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Distribution of Activation Enthalpies in Viscoelastic Relaxations

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ABSTRACT: The distribution of relaxation times in viscoelastic relaxations can be expressed as the corresponding distribution of activation enthalpies, assuming that the activation entropy is constant. When this is done, the earlier finding that certain simple, noncooperative motions have activation entropies close to zero is confirmed. The widths of the distributions of activation enthalpy for many relaxations are quite similar, even though the distribution of relaxation times is much broader for secondary relaxations, which are observed at low temperatures, than for glass transitions. This is shown to be a natural property of the formalism. When the frequency–temperature behavior of local-mode relaxations is analyzed, it is found that the data on the low-temperature side of the loss peak correspond to an activation entropy close to zero while those on the high-temperature side give much larger activation energies and entropies.

Previously, we have described a category of simple, noncooperative relaxations having activation entropies close to zero.[1,2] These include rotations of methyl groups,[1] certain side-group motions,[2] local-mode relaxations which are restricted to short polymethylene sequences,[2] the crystalline α-relaxation in poly(oxymethylene),[3] and grain boundary relaxations in metals.[2] A puzzling aspect of these relaxations, which frequently reflect motions of small submolecular fragments, is that they are often much broader on a time or frequency scale than glass transitions, which are highly cooperative and are characterized by large activation enthalpies and entropies. We have now found that some understanding of this contrast can be gained through consideration of distributions of activation parameters.

Viscoelastic relaxations in solids or liquids are always broader than a Debye relaxation. This broadening can be expressed in many different ways, such as distribution of relaxation times[4] or a stretched exponential function.[5,6] A distribution of relaxation times might in turn reflect a distribution of activation energies, a distribution of preexponential factors, or both.

The quantity $\Phi(\ln \tau)\mathrm{d}\ln \tau$ is the fraction of the relaxation process having relaxation times between $\ln \tau$ and $(\ln \tau + \mathrm{d}\ln \tau)$.[4] Thus

$$\int_{-\infty}^{\infty}\Phi(\ln \tau)\mathrm{d}\ln \tau = 1 \tag{1}$$

In a stress relaxation experiment, the relaxation modulus, $E(t)$, is given by

$$E(t) = E_r + (E_u - E_r)\int_{-\infty}^{\infty}\Phi(\ln \tau)e^{-t/\tau}\,\mathrm{d}\ln \tau \tag{2}$$

where E_u and E_r are the limiting unrelaxed and relaxed moduli.

In a dynamic mechanical experiment, the storage and loss moduli, E' and E'', are

$$E'(\omega) = E_r + (E_u - E_r)\int_{-\infty}^{\infty}\frac{\Phi_E(\ln \tau)\omega^2\tau^2\,\mathrm{d}\ln \tau}{1+\omega^2\tau^2} \tag{3}$$

$$E''(\omega) = (E_u - E_r)\int_{-\infty}^{\infty}\frac{\Phi_E(\ln t)\omega\tau\,\mathrm{d}\ln \tau}{1+\omega^2\tau^2} \tag{4}$$

Analogous expressions can be written for the dielectric permittivity and loss factor.

$$\epsilon'(\omega) = \epsilon_u + (\epsilon_r - \epsilon_u)\int_{-\infty}^{\infty}\frac{\Phi_\epsilon(\ln \tau)\,\mathrm{d}\ln \tau}{1+\omega^2\tau^2} \tag{5}$$

$$\epsilon''(\omega) = (\epsilon_r - \epsilon_u)\int_{-\infty}^{\infty}\frac{\Phi_\epsilon(\ln \tau)\omega\tau\,\mathrm{d}\ln \tau}{1+\omega^2\tau^2} \tag{6}$$

There are a number of approximations for obtaining the relaxation spectrum from experimental data.[4]

The one used here is

$$\Phi_E(1/\omega) = \frac{2E''(\omega)}{\pi(E_u - E_r)} \tag{7}$$

The distribution can also be obtained from the following equation or analogous expressions for data from creep or stress relaxation experiments.

$$\Phi_E(1/\omega) = -\frac{\mathrm{d}\,E'(\omega)}{\mathrm{d}\ln \omega}\frac{1}{(E_u - E_r)} \tag{8}$$

The relationship between the frequency of a relaxation, $f = 1/(2\pi\tau)$, and the temperature is given by the following expression due to Eyring.

$$f = \frac{kT}{2\pi h}e^{-\Delta H^\ddagger/RT}e^{\Delta S^\ddagger/R} = \frac{kT}{2\pi h}e^{-\Delta F^\ddagger/RT} \tag{9}$$

The activation enthalpy, $\Delta H^\ddagger$, is related to the Arrhenius activation energy, E_a, by[1]

$$E_a = \Delta H^\ddagger + RT \tag{10}$$

Rearranging eq 9 to solve for $\Delta F^\ddagger$

$$\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = RT[\ln (k/2\pi h) + \ln (T/f)] \tag{11}$$

In our previous work,[1-3] we used the following relationship between E_a and T', the temperature of a loss maximum at a frequency of 1 Hz when $\Delta S^\ddagger = 0$.

$$E_a = RT'[1 + \ln (k/2\pi h) + \ln T'] \tag{12}$$

We will now use eq 11 to characterize an entire loss peak, not just the maximum. Dynamic mechanical or dielectric data are taken over a range of temperature and frequency. The unrelaxed and relaxed moduli or permittivities are obtained from a complex plane plot of E'' vs E' or ϵ'' vs ϵ'. For each combination of temperature and frequency, Φ is calculated from eq 7 and plotted against $\Delta F^\ddagger$ from eq 11.

If the data for all the temperatures form a common pattern, $\Delta S^\ddagger = 0$ and $\Delta H^\ddagger = \Delta F^\ddagger$. This may already be known through the application of eq 12. The plot then represents the distribution of activation enthalpies.

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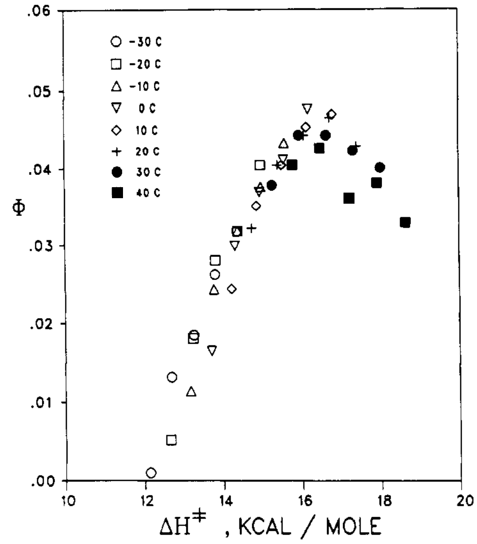

Figure 1. β-Relaxation in PMMA.

If the data from different temperatures do not fall on a single relationship of Φ vs $\Delta F^\ddagger$, it may be possible to bring them into concert by shifting along the $\Delta F^\ddagger$ axis. If the distribution of relaxation times reflects a constant $\Delta S^\ddagger$ and a distribution of $\Delta H^\ddagger$, that can be evaluated through the following equations.

$$\Delta S^\ddagger = -\mathrm{d}\Delta F^\ddagger/\mathrm{d}T \qquad \Delta H^\ddagger = \Delta F^\ddagger + T\Delta S^\ddagger \tag{13}$$

If, on the other hand, $\Delta H^\ddagger$ is constant and $\Delta S^\ddagger$ is distributed, the following equations are applicable.

$$\Delta H^\ddagger = \frac{\mathrm{d}(\Delta F^\ddagger/T)}{\mathrm{d}(1/T)} \qquad \Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta F^\ddagger}{T} \tag{14}$$

Dynamic mechanical data were obtained with either the Du Pont Dynamic Mechanical Analyzer (DMA) Model 983 or the Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA). With both of these instruments, data can be taken over a range of defined frequencies. Dielectric data were obtained as described in ref 7.

Simple Noncooperative Relaxations

The β-relaxation in poly(methyl methacrylate) (PMMA) has been identified as one in which the activation entropy is close to zero.[2] It has been attributed to the local motion of ester side groups and the atoms immediately adjacent. A plot of Φ vs $\Delta H^\ddagger$ ($=\Delta F^\ddagger$) is shown in Figure 1. The fact that the data from various temperatures conform to a single relationship confirms the earlier conclusion that $\Delta S^\ddagger$ is close to zero.

We have found that, in the case of the β-relaxation in polycarbonate, $\Delta S^\ddagger$ is close to zero for dielectric but not dynamic mechanical data.[7] This is confirmed by the plot of Φ vs $\Delta H^\ddagger$ ($=\Delta F^\ddagger$) for the dielectric data in Figure 2.

A different kind of internal motion that has also been found to have an activation entropy close to zero is the crystalline α-relaxation in poly(oxymethylene).[3] This process, for which the maximum in E'' occurs at 104 °C at 1 Hz, dominates the long-term mechanical behavior near room temperature. A plot of Φ vs $\Delta H^\ddagger$ ($=\Delta F^\ddagger$) based on the data in ref 3 is shown in Figure 3. In this case, the variation of the unrelaxed modulus, E_u, with temperature was taken into account in applying eq 7. While the data are limited at high temperatures by the onset of melting, it is clear that this relaxation fits the same pattern as those discussed above.

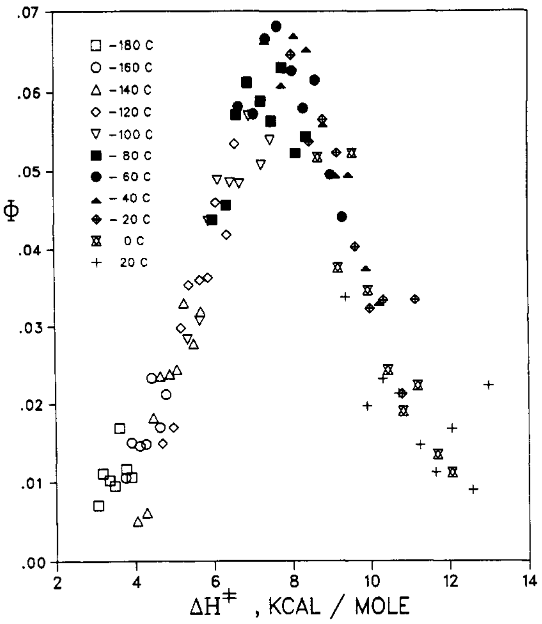

Figure 2. β-Relaxation in polycarbonate (dielectric data).

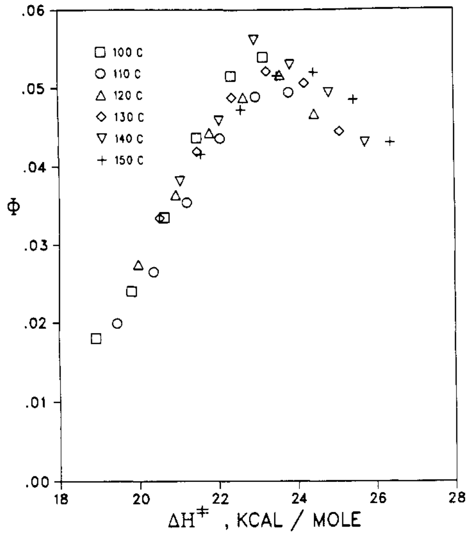

Figure 3. α-Relaxation in poly(oxymethylene).

Glass Transitions

The glass transition in polycarbonate is a particularly suitable subject for study because it is well separated from the secondary β-relaxation. Figure 4 is a plot of Φ from eq 7 vs the free energy of activation, $\Delta F^\ddagger$, from eq 11. It is clear that the data from different temperatures would fall on the same relationship only after shifting along the horizontal axis. Those shift factors, using 145 °C as the reference temperature, are shown in Figure 5. The slope of the line corresponds to an activation entropy of 507 cal deg^{-1} mol^{-1}. Through the application of eq 13, one can compute the distribution of activation enthalpies shown in Figure 6.

We have also used eq 14 to treat the data in terms of a distribution of activation entropies and a fixed activation enthalpy of 234 kcal/mol. Statistically, both approaches give equally good fits. We prefer to consider a fixed value of $\Delta S^\ddagger$ and a distribution in $\Delta H^\ddagger$, since that model seems to work well for the noncooperative relaxations where $\Delta S^\ddagger$ is close to zero. Distributions in both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ cannot be ruled out, but at present we see no way to define them uniquely.

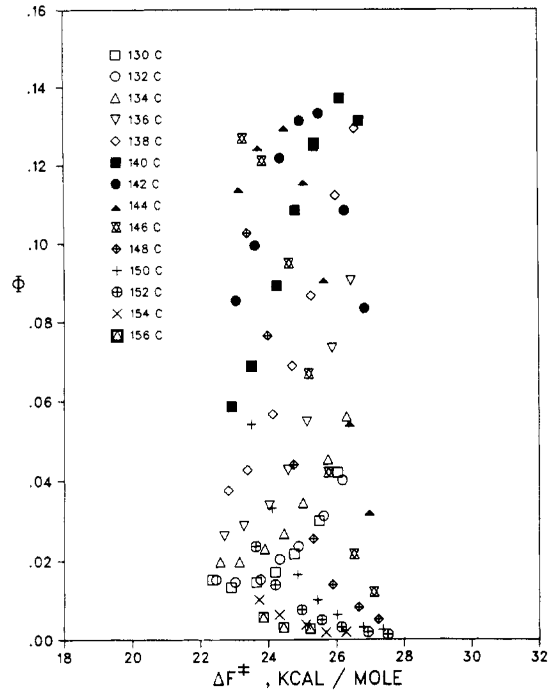

Figure 4. Φ vs ΔF^* for the glass transition in polycarbonate.

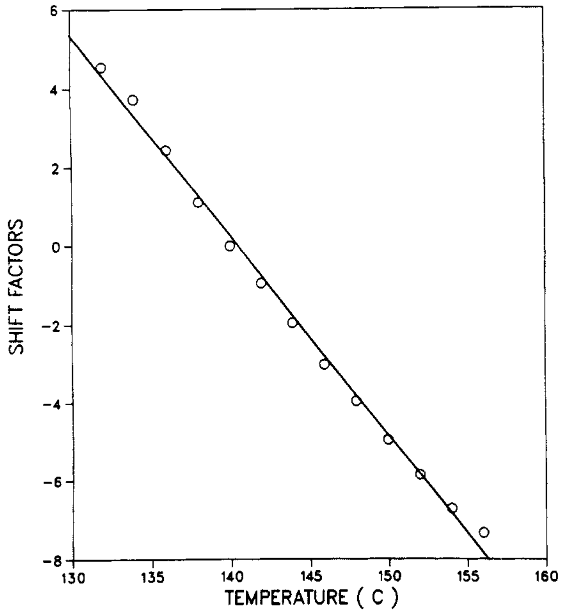

Figure 5. Shift factors for the glass transition in polycarbonate.

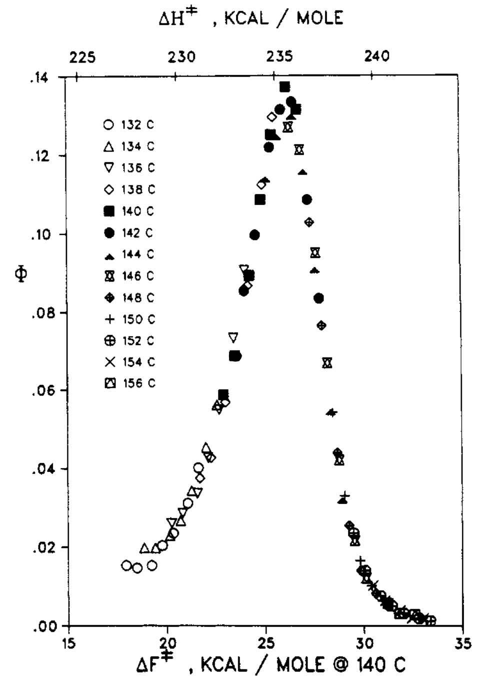

Figure 6. Φ vs ΔF^* for the glass transition in polycarbonate.

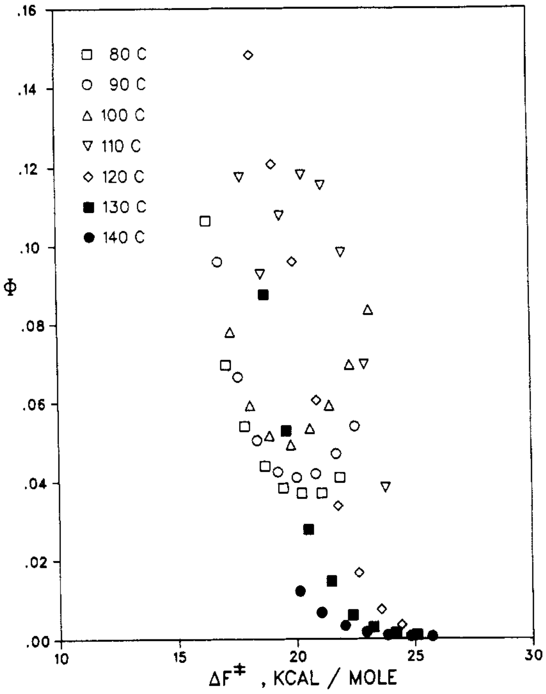

Figure 7. Φ vs ΔF^* for the glass transition in PMMA.

The glass transition in PMMA is impacted by the proximity of the β-relaxation. When the isotherms for Φ vs ΔF^* in Figure 7 were shifted along the horizontal axis to form a common curve, the shift factors varied linearly with temperature only at 110 °C and above. The calculated activation entropy was 168 cal deg^{-1} mol^{-1}. The resulting relationship between Φ and ΔH^* derived from eq 13 is shown in Figure 8.

This behavior is not limited to glass transitions in polymers. The distribution of activation enthalpies for soda–lime–silica glass is shown in Figure 9. This was based on stress relaxation data[8] treated according to eq 8. For this material, the activation entropy was 136 cal deg^{-1} mol^{-1}.

All of the samples discussed here were cooled rapidly from the melt and are thus far from equilibrium below T_g. It would be of interest to study the effect of physical aging on the distribution of activation parameters.

Local-Mode Relaxations

Traditionally, the activation energies of viscoelastic relaxations have been calculated from the frequency–temperature relationships for the maxima in tan δ, the loss modulus, E'', or the dielectric loss factor, ϵ''. When this procedure is followed, most local-mode (γ) relaxations exhibit substantial positive activation entropies.[1,2] If, however, the motion is limited to a short sequence of chain atoms, the activation entropy is close to zero.

A plot of Φ vs ΔF^* for the γ-relaxation in high-density polyethylene is shown in Figure 10. The data from the low-temperature (low ΔF^*) side of the peak lie on a common relationship, indicating that, for this portion of

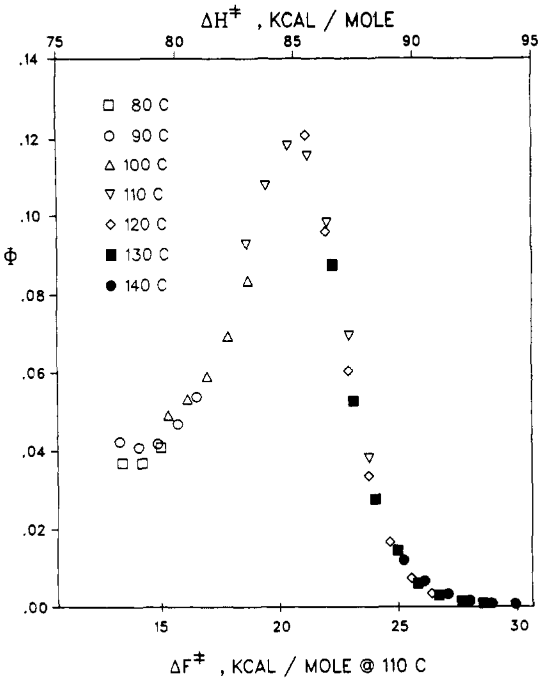

Figure 8. Φ vs ΔH^* for the glass transition in PMMA.

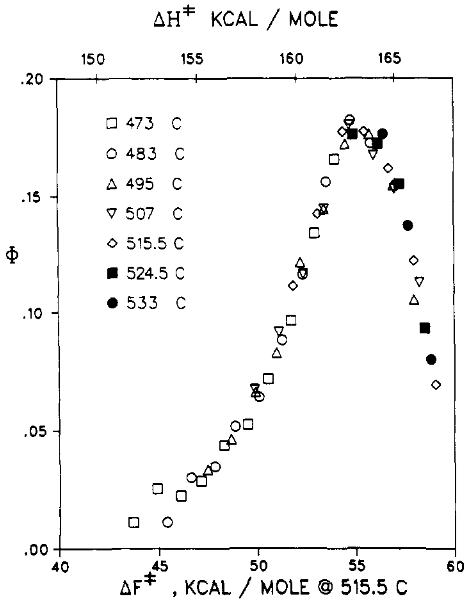

Figure 9. Φ vs ΔF^* for soda-lime-silica glass.

the relaxation, the activation entropy is close to zero. On the other hand, the points corresponding to the high temperature side of the peak would form a common relationship only if shifted along the ΔF^* axis by a different amount for each temperature. This property, which we have already found to apply to glass transitions, is indicative of a finite, positive activation entropy.

We have already described a somewhat similar situation, which was found for poly(butylene terephthalate).[2] In that case, there was a shoulder on the low-temperature side of the β-relaxation, which unlike the main peak was characterized by an activation entropy near zero.

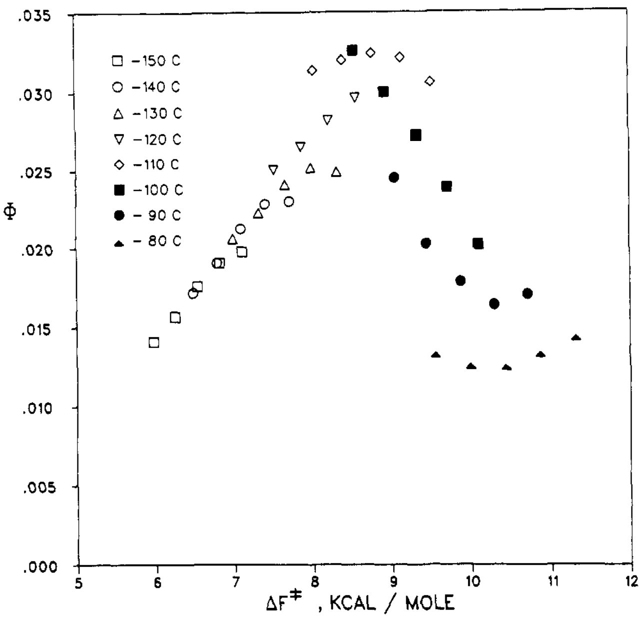

Figure 10. Distribution of activation free energies for the γ-relaxation in high-density polyethylene.

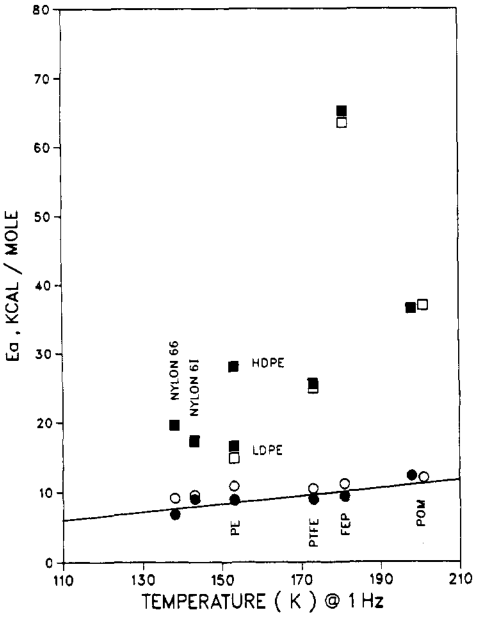

Figure 11. Activation energies of local-mode relaxations: (open points) from tan δ; (filled points) from E''; (circles) from the low-temperature side of the peak; (squares) from the high-temperature side of the peak; (line) $\Delta S^* = 0$.

When frequency-temperature shifting is done carefully for local-mode relaxations, radically different activation energies are determined from the data on the low- and high-temperature sides of the loss peaks. As shown in Figure 11, the low-temperature data give activation energies corresponding to activation entropies close to zero. The data from the high-temperature sides of the loss peaks give much larger activation energies and entropies. The figure includes data for high- and low-density polyethylene (HDPE, LDPE), poly(tetrafluoroethylene) (PTFE), poly(oxymethylene) (POM), and nylons 66 and 6I. The nylon samples were dry. FEP resin, the copolymer of tetrafluoroethylene and hexafluoropropylene, has an extremely high apparent activation energy on the high-temperature side of the peak because the β-relaxation, which is associated with the room-temperature crystalline transitions in PTFE, has been shifted downward in temperature to the point where it is merged with the γ-relaxation. Activation energies computed from the temperature-frequency relationships from the loss maxima may occur anywhere between the limits discussed here.

We suspect that, in many cases, local-mode relaxations reflect a spectrum of internal motions. The component that is prominent at the lowest temperatures

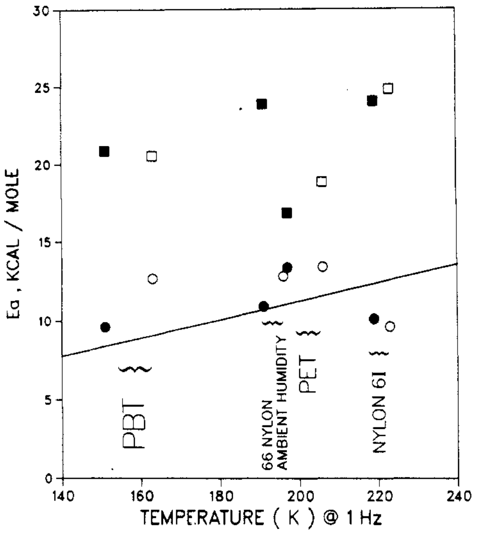

Figure 12. β-Relaxations in condensation polymers (symbols same as Figure 11).

Table I
Distribution of Activation Enthalpies

polymer	relaxation	$\delta\Delta H^*$ (width at half-maximum), kcal/mol	cohesive energy, kcal/mol of anonomer units
PMMA	β	5.4	7.2
	α^a	6.1	
polycarbonate	β	5.6	12.9
	α^a	4.8	
poly(oxymethylene)	α	6.0	2.5
silica glass	a	7.5	1.35

[a] Glass transition.

involves the minimum number of chain atoms. At slightly higher temperatures, cooperative motions of longer chain segments come into play.

Other Secondary Relaxations

The activation energies determined from the low- and high-temperature sides of the dynamic mechanical loss peaks for the β-relaxations in several condensation polymers are plotted against the peak temperature at a frequency of 1 Hz in Figure 12. The examples include two polyesters, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), and two polyamides, nylons 66 and 6I. The sample of nylon 66 was equilibrated to ambient humidity (about 2% water) where the β-relaxation is most prominent. In all cases, the low-temperature activation energy corresponded to an activation entropy close to zero, and the high-temperature activation energies and entropies were much larger.

Discussion

We have found that a variety of dynamic mechanical and dielectric relaxations can be characterized in terms of a distribution of activation enthalpies. This applies both to simple, noncooperative relaxations for which the activation entropy is close to zero and glass transitions, which have large positive activation entropies. A surprising finding is that the breadth of the distribution of activation enthalpies is similar for both categories. As summarized in Table I, the full-width at half-maximum is 5–6 kcal/mol for the organic polymers and 7.5 kcal/mol for the silica glass. When eq 9 is differentiated, it is seen that the width of the distribution in frequency ($\delta \ln f$) is related to the corresponding width in activation enthalpy ($\delta\Delta H^*$) by the following expression.

$$\delta \ln f = -\frac{\delta\Delta H^*}{RT} \qquad (15)$$

Thus, for relaxations having similar values of $\delta\Delta H^*$, those which occur at low temperatures will be much more diffuse in frequency and will exhibit a much broader distribution of relaxation times.

It has been suggested[9] that the distribution of activation enthalpies may reflect a modulation of the average value by a quantity corresponding to the cohesive energy associated with a small polymer segment. These quantities are compared in Table I. The cohesive energies of polymers were taken from the tabulations of Van Krevelen.[10] The agreement is within a factor of 2.5. For soda–lime–silica glass, $\delta\Delta H^*$ corresponds to the cohesive energy associated with about six SiO_2 units.[11]

Earlier work on the distribution of activation enthalpies in dielectric relaxations reviewed by Kauzmann[12] did not include secondary relaxations. He suggested that the distribution might arise from fluctuations due to the thermal energy or in the case of polymers "from the indefiniteness in the size of the segments which are acting as the kinetic units in the relaxation process". The latter suggestion does not seem likely for the noncooperative relaxations and certainly should not apply equally to all categories discussed here.

Registry No. PMMA, 9011-14-7; poly(oxymethylene), 9002-81-7; polyethylene, 9002-88-4.

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