

# Aspects of simple, non-cooperative relaxations

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The lower limit for the activation energies of internal motions in polymers is defined by a relationship corresponding to an activation entropy of zero. We associate this characteristic with non-cooperative motions of molecular segments. While these motions are localized in space, they are very diffuse in frequency or time. Examples are side-group relaxations and certain motions within the crystalline regions. Local-mode  $\gamma$  relaxations of the main chain appear to involve a spectrum of motions in which the limiting low-temperature, high-frequency component has an activation entropy close to zero. Glass transitions characteristically have very large apparent activation energies and entropies. This is attributed to a spectrum of motions that is sampled differently at different temperatures. At temperatures well above  $T_g$ , the apparent activation energy again approaches a value corresponding to a zero activation entropy. For a wide variety of relaxations, the distribution of relaxation times corresponds to a distribution of activation enthalpies having a width at half-maximum of 5–6 kcal mol<sup>-1</sup>.

(Keywords: relaxation; activation energy; molecular motion; glass transition)

## INTRODUCTION

It is well known that the frequency of a viscoelastic relaxation, like the rate of a chemical reaction, increases with increasing temperature. This relationship can be expressed in terms of an Arrhenius equation:

$$f = A \exp(-E_a/RT) \quad (1)$$

An alternative expression comes from the Eyring theory of absolute reaction rates:

$$f = \frac{kT}{2\pi h} \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (2)$$

The Arrhenius activation energy  $E_a$  is thus:

$$E_a = -R \, d \ln f / d(1/T) \quad (3)$$

and the Eyring activation enthalpy  $\Delta H^\ddagger$  is:

$$\Delta H^\ddagger = -R \, d \ln(f/T) / d(1/T) \quad (4)$$

The relationship between them is:

$$E_a = \Delta H^\ddagger + RT \quad (5)$$

Combining equations (2) and (5), one obtains:

$$E_a = RT[1 + \ln(k/2\pi h) + \ln(T/f)] + T\Delta S^\ddagger \quad (6)$$

We have found<sup>1,2</sup> that for many relaxations, particularly those involving small, submolecular fragments moving independently of one another, the activation entropy  $\Delta S^\ddagger$  is close to zero. If this is the case and  $T'$  is the temperature in kelvins at which the frequency of the relaxation is 1 Hz,  $E_a$  follows a simple, almost linear, dependence on temperature:

$$E_a = RT'[1 + \ln(k/2\pi h) + \ln T'] \quad (7)$$

The extent to which the activation energy exceeds this value is equal to  $T'\Delta S^\ddagger$ .

Equation (7) defines an effective lower limit for the

activation energies of viscoelastic relaxations. That is, few if any relaxations have significantly negative activation entropies.

For the class of relaxations for which  $\Delta S^\ddagger = 0$ , equation (2) has the advantage over equation (1) in that only a single parameter is needed to define the relationship between the temperature and the frequency. Equation (7) corresponds to a pre-exponential factor  $A$  in equation (1) of  $9.0 \times 10^9 T'$  or  $2.7 \times 10^{12}$  for a relaxation having a frequency of 1 Hz at 300 K.

## RELAXATIONS

### *Side-group relaxations*

The Arrhenius activation energy  $E_a$  is plotted against the temperature at 1 Hz for relaxations that have been attributed to alkyl<sup>1</sup> and ester<sup>2</sup> side-groups in *Figure 1*. All of these data lie close to the line that corresponds to equation (7).

The alkyl groups include the main-chain methyl groups in several methacrylate polymers (poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and poly(butyl methacrylate) (PBMA)) as well as the ethyl group in poly(ethyl methacrylate). In some references, motions attributed to the main-chain methyls in heterotactic and syndiotactic sequences in poly(methyl methacrylate) have been distinguished, and these relaxations also fit the pattern. This is also true of relaxations assigned to motions of the methyl side-groups in polypropylene (PP) and polyisobutylene (PIB). A low-temperature relaxation in FEP fluorocarbon resin, a copolymer of tetrafluoroethylene and hexafluoropropylene, has been assigned to the motion of CF<sub>2</sub>H groups<sup>3</sup>.

The  $\beta$  relaxations in poly(methyl methacrylate) and poly(vinyl acetate) (PVAc) are attributed to the local

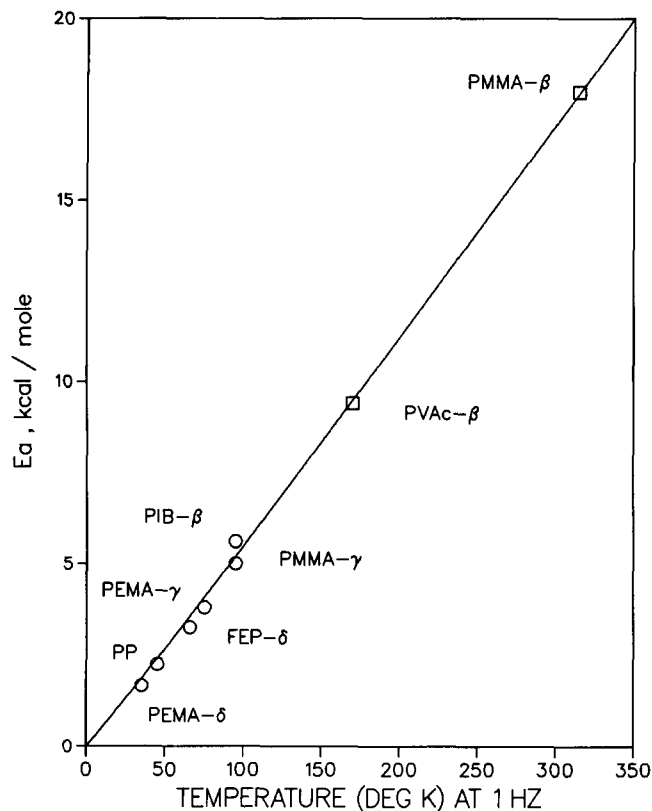


Figure 1 Side-group relaxations: (—)  $\Delta S^\ddagger = 0$ ; (O) alkyl groups; (□) ester groups

motions of ester side-groups<sup>4</sup>. In the case of PMMA, this has been supported by calculations of the energy involved using the methods of molecular mechanics<sup>5,6</sup>. As shown in Figure 1, these relaxations conform closely to the conditions for a zero activation entropy. For PMMA, the activation energy is close to that computed by Heijboer and coworkers<sup>6</sup>.

Further support for the belief that the  $\beta$  relaxations in poly(vinyl acetate) and poly(methyl methacrylate) involve non-cooperative motions comes from the observations that they are unaffected by additives such as toluene<sup>2</sup>, acetone<sup>2</sup> and dibutyl phthalate<sup>7,8</sup>, all of which shift the glass transition to lower temperatures.

#### Local-mode relaxations

It has long been recognized that all polymers having sequences of four or more methylene units exhibit a loss peak similar to the  $\gamma$  relaxation in polyethylene<sup>9</sup>. It has also been recognized that local motions of the main chain may also involve somewhat longer sequences<sup>10,11</sup>. Similar relaxations occur in other simple chain structures such as polytetrafluoroethylene and polyoxymethylene<sup>4</sup>.

The relationship between the activation energy calculated from the loss maxima and the temperature at 1 Hz for the local-mode relaxations in a number of polymers is shown in Figure 2. In poly(butylene terephthalate) (4GT) and nylon-6,I, which contain sequences of only four or six methylene units, the data conform to the relationship for a zero activation entropy. For nylon-6,6, the activation entropy is positive when dry and near zero when wet. We believe that, at these low temperatures, water forms mechanically stable bridges between amide groups in the amorphous regions. This limits the local

motions to the individual sequences of four or six methylene units. In copolymers of ethylene, the activation entropy increases as the mole fraction of ethylene and the average number of methylene units per sequence are increased. Not surprisingly, the largest activation entropy was found in high-density polyethylene (HDPE).

A somewhat different picture was found when activation energies were calculated by separately performing frequency-temperature shifting of data on the low- and high-temperature sides of the loss peaks<sup>12</sup>. As shown in Figure 3, the data from the low-temperature side lie close to the line for a zero activation entropy, while the activation energies from data on the high-temperature side are 2–4 times as large. The very large value for FEP resin is attributed to overlapping of the  $\gamma$  and  $\beta$  relaxations.

We conclude that in many polymers the local-mode relaxation involves the motion of a spectrum of chain segment lengths with a well defined minimum value. The data at the lowest temperatures reflect the motions of the shortest chain segments, which are most easily excited.

The behaviour of the  $\beta$  relaxations in polyamides and polyesters is similar to that for the polymethylene local-mode relaxations<sup>12</sup>. There, as well, the data on the low-temperature side of the loss peaks correspond to activation entropies close to zero, while the activation energies computed from data on the high-temperature side are about twice as large. Here again, we surmise that the relaxations reflect motions of a distribution of segment lengths with a well defined minimum.

In another study<sup>13</sup>, the dynamic mechanical and dielectric properties were compared for the  $\beta$  relaxations in a series of polymers having phenylene linkages in their chains. These included polycarbonate, poly(ether ether ketone) (PEEK) and BPA-I/T (50/50), a polyester made from bisphenol A and an equimolar mixture of isophthalic and terephthalic acids. In each case, the

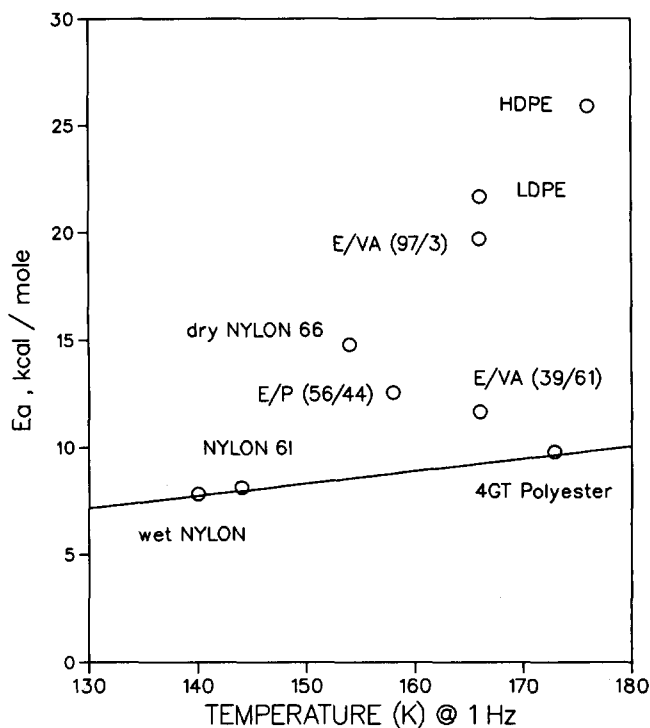


Figure 2 Activation energies for local-mode relaxations based on the positions of the loss maxima: (—)  $\Delta S^\ddagger = 0$

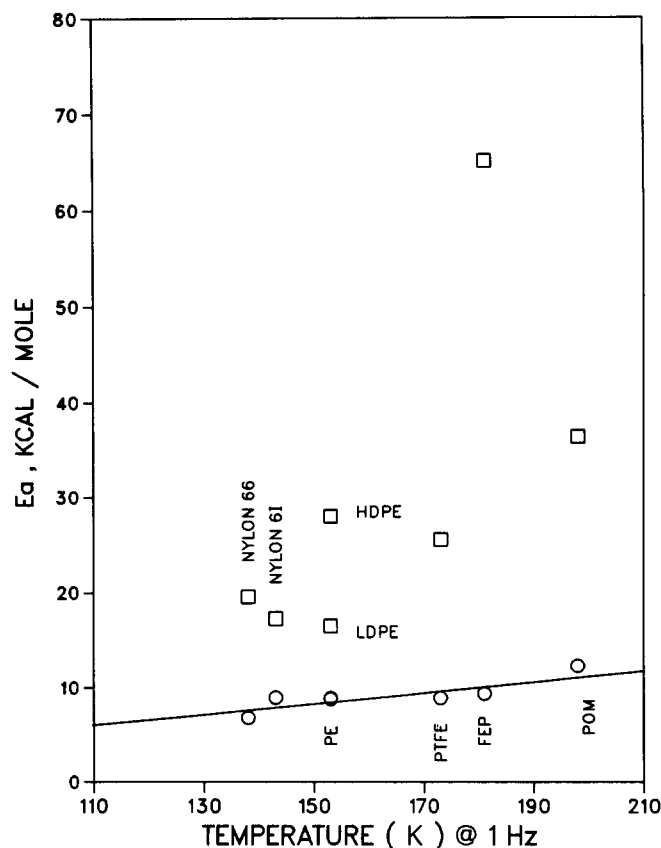


Figure 3 Activation energies of the low- and high-temperature components of local-mode relaxations: (—)  $\Delta S^\ddagger = 0$ ; (○) low-temperature side of the peak; (□) high-temperature side of the peak

mechanical relaxation was observed at a higher temperature or a lower frequency than the dielectric relaxation. The dielectric relaxations had activation entropies close to zero, while the apparent activation energies of the mechanical relaxations were 1.5–2 times as large. It was concluded that the dielectric relaxation represents the high-frequency, low-temperature component of a broader mechanical relaxation.

In contrast with these polymers, the mechanical and dielectric  $\gamma$  and  $\beta$  relaxations in nylon-6,I followed the same frequency–temperature relationships. Since the activation entropies for these relaxations are close to zero, it is believed that the internal motions are more sharply defined on a segmental level.

#### Crystalline relaxations

Perhaps the first relaxation in a polymer that was recognized to have a zero activation entropy was the  $\gamma_c$  relaxation in poly(chlorotrifluoroethylene)<sup>14</sup>. It is associated with local chain motions in the crystal. There have been occasional reports of what may be a similar process, called the  $\gamma_{III}$  relaxation, in polyethylene<sup>15,16</sup>.

Other crystalline relaxations in polymers are thought to involve longer-range effects. An important example is the  $\alpha$  relaxation in polyoxymethylene (POM), which has been found to have an activation entropy near zero<sup>17</sup>. The  $\alpha$  relaxation in polyethylene may also have this property, but this is uncertain because of the complexity due to multiple motions in the crystals. These relaxations are thought to involve conformational irregularities, which act as point defects or solitons and permit the transport of matter through the crystal in the direction

of the chains. The zero activation entropy is consistent with the view that these defects move independently of each other.

The  $\beta$  relaxation in polytetrafluoroethylene (PTFE) is a viscoelastic process that changes abruptly at the first-order thermodynamic transition at 19°C<sup>18</sup>. The strength of the relaxation increases with increasing crystallinity<sup>19</sup>. On the basis of these observations, it is assigned to the crystalline phase. A detailed analysis indicates that the relaxation that exists below the 19°C transition has an activation entropy close to zero<sup>20</sup>.

This characteristic is not limited to polymers. Grain boundary relaxations in several metals have activation entropies close to zero. Examples are tin, copper, aluminium and iron<sup>2</sup>.

#### GLASS TRANSITIONS

The apparent activation energies reported for glass transitions based on equation (3) are generally very large, frequently from 50 to 100 kcal mol<sup>-1</sup> or more. Let us rearrange equation (2) to give the activation free energy:

$$\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = RT[\ln(k/2\pi h) + \ln(T/f)] \quad (8)$$

As shown in Figure 4, the range of temperature and frequency of interest corresponds to activation free energies no greater than about 30 kcal mol<sup>-1</sup>. Therefore,

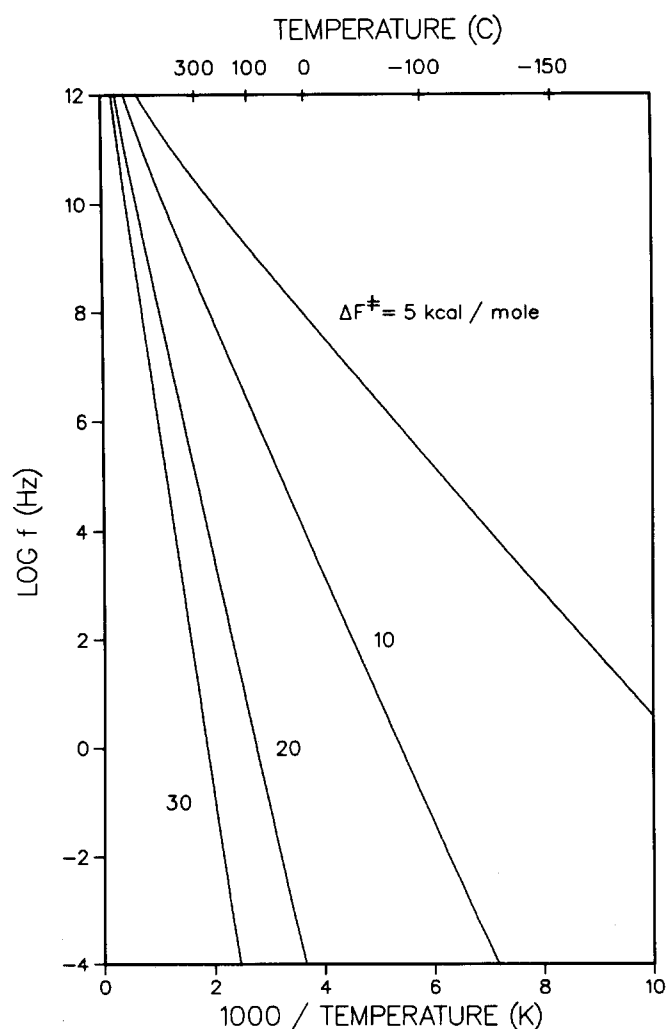


Figure 4 Arrhenius plot for various values of the activation free energy

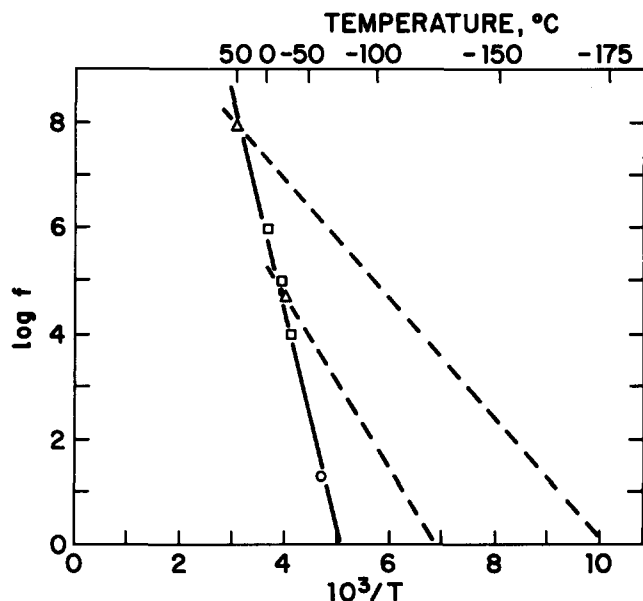


Figure 5 Relaxation map for the glass transition of an ethylene/propylene copolymer: (—) overall relaxation; (---) component relaxations from  $T_1$  and  $T_{1\rho}$ ; (○) mechanical; (□) dielectric; (Δ) n.m.r.

very large values for the apparent activation energy or enthalpy from equations (3) or (4) must go hand in hand with large activation entropies. The physical significance of a large positive activation entropy is even harder to understand than an activation energy greater than the strength of a chemical bond.

The contrast between complex viscoelastic relaxations such as the glass transition and chemical reactions is particularly striking. Many reactions have small pre-exponential factors corresponding to negative activation entropies. This indicates that the activated complex is more ordered than the reactants. On the other hand, this situation is rarely if ever observed for viscoelastic relaxations.

One possible explanation is that the glass transition reflects a spectrum of internal motions having different activation energies and involving molecular segments of varying sizes. As the frequency is increased, the absorption of energy is dominated by components having progressively smaller activation energies. This results in an apparent overall activation energy that is much larger than that of the simple, component relaxations and a large, positive apparent activation entropy.

An example of how this could happen is shown in Figure 5, which is an Arrhenius plot for the glass transition of an ethylene/propylene copolymer<sup>1</sup>. Data from dynamic mechanical, dielectric and proton n.m.r. measurements were combined to give a relationship having an apparent activation energy of  $18 \text{ kcal mol}^{-1}$  and an apparent activation entropy of  $40 \text{ cal K}^{-1} \text{ mol}^{-1}$ . Activation energies computed from the temperature dependence of the spin-lattice relaxation times,  $T_1$  and  $T_{1\rho}$ , correspond to the condition for a zero activation entropy. These relationships are indicated by the broken lines in Figure 5. A similar analysis has been done for a number of other elastomeric polymers including natural rubber and polyisobutylene<sup>1</sup>. In those cases as well, n.m.r. data gave activation energies of  $5\text{--}8 \text{ kcal mol}^{-1}$  and activation entropies close to zero, while Arrhenius

relationships based on mechanical and dielectric data gave activation energies on the order of  $30 \text{ kcal mol}^{-1}$ .

B. B. Sauer has collected data on the temperature dependence of the activation enthalpy based on thermally stimulated currents following charging in narrow temperature intervals<sup>21</sup>. An example is shown in Figure 6 for polycarbonate. Up to about 400 K, a region that includes the  $\beta$  relaxation, the data lie close to the relationship from equation (8) for the activation free energy  $\Delta F^\ddagger$ , indicating that  $\Delta S^\ddagger = 0$ . In the region of the glass transition, the activation enthalpy becomes very large, as much as five times  $\Delta F^\ddagger$ . At higher temperatures,  $\Delta H^\ddagger$  again decreases and approaches the relationship for a zero activation entropy.

It is well known that in many polymers the glass transition follows the relationship of Williams, Landel and Ferry<sup>22</sup>. In that treatment, the time-temperature shift factors are given by:

$$\ln a = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)} \quad (9)$$

where  $T_0$  is a reference temperature, sometimes the glass temperature, and  $C_1$  and  $C_2$  are constants. Combining equations (3) and (9), one obtains the following expression for the Arrhenius activation energy:

$$E_a = \frac{RT^2 C_1 C_2}{[C_2 + (T - T_0)]^2} \quad (10)$$

This relationship gives an activation energy that decreases with increasing temperature above  $T_0$ . For glass temperatures of  $50\text{--}100^\circ\text{C}$ ,  $E_a$  would cross the value for a zero activation entropy about  $60^\circ\text{C}$  above  $T_g$ . Examination of experimental data for a number of polymers<sup>4</sup> indicates that, at high temperatures,  $E_a$  approaches but does not fall below the value for a zero activation entropy when both the temperature and frequency of the measurements are considered.

In the treatment of Adam and Gibbs<sup>23</sup>, it was assumed that the activation energy is proportional to the size of the unit that must move cooperatively. A similar assumption was made by Matsuoka<sup>24</sup>. If the zero activation entropy condition corresponds to the non-cooperative motion of minimal submolecular units,

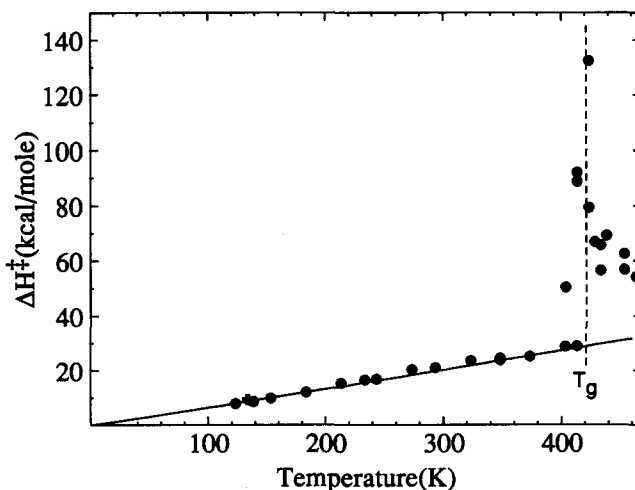


Figure 6 Activation energy versus temperature for polycarbonate based on measurements of thermally stimulated currents: (—)  $\Delta F^\ddagger$ ; (---)  $T_g$ .

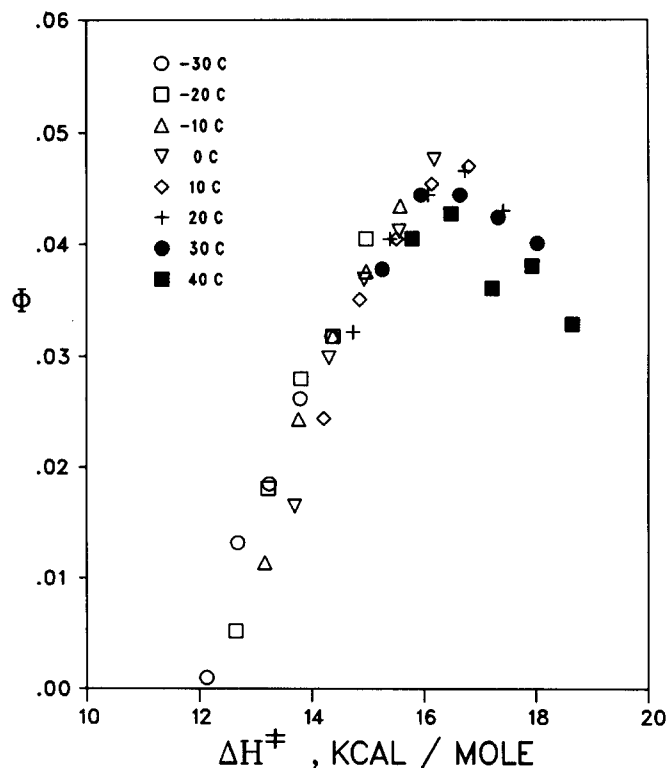


Figure 7 Distribution of activation enthalpies for the  $\beta$  relaxation in poly(methyl methacrylate)

a typical glass transition involves the cooperative motion of five to ten such units. The local-mode relaxations discussed above involve a spectrum of degrees of cooperation from one (non-cooperative) to two or three. At temperatures sufficiently far above the glass transition, the motion again becomes non-cooperative.

If the activation entropy associated with cooperativity is  $R \ln n$ , where  $n$  is the degree of cooperation, the maximum contribution to the apparent activation energy, i.e.  $RT \ln n$ , will be a few tenths of a kcal mol<sup>-1</sup> for a local-mode relaxation and about 2 kcal mol<sup>-1</sup> for glass transitions. These quantities are within experimental uncertainty for the Arrhenius activation energy. This is another reason why we believe that large apparent activation energies and entropies reflect temperature- and frequency-dependent sampling of a spectrum of related internal motions.

#### DISTRIBUTION OF ACTIVATION ENTHALPIES

Viscoelastic relaxations in solids or liquids are always broader than a Debye relaxation. This broadening can be expressed as a distribution of relaxation times<sup>4</sup>, which might in turn reflect a distribution of activation energies, a distribution of pre-exponential factors, or both.

The quantity  $\Phi(\ln \tau) d \ln \tau$  is the fraction of the relaxation process having relaxation times between  $\ln \tau$  and  $(\ln \tau + d \ln \tau)$ <sup>4</sup>. Thus:

$$\int_{-\infty}^{\infty} \Phi(\ln \tau) d \ln \tau = 1 \quad (11)$$

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

$$E'(\omega) = E_r + (E_u - E_r) \int_{-\infty}^{\infty} \frac{\Phi_E(\ln \tau) \omega^2 \tau^2 d \ln \tau}{1 + \omega^2 \tau^2} \quad (12)$$

$$E''(\omega) = (E_u - E_r) \int_{-\infty}^{\infty} \frac{\Phi_E(\ln \tau) \omega \tau d \ln \tau}{1 + \omega^2 \tau^2} \quad (13)$$

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

Analogous expressions can be written for the dielectric permittivity and loss factor. Two approximations for obtaining the relaxation spectrum from experimental data<sup>4</sup> are:

$$\Phi_E(1/\omega) = \frac{2E''(\omega)}{\pi(E_u - E_r)} \quad (14)$$

$$\Phi_E(1/\omega) = -\frac{dE'(\omega)}{d \ln \omega} \frac{1}{(E_u - E_r)} \quad (15)$$

Equation (8) is now used 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  $E''$  versus  $E'$  or  $\epsilon''$  versus  $\epsilon'$ . For each combination of temperature and frequency,  $\Phi$  is calculated from equation (14) or (15) and plotted against  $\Delta F^\ddagger$  from equation (8).

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 equation (7). The plot then represents the distribution of activation enthalpies.

The  $\beta$  relaxation in poly(methyl methacrylate) (PMMA) has been identified as one in which the activation entropy is close to zero<sup>2</sup>. It has been attributed to the local motion of ester side-groups and the atoms immediately adjacent. A plot of  $\Phi$  versus  $\Delta H^\ddagger$  ( $= \Delta F^\ddagger$ ) is shown in Figure 7. 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. The same pattern has been found for the dielectric  $\beta$  relaxation in polycarbonate and the crystalline  $\alpha$  relaxation in polyoxymethylene<sup>12</sup>.

A plot of  $\Phi$  versus  $\Delta F^\ddagger$  for the local-mode  $\gamma$  relaxation in high-density polyethylene is shown in Figure 8. The

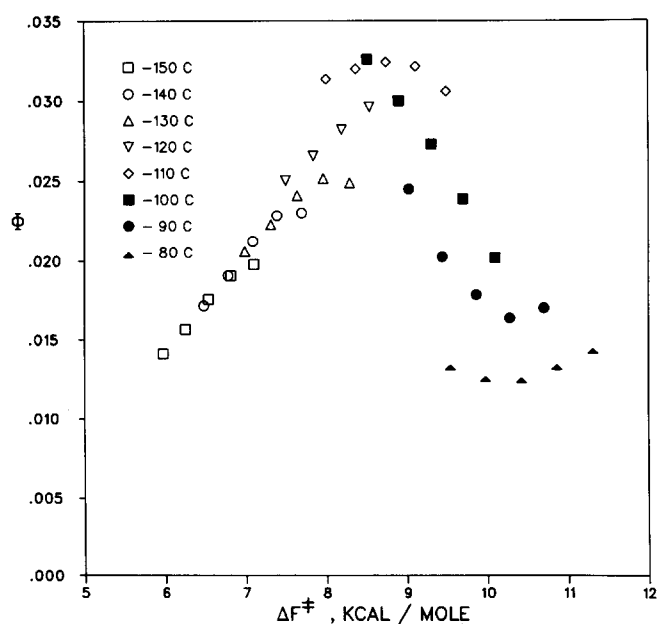


Figure 8 Distribution of activation free energies for the local-mode  $\gamma$  relaxation in high-density polyethylene

data from the low-temperature (low  $\Delta F^\ddagger$ ) side of the peak lie on a common relationship, indicating that, for this portion of 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  $\Delta F^\ddagger$  axis by a different amount for each temperature. This property is indicative of a finite, positive activation entropy and is consistent with the presentation in Figure 3.

For glass transitions, data from different temperatures in plots of  $\Phi$  versus  $\Delta F^\ddagger$  form a single relationship only after shifting along the  $\Delta F^\ddagger$  axis. From these shift factors, apparent activation entropies of  $507 \text{ cal K}^{-1} \text{ mol}^{-1}$  for polycarbonate and  $168 \text{ cal K}^{-1} \text{ mol}^{-1}$  for PMMA were computed<sup>12</sup>. As indicated earlier, these values seem to be unphysically large. We think that it is more reasonable that the very large apparent activation energies and entropies reflect distributions of internal motions that are sampled differently at different temperatures. A variety of dynamic mechanical and dielectric relaxations can be characterized in terms of a distribution of activation enthalpies. This applies both to simple, non-cooperative relaxations, for which the activation entropy is close to zero, and to glass transitions, which have large positive apparent activation entropies. A surprising finding is that the breadth of the distribution of activation enthalpies is similar for both categories. The full width at half-maximum is  $5\text{--}6 \text{ kcal mol}^{-1}$  for organic polymers and  $7.5 \text{ kcal mol}^{-1}$  for silica glass. When the logarithmic form of equation (2) 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 ( $\delta \Delta H^\ddagger$ ) by the following expression:

$$\delta \ln f = -\delta \Delta H^\ddagger / RT \quad (16)$$

Thus, for relaxations having similar values of  $\delta \Delta H^\ddagger$ , 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 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 agree within a factor of 2.5. For soda lime-silica glass,  $\delta \Delta H^\ddagger$  corresponds to the cohesive energy associated with about six  $\text{SiO}_2$  units<sup>12</sup>.

## CONCLUSIONS

There is a good deal of evidence that the fundamental internal motions in polymers and probably other materials have activation entropies close to zero. For relaxations involving side-groups and certain processes in crystals, these are simple, non-cooperative motions. Even though these motions are localized in space, they are highly diffuse in frequency or time. Local, main-chain motions frequently involve a distribution of processes with a well defined limit at low temperatures and high frequencies. In some cases, the molecular structure may restrict this motion to a single segment length, e.g. four methylene units. Glass transitions generally have very large apparent activation energies and entropies. This is thought to be due to a degree of cooperativity that is highly dependent on the temperature. In the limit of high temperatures above the glass transition, the apparent activation entropy again approaches zero, suggesting minimal cooperativity in the motion of chain segments.

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