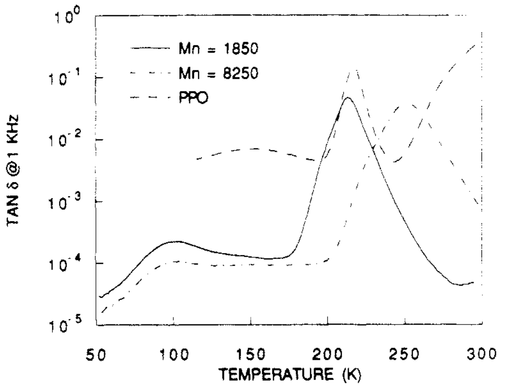

Figure 4. Comparison of Krytox and PPO: tan δ at 1 kHz vs temperature.

the densities are 1.867, 1.894, and 1.910 g/cm^3 for Krytox 143 AZ, AB, and AD, respectively.[2]

Comparison with Poly(propylene oxide)

Early work on PPO included several studies of the α-relaxation and a few isolated observations of the β- and γ-relaxations.[8] The T_g as measured by DSC is 211 K,[9] and the temperature of the dielectric α-relaxation at 1 kHz is 223 K.[10] The data were fitted to the WLF equation with C_1 = 11.6, C_2 = 38.3, and T_0 = 211 K.[9] Thus the temperature of the α-relaxation of PPO falls within the range of those for the samples of poly(perfluoropropylene oxide) of the present study. This is shown in Figure 4 for tan δ at 1 kHz vs temperature.

Both the temperature and the magnitude of the loss peak for the β-relaxation are much higher for PPO. At a frequency of 1 kHz, this relaxation occurs at 168 K in isochronal temperature scans and 156 K in isothermal frequency scans. The Eyring activation free energy, $\Delta F^{\ddagger}$, is 6.7 kcal/mol and is independent of temperature within 1%. This means that the activation entropy, $\Delta S^{\ddagger}$, is close to zero, a property of a local noncooperative internal motion.[5,6] The Arrhenius activation energy, E_a, is 6.9 kcal/mol. An Arrhenius plot comparing the β-relaxations of the two polymers is shown in Figure 5. The properties of their relaxations are compared in Table I.

Although they both have activation entropies close to zero, the β-relaxations in the two classes of polymers may not arise from similar mechanisms. As stated earlier, the β-relaxation in Krytox seems to be similar to the low-temperature relaxation which is present in FEP but not in PTFE.[1] It is probably due to motions of the CF_3 side groups. We would expect a corresponding motion of the CH_3 groups in PPO to occur at a lower, not a higher, temperature. Also, we would not expect the peak height to be as much higher as that shown for PPO in Figure 4. It has been suggested that the β-relaxation in PPO involves a cooperative motion of three or four repeat units.[8] It could be somwhat more localized than that and still involve motions of the main chain. The fact that the activation entropy is close to zero is characteristic of a noncooperative relaxation.[5,6] There is a γ-relaxation at still lower temperatures or higher frequencies with an activation energy of 3–4 kcal/mol.[8] The suggestion that it is associated with the methyl groups seems plausible. There is a similar relaxation in polypropylene.[5] If this idea is correct, the γ-relaxation in PPO is analogous to the β-relaxation in Krytox.

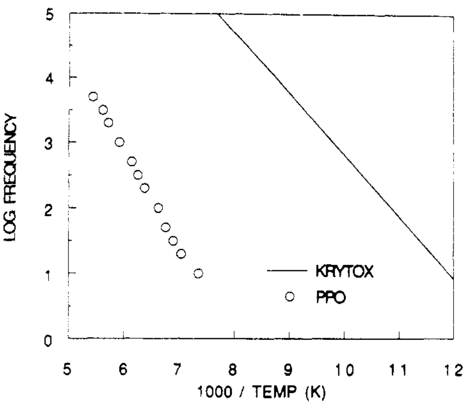

Figure 5. Comparison of Krytox and PPO: Arrhenius plot for the β-relaxations.

Table I
Effect of Fluorination on Relaxations

	poly(propylene oxide)	poly(perfluoropropylene oxide)
T_g (K) by DSC	211	195–219
dielectric α-relaxation at 1 kHz (K)	223	213–252
dielectric β-relaxation at 1 kHz (K)	168 (T scans) 156 (f scans)	100
$\Delta F^{\ddagger}$ (kcal/mol)	6.7	4.0
E_a (kcal/mol)	6.9	4.4

References and Notes

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Registry No. Krytox 143AZ, 65863-23-2.