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Ultralow Temperature Dielectric Relaxations in Polyolefins

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ABSTRACT: Dielectric measurements were made on polyethylene, polypropylene, and a stabilizer, Irganox 1010, down to and below the temperature of liquid helium. All three materials exhibited a relaxation in which the frequency is proportional to the absolute temperature with $f/T \simeq 1$ kHz/K. This phenomenon is indicative of quantum mechanical tunneling with an activation enthalpy close to zero and a negative activation entropy. Alternatively, the relationship may be expressed in terms of a transmission coefficient of about 3×10^{-7}. There is evidence that the presence of a stabilizer such as Irganox 1010 may be responsible for the ultralow temperature relaxation in the polymer samples.

Introduction

Internal motions in polymers have both theoretical and practical significance. They can be studied by dielectric or dynamic mechanical techniques or by nuclear magnetic resonance. Low-temperature relaxations can frequently be assigned to the motion of small submolecular units and thus are of special interest in the study of structure–property relationships. Many of these relaxations can be studied with liquid nitrogen or liquid helium techniques. There are, however, a few relaxations which occur at temperatures below the boiling point of helium. These phenomena at temperatures very close to absolute zero have unusual properties such as quantum mechanical tunneling and can add to our understanding of polymer behavior.

The relationship between the frequency and temperature for dielectric or dynamic mechanical relaxations can be expressed in a manner analogous to Eyring's theory of absolute reaction rates.

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

This equation can be rearranged in terms of the activation free energy

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

We have found a large number of relaxations for which $\Delta F^{\ddagger}$ is independent of temperature, and the activation entropy, $\Delta S^{\ddagger}$, is therefore close to zero.[1-3] This behavior is associated with simple, noncooperative situations such as the motions of side groups or dislocations in crystals.

There is another class of relaxations at temperatures close to absolute zero for which $\Delta F^{\ddagger}$ is proportional to the absolute temperature, T, and the frequency, f, is also proportional to T. From eq 2, we see that this means that the activation enthalpy, $\Delta H^{\ddagger}$, must be close to zero. This phenomenon has been attributed to phonon-assisted quantum mechanical tunneling.[4]

In 1969, Vincent[4] reported a maximum in the dielectric tan δ of polyethylene at the following combinations of temperature and frequency, 1.35 K, 1.3 kHz; 2 K, 1.9 kHz, 4.2 K, 4 kHz, and suggested the quantum mechanical tunneling mechanism. Phillips[5] made dielectric measurements on polyethylene from 10 to 10^6 Hz and 1–4.2 K and developed the quantum mechanical model in more detail. He reported that the low-temperature relaxation corresponded closely to the Debye model for a single relaxation time. He stated that the relaxation is intrinsic to polyethylene and that neither an antioxidant nor a catalyst is responsible for the loss which he attributed to hydroxyl groups attached to the main chain within the crystalline regions. He stated that the frequency is proportional to the temperature below 3 K, with a more complex relationship between 4 and 10 K. Phillips reported that in contrast to polyethylene, the dielectric tan δ in polypropylene and polystyrene is independent of temperature and frequency in this region.

Carson[6] found that the peak at about 4 kHz and 4.2 K could be removed by steaming in H_2O or D_2O. He found a second, broader peak at 4×10^6 Hz, which was shifted reversibly to 3×10^4 Hz by deuteration. He reported that the 4-kHz peak was not entirely absent in unoxidized polyethylene but that the higher frequency peaks were present only in oxidized samples. Low-density polyethylene showed only the low-frequency peak. Thomas and King[7] concluded that the intrinsic dielectric loss of polyethylene at 4.2 K is about 5×10^{-6}, independent of frequency between 50 and 10^5 Hz.

Yano and co-workers[8] reported that the loss maximum was broader in low-density polyethylene or ethylene(vinyl alcohol) copolymers than in high-density polyethylene. The maximum loss was found at 7.5% vinyl alcohol. It was thought that larger concentrations of hydroxyl groups tended to couple and depress the effect. Working with oriented polyethylene, the same group found evidence that the loss is associated with motions of protons parallel to the chain axes.[9] They found that the relationship between frequency and temperature in the stabilizer, Ionox 330, differs from that in polyethylene and appears to reflect overlapping of tunneling and thermally activated processes.

Gilchrist[10] showed that the ultralow temperature relaxation can be reproduced both by synthetically introducing hydroxyl groups into the polymer molecules or by adding long-chain secondary alcohols. Antioxidants such as 2,6-di-*tert*-butylphenol can also produce low-temperature dielectric losses,[11] as can mercaptans and amines.[12]

Other workers have reported low-temperature relaxations in polyethylene which were observed only in samples which had been mechanically deformed. Examples are the dielectric study by Heybey and Müller[13] and the dynamic mechanical measurements by Papir and Baer.[14] The latter observed peaks at 20 and 48 K in linear

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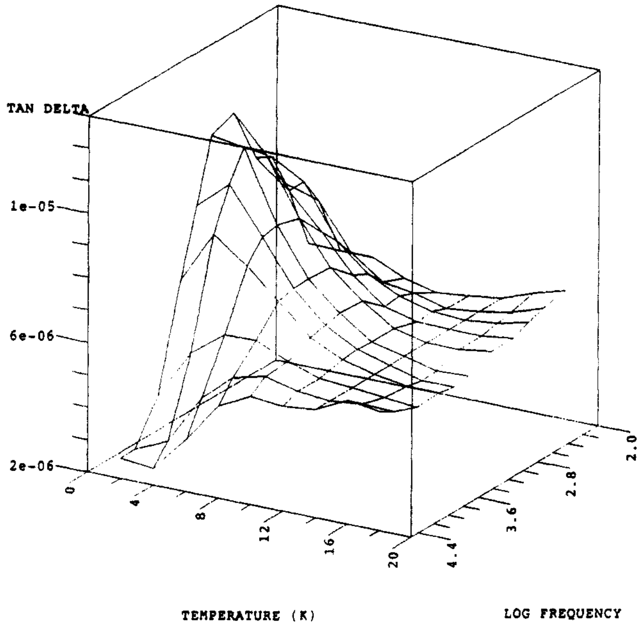


Figure 1. Three-dimensional plot of the dielectric tan δ of polyethylene vs frequency and temperature.

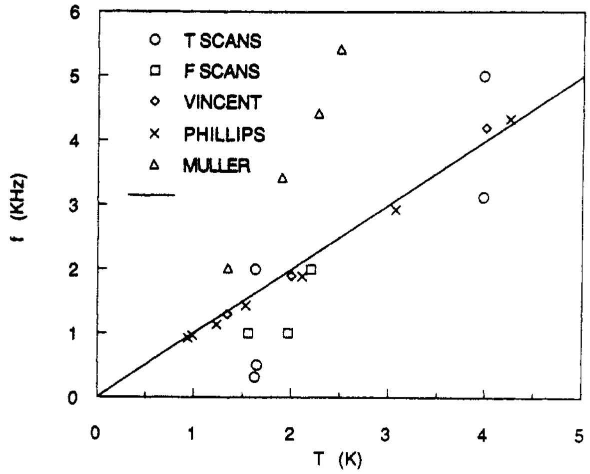


Figure 2. Relationship between frequency and temperature for the ultralow temperature relaxation in polyethylene.

polyethylene using a frequency of 1 Hz. For the higher temperature process, the activation energy was reported to be 3–4 kcal/mol.

In polypropylene, Vincent[4] found no dielectric loss peak at 4.2 K between 50 Hz and 20 kHz. However, Sinnott[15] reported dynamic mechanical loss peaks at 19 K (6 Hz) and 53 K (7 Hz) which he attributed to hindered rotation of methyl groups. Crissman et al.[16] observed a broad maximum at 10–30 K (10 kHz). Several workers have attributed these low-temperature relaxations to quantum mechanical tunneling. Stejskal and Gutowsky[17] concluded that the tunneling rate should exceed the classical rate at low temperatures and that below 70 K the tunneling frequency for the rotation of methyl groups is practically independent of temperature.

Gilchrist and Vij[18,19] studied the effect of compounds of low molecular weight absorbed in polypropylene on the low-temperature dielectric properties. The normal alkanes caused a peak at 1.2 kHz and a temperature which increased with chain length from 25 K for propane and 40 K for butane to 95 K for decane.[18] The relaxation time at 92 K increased from 10^{-4} s for propane to about 0.3 s for $C_{22}H_{46}$. Additional features were found in branched compounds and those with polar substituents. A peak near 80 K at 1.2 kHz in several compounds was attributed to ethyl rotations. A subsequent study[19] concerned polypropylene films containing CCl_4, tetramethylsilane, or CS_2. At 1.2 kHz, peaks characteristic of each compound were observed at temperatures from 24 to 86 K.

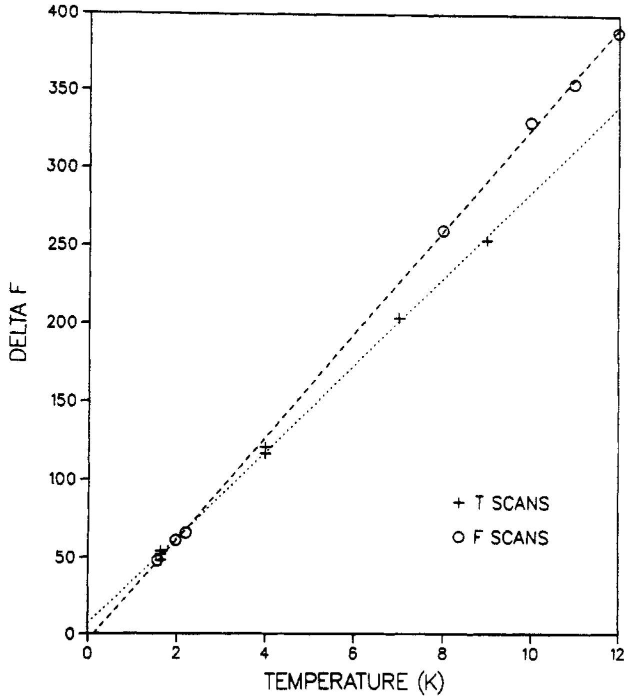


Figure 3. Dependence of the activation free energy on temperature for the ultralow temperature relaxation in polyethylene.

Experimental Section

Dielectric measurements were made at 17 frequencies from 10 to 10^5 Hz from room temperature down to about 5 K in the manner which has previously been described.[20] For some of the samples, measurements were made from 1.5 to 4.2 K by immersing them in liquid helium which was then pumped on to achieve the low temperatures. The temperature was measured using a silicon diode in conjunction with a LakeShore Cryotronics DRC-82C temperature controller. For other samples, measurements from 0.2 to 4.2 K were carried out by attaching them to the mixing chamber of a dilution refrigerator which was originally constructed by S. H. E. Corp. In that case the temperature was measured and controlled using a germanium resistance thermometer in conjunction with a Biomagnetics Technology Model 1000 temperature controller. In all three cases, the same sample holder was used.

Results

Polyethylene. Figure 1 is a three-dimensional plot of the dielectric tan δ vs frequency and temperature between 2 and 20 K. The loss rises sharply at low temperatures and does not reach a global maximum within the range of these experiments. Nevertheless, maxima do appear in isothermal frequency scans and isochronal temperature scans. As shown in Figure 2, the relationship between frequency and temperature is in reasonable accord with the data of Vincent[4] and Phillips[5] which follow the constant ratio expected for a tunneling mechanism. The line is drawn with a slope of 1 kHz/K. Another study by Müller and co-workers[21] reported a frequency which increased much more rapidly with temperature.

The dependence of the activation free energy on temperature for the temperature and frequency scans is shown in Figure 3. The data conform to the proportionality expected for an activation enthalpy close to zero.

A sample of high-density polyethylene which was made without any antioxidant and molded and handled in the

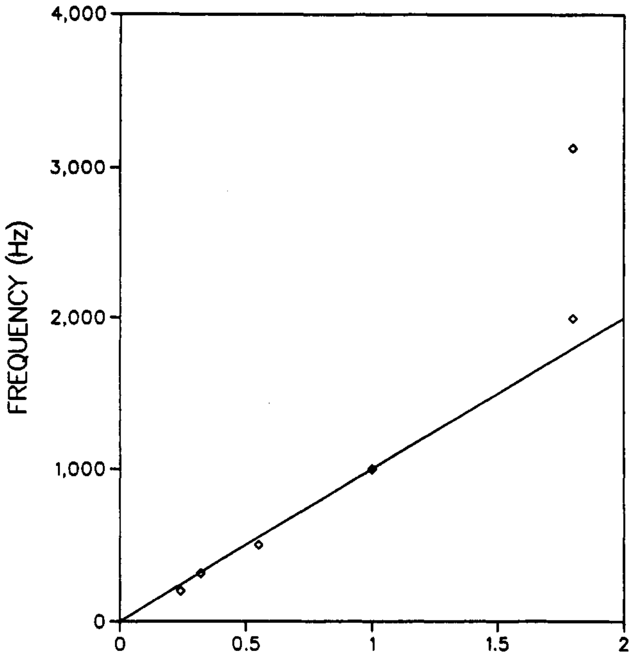
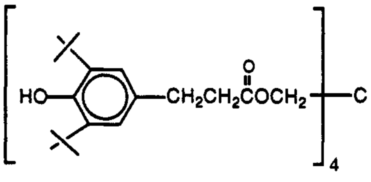


Figure 4. Dependence of the frequency on temperature for the ultralow temperature relaxation in polypropylene.

absence of moisture and oxygen did not show the ultralow temperature dielectric relaxation.[22]

Polypropylene. The relationship between the frequency and the temperature for the ultralow temperature dielectric relaxation in polypropylene is shown in Figure 4. Below 1 K, it conforms to a line with a slope of 1 kHz/K, as was found with polyethylene. At higher temperatures, the frequency increases more rapidly. Polypropylene exhibits a number of other dielectric relaxations. The β-relaxation or glass transition occurs at 290 K and 1 kHz with an activation energy of 40–50 kcal/mol. The γ-relaxation is observed near 150 K with an activation free energy of 5.6 kcal/mol and an activation entropy close to zero. The δ-relaxation occurs at 33 K and 1 kHz with an activation free energy of about 1 kcal/mol. Since the maximum value of tan δ increases strongly with increasing frequency, it can be observed only in temperature scans.

Irganox 1010. Irganox 1010 is widely used as an antioxidant in polyolefins. It has the following chemical formula.



This compound is a crystalline solid melting at 116 °C which was cold pressed to form samples for dielectric measurements. The dielectric tan δ from 5 to 300 K is shown in Figure 5 at frequencies from 30 to 10^5 Hz. We will name the relaxations by analogy with those in polypropylene. The strong β-relaxation near 280 K has an activation free energy of 13.86 ± 0.06 kcal/mol. The weak γ-relaxation near 200 K has an activation free energy of 6.7 ± 0.3 kcal/mol and an activation entropy close to zero. The frequency of the stronger δ-relaxation increased from 5 kHz at 33 K to 100 kHz at 55 K. This corresponds to an activation enthalpy, $\Delta H^{\ddagger}$, of 0.4 kcal/mol and an activation entropy, $\Delta S^{\ddagger}$ of -21 cal deg^{-1} mol^{-1}. While this relaxation does not exhibit the proportionality between frequency and temperature which is characteristic of quantum mechanical tunneling, there are the common properties of a negative $\Delta S^{\ddagger}$ and a very small $\Delta H^{\ddagger}$.

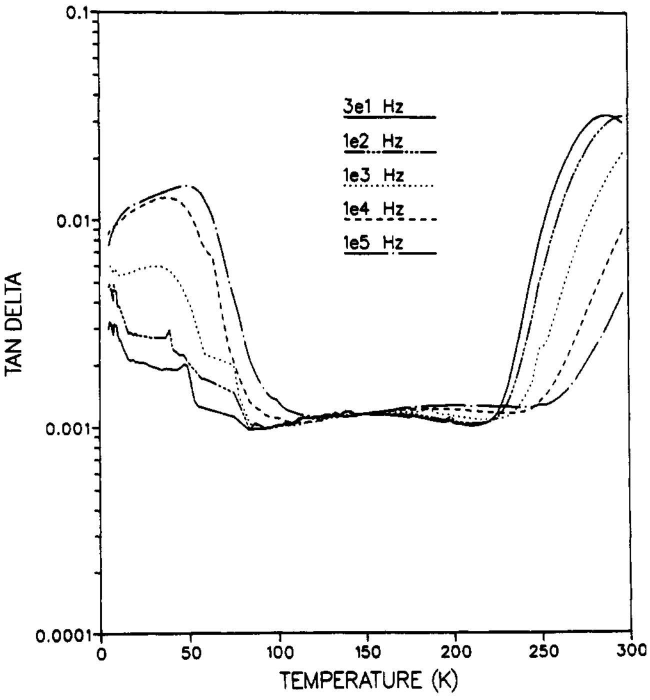


Figure 5. tan δ vs temperature for Irganox 1010.

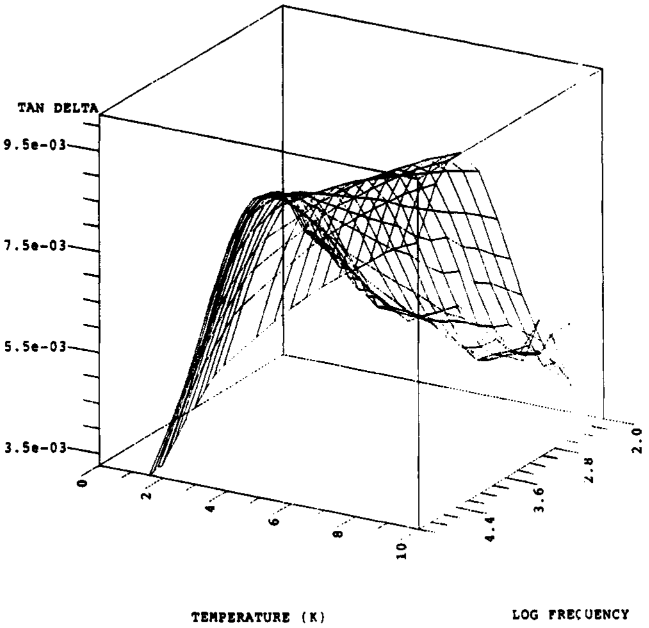


Figure 6. Three-dimensional plot of tan δ vs temperature and frequency for the ultralow temperature relaxation in Irganox 1010.

Figure 6 is a three-dimensional plot of the ultralow temperature ϵ-relaxation in Irganox 1010. The frequency increases from 2 kHz near 2 K to 20 kHz at 8 K. At the lowest temperature, it conforms to the relationship which applies to polyethylene and polypropylene, i.e., $f/T \simeq 1$ kHz/K.

The frequency–temperature relationships for the ultralow temperature relaxations in polyethylene, polypropylene, and Irganox 1010 are compared in Figure 7. At the lowest temperatures where quantum effects are likely to dominate, they all seem to behave in the same manner. At slightly higher temperatures where thermally activated effects begin to contribute, polypropylene and Irganox 1010 deviate from the linear relationship between fre-

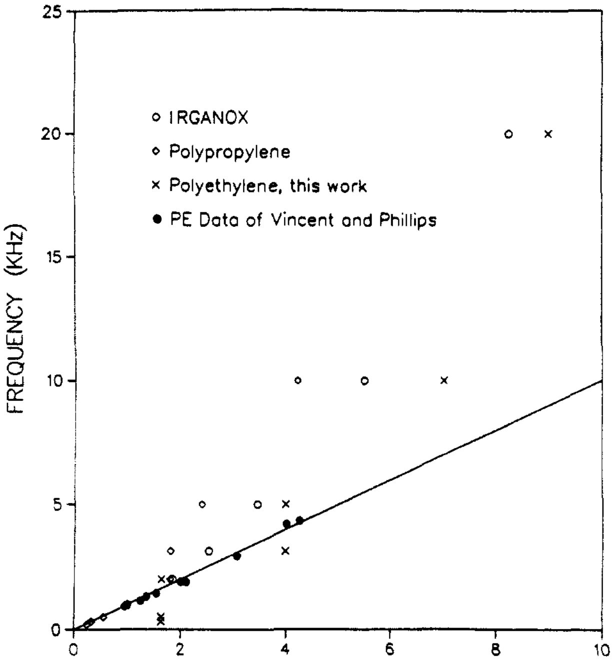


Figure 7. Comparison of the frequency–temperature relationships for the ultralow temperature relaxations in polyethylene, polypropylene, and Irganox 1010.

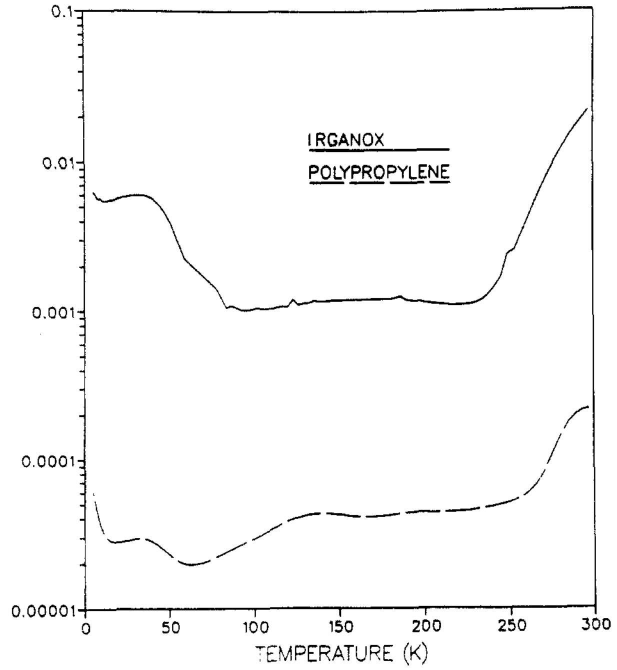


Figure 8. Dependence of tan δ at 1 kHz on temperature in Polypropylene and Irganox 1010.

quency and temperature sooner than polyethylene. Figure 8 is a comparative plot of the dependence of tan δ at 1 kHz on temperature in polypropylene and Irganox 1010. At the δ-relaxation near 33 K, tan δ is 200 times as large in Irganox 1010. If that compound is responsible for the relaxation in polypropylene, it would suggest a concentration of 0.5%. This is about the highest loading which is used in commercial practice.

Discussion

In earlier work,[1-3] we found that the activation entropies of relaxations in polymers were either zero or positive. From eq 2, it follows that if f/T for the ultralow temperature relaxation is 1 kHz/K, $\Delta H^{\ddagger}$ is zero and $\Delta S^{\ddagger}$ is −29.8 cal deg^{-1} mol^{-1}. Another approach is based on the hypothesis that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are both equal to zero. We then replace eq 1 with the following relationship where κ is the transmission coefficient.

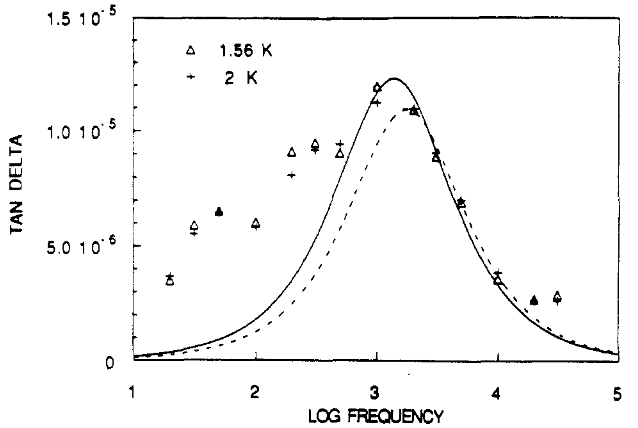


Figure 9. tan δ vs frequency for the ultralow temperature relaxation in polyethylene: (curves) form for a Debye relaxation having a single relaxation time; (solid) 1.56 K; (dashed) 2 K.

$$f = \kappa kT/2\pi h \qquad (3)$$

If $f/T = 1$ kHz/K, κ is 3×10^{-7}.

Eyring has stated[23] that for internal motions in solids, the transmission coefficient is usually equal to 1. On the other hand, very small transmission coefficients are common for chemical reactions. The very low temperature relaxations discussed here are an exception, a reasonable one for quantum mechanical tunneling.

Relaxations at slightly higher temperatures may also have small transmission coefficients. An example is the δ-relaxation in Irganox 1010 discussed above. Here $\Delta H^{\ddagger}$ is not zero but 0.4 kcal/mol, an extremely small value compared to the familiar relaxations which occur at higher temperatures. The negative apparent activation entropy, −21 cal deg^{-1} mol^{-1} would correspond to a transmission coefficient of 2.6×10^{-5} if one replaces $\exp(\Delta S^{\ddagger}/R)$ in eq 1 with κ.

The hypothesis that the true activation entropies of these low-temperature relaxations is zero is reasonable. A positive activation entropy is indicative of a cooperative process, and internal motions which occur at low temperatures are almost certainly noncooperative. A large class of secondary relaxations occurring at temperatures somewhat higher than those discussed here have activation entropies close to zero and are considered to be noncooperative.[1-3]

As mentioned earlier, Phillips stated that the low-temperature relaxation in polyethylene could be fitted very well by the Debye model for a single relaxation time.[5] However, Carson[7] and Yano and co-workers[8] found that the peak was slightly broader. Our data at 1.56 and 2 K are plotted against the frequency in Figure 9. While the peaks are well fitted by Debye model on the high-frequency side, they are broader on the low-frequency side. The overall width at half-maximum is about 2 decades compared to 1.14 decades for the Debye model. The widths at half-maximum were about 2.25 decades for polypropylene and 3.2 decades for Irganox 1010.

We conclude that the ultralow temperature relaxation is due to the motion of hydroxyl groups either on an antioxidant or on the polymer as a result of oxidation. If the concentration of hydroxyl groups is very low, the relaxation is very close to the Debye model. At higher concentrations in polypropylene and especially in Irganox

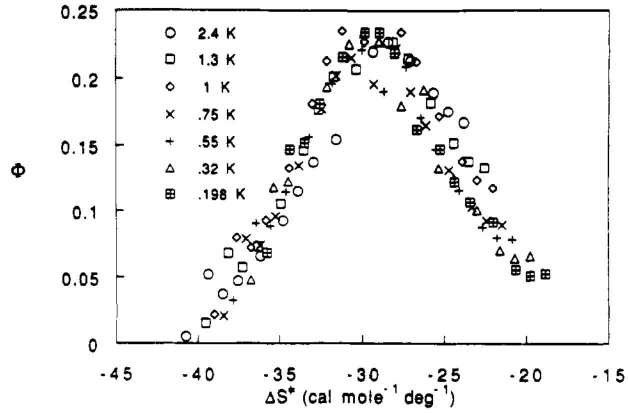


Figure 10. Distribution of activation entropies for the ultralow temperature relaxation in polypropylene.

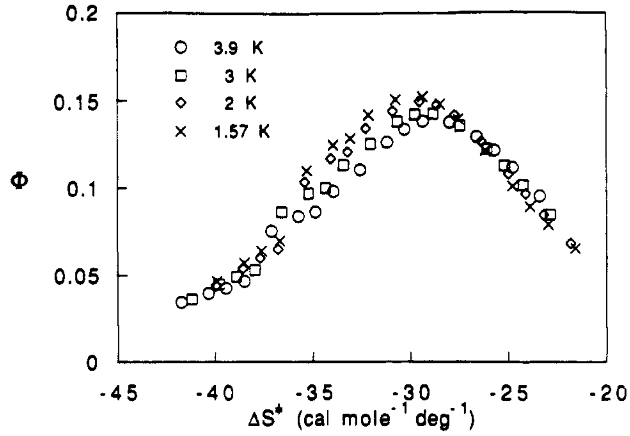


Figure 11. Distribution of activation entropies for the ultralow temperature relaxation in Irganox 1010.

1010, the distribution of relaxation times is broadened significantly.

In an earlier paper,[24] we discussed the distribution of activation enthalpies for relaxations for which the activation entropy was zero or a positive constant. A similar approach can be taken to determine the distribution of activation entropies when the activation enthalpy is zero. Provided a relaxation is not too close to the Debye model, the distribution of relaxation times or the corresponding activation entropies can be given by the following equation where $\Phi(\ln \tau) d \ln \tau$ is the fraction of the relaxation having relaxation times between $\ln \tau$ and $(\ln \tau + d \ln \tau)$.[25]

$$\Phi(1/\omega) = \frac{2}{\pi} \frac{\epsilon''(\omega)}{\epsilon_r - \epsilon_u} \qquad (4)$$

Here, ϵ'' is the dielectric loss factor and ϵ_r and ϵ_u are the relaxed and unrelaxed permittivities as determined from Cole–Cole plots.

It follows from eq 2 that if $\Delta H^{\ddagger} = 0$

$$-\Delta S^{\ddagger} = \Delta F^{\ddagger}/T = R[\ln (k/2\pi h) + \ln (T/f)] \qquad (5)$$

Then, a plot of Φ vs $\Delta S^{\ddagger}$ gives the distribution of activation entropies. If $\Delta H^{\ddagger}$ is indeed zero, this distribution should be independent of temperature.

These distributions are shown for polypropylene in Figure 10 and Irganox 1010 in Figure 11. In both cases, the distributions are substantially independent of temperature. The widths at half-maximum are about 11 cal mol^{-1} deg^{-1} for polypropylene and about 15 cal mole^{-1} deg^{-1} for Irganox 1010. It should be noted that if this procedure had been applied inappropriately to a Debye relaxation, the apparent width at half-maximum would have been about 5 cal mol^{-1} deg^{-1}.

Conclusions

There is a dielectric relaxation in polyethylene, polypropylene, and the stabilizer, Irganox 1010, within a few degrees of absolute zero. For these relaxations, both the frequency and the activation free energy are proportional to the absolute temperature with $f/T \cong 1$ kHz/K. These relationships are attributed to quantum mechanical tunneling with an activation enthalpy of zero.

This ultralow temperature relaxation was absent in a sample of polyethylene containing no stabilizer and which had never been exposed to oxygen or moisture. Combining our observations with those of earlier workers,[4-19] we conclude that this relaxation probably reflects the motion of hydroxyl groups either on a stabilizer or on the polymer through oxidation or some other chemical process.

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Registry No. Polyethylene, 9002-88-4; polypropylene, 9003-07-0; Irganox 1010, 6683-19-8.