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(13) Actually, two types of divergences appear, those which behave like ln a and those which behave like $1/a$. Discarding the latter corresponds to an arbitrary shifting of the zero of the free energy per monomer (see e.g., ref 14).

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(15) The unusual dimensionality of the conformation **C** arises from our choice of (II.1) for the Hamiltonian. If **r** is the real space conformation, then $\mathbf{r} = (l/d)^{1/2}\mathbf{C}$, where l is the usual Kuhn length.

(16) First introduced by t'Hooft: t'Hooft, G.; Veltman, M. *Nucl. Phys. B* **1972**, *B44*, 189.

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(18) It is interesting to note that the same analysis may be carried through with u not equal to u^*. It is found[19] that (III.12) takes the more general form

$$G = \exp\left[-\int_{u_1}^{u} \frac{A(u)}{L\dfrac{\partial u}{\partial L}}\,\mathrm{d}u\right] \times F\left(L \exp\left[-\int_{u_1}^{u} \frac{\mathrm{d}u}{L\dfrac{\partial u}{\partial L}}\right], N \times \exp\left[-\int_{u_1}^{u} \frac{\mathrm{d}u}{L\dfrac{\partial u}{\partial L}}\right], \mathbf{R}, \theta\right)$$

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Simple and Complex Relaxations

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ABSTRACT: Viscoelastic relaxations are considered to be simple or complex depending on their activation entropies. Simple relaxations have activation entropies near zero and reflect the motion of small molecular fragments without much cooperative involvement. Complex relaxations have large positive activation entropies and involve cooperative motions of neighboring groups or molecules. By these tests, alkyl group relaxations and relaxations due to the motion of small absorbed molecules are simple. Many main-chain local mode relaxations are complex, but some which are restricted due to crystallinity or hydrogen bonding are simple. Relaxations associated with the motion of polar groups may be either simple or complex. Glass transitions have large activation entropies. In some cases, however, they may consist of a spectrum of relaxations in which the individual components are simple.

Introduction

A puzzling aspect of viscoelastic relaxations in polymers is the large magnitude for the activation energies derived from Arrhenius plots. For glass transitions, it is not unusual to find activation energies of 50–100 kcal/mol, greater than the energy of a primary chemical bond. Clearly, such large activation energies indicate that there is a high degree of complexity in the motion associated with the relaxations. This impression of complexity is confirmed by large activation entropies for many of these relaxations. Moreover, this behavior is not limited to polymers.

In 1942 Kauzmann of Westinghouse published a survey on the application of absolute rate theory to relaxations in low molecular weight solids and liquids as well as polymers.[1] Chloropentamethylbenzene is one of several related compounds which exhibit relaxations in the solid state having small activation energies and zero or small activation entropies. The behavior of cyclopentanol, cyclohexanol,[2] and 2,3-dimethylbutane[2] is similar. Clearly, these relaxations involve very simple motions within the solids. In contrast with this, benzophenone has a dielectric relaxation in the solid with an activation energy of 45 kcal/mol and an activation entropy of 103 eu. This must be a much more complex relaxation.

Similar contrasts occur among low molecular weight liquids. Ethyl alcohol has a relaxation with an activation energy of only 4.7 kcal/mol and an activation entropy of 6 eu whereas supercooled propylene glycol has a relaxation with an activation energy of 20 kcal/mol and an activation

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entropy of 66 eu. Many alcohols exhibit secondary relaxations with very low activation energies and activation entropies near zero.[3-5]

Liquid water has a dielectric relaxation in the microwave region. Its activation entropy decreases from about 7.5 eu at room temperature to about 2 eu at higher temperatures.[6] When certain polymers are saturated with water and cooled, microscopic water-filled cavities are formed.[7] This water exhibits a dielectric relaxation having an activation energy of 7 kcal/mol and a temperature extrapolated to 1 Hz of about 125 K. This corresponds to an activation entropy near zero.

As in the case of low molecular weight solids and liquids, there are some secondary relaxations in polymers which have little or no activation entropy and relatively small activation energies. The relationship between frequency and temperature can be expressed in terms of an Arrhenius equation:

$$f = Ae^{-E_a/RT} \tag{1}$$

An alternative equation is derived from the theory of absolute reaction rates:

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

Although these equations are slightly different in form, it is usually difficult to decide which provides a better fit for experimental data. The activation enthalpy, ΔH^*, from eq 2 is given by

$$\Delta H^* = -R \text{ d} \ln (f/T)/\text{d}(1/T) \tag{3}$$

The activation energy, E_a, from the Arrhenius equation is

$$E_a = -R \text{ d} \ln f/\text{d}(1/T) \tag{4}$$

It is easily shown that

$$E_a = \Delta H^* + RT \tag{5}$$

The relationship between the activation energy and the temperature T' at which $f = 1$ Hz is

$$\begin{gathered} E_a = RT'[1 + \ln (kT'/2\pi h)] + T'\Delta S^* \\ (f = 1 \text{ Hz}) \end{gathered} \tag{6}$$

For relaxations having a zero activation entropy, this reduces to the following simple, not quite linear relationship:

$$\begin{gathered} E_a = RT'[1 + \ln (kT'/2\pi h)] \\ (f = 1 \text{ Hz}, \Delta S^* = 0) \end{gathered} \tag{7}$$

Thus the difference between the observed activation energy and that calculated from eq 7 is $T'\Delta S^*$.

For a number of relaxations the activation entropy is very small and eq 7 is obeyed. Since the experimental uncertainty in the activation energy is frequently at least 1 kcal/mol, it is not certain whether the activation entropy is exactly zero or has a small positive or negative value. In any case, such phenomena may be called simple relaxations, and they are believed to involve the motion of small groups of atoms with little interaction with other portions of the molecule or neighboring molecules. Other relaxations having very large activation entropies may be designated complex relaxations. They, in turn, are believed to involve a spectrum of related motions with extensive intra- and intermolecular interactions. An activation entropy of zero corresponds to $f/T \rightarrow 3.3 \times 10^9$ s^{-1} deg^{-1} as $1/T \rightarrow 0$ or a limiting frequency near 10^{12} Hz in an Arrhenius plot. For positive activation entropies, the limiting frequency can be much higher.

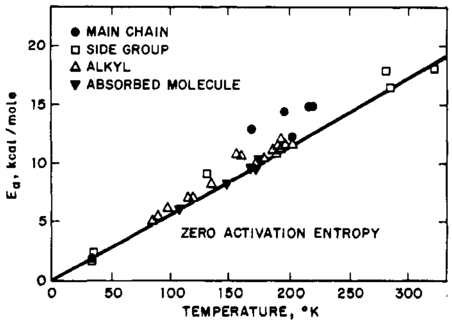

Figure 1. Activation energy vs. the temperature at a frequency of 1 Hz for secondary relaxations in polymers (derived from a plot by Heijboer[8-10]). The line corresponds to a zero activation entropy.

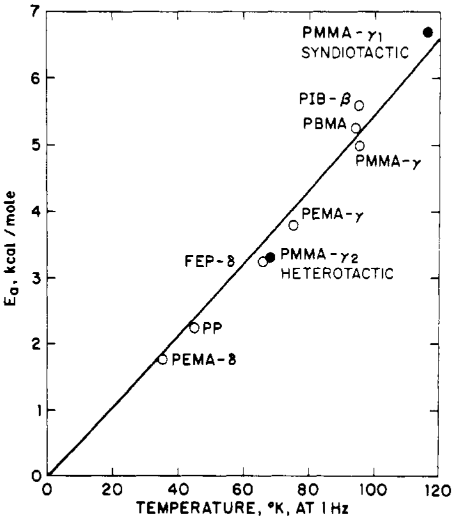

Figure 2. Alkyl group relaxations. Line: $\Delta S^* = 0$. The solid points represent the γ relaxation in syndiotactic and heterotactic PMMA (ref 15).

Figure 1 is a plot of the activation energies of secondary relaxations vs. the temperature at 1 Hz and is derived from a chart published by Heijboer.[8-10] The line corresponding to zero activation entropy represents, in general, a lower limit for the value of the activation energy. Heijboer gave the following slightly higher empirical relationship which runs through the center of the population of most of the points:

$$E_a = 0.060T' \quad (1 \text{ Hz}) \tag{8}$$

He divided secondary relaxations into four general categories. The first are main-chain motions which in many cases have substantial positive activation entropies and lie far above the line. The points corresponding to relaxations of side groups attached to the main chain are generally somewhat closer to the line but vary considerably in this respect. Most relaxations due to motions of alkyl groups at the end of side chains are quite close to the zero activation entropy line. Finally, relaxations associated with dissolved small molecules appear to have zero activation entropies within experimental uncertainty.

These categories were explored in more detail with data taken from three reviews.[11-13]

Alkyl Group Relaxations

Figure 2 shows the relationship between E_a and T' at 1 Hz for relaxations associated with motions of alkyl side groups on an expanded scale. Most of these relaxations have zero activation entropies within experimental uncertainty. The δ relaxation in FEP fluorocarbon resin has been assigned to the motion of CF_2H groups.[14]

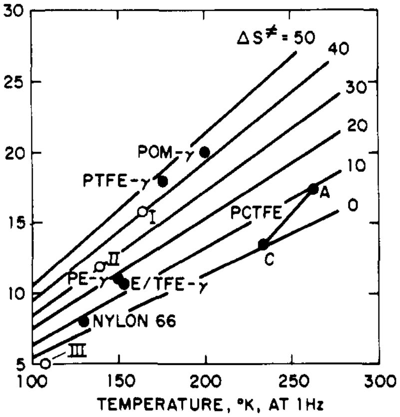

Figure 3. Local mode relaxations. The open points represent the components of the γ relaxation in polyethylene (ref 17).

The present discussion is based on the portions of the data which give linear Arrhenius relationships. In some cases, the frequency for a methyl group relaxation levels off with decreasing temperature due to quantum mechanical tunneling. Williams and Eisenberg[15] reported this phenomenon for the γ relaxation in poly(methyl methacrylate), which is attributed to the main-chain methyls. A nonlinear Arrhenius plot was found when these methyls were protonated but not when they were deuterated. This contrast was expected because of the differences in mass. They also found that the relaxation contained two components due to tacticity effects. The γ_1 relaxation, attributed to syndiotactic units, had an activation energy of 6.7 kcal/mol and a temperature at 1 Hz of 116 K, whereas the γ_2 relaxation, associated with heterotactic units, had an activation energy of 3.3 kcal/mol and a temperature of 68 K extrapolated to 1 Hz. The activation entropies for both relaxations are very close to zero.

Local Mode Relaxations

A number of local mode main-chain relaxations are plotted in Figure 3. Some of these relaxations, especially those for polyethylene, poly(tetrafluoroethylene), and poly(oxymethylene), have quite large activation entropies. However, the activation entropy for the γ relaxation in nylon 66 is relatively small. This relaxation is commonly considered to be very similar to the γ relaxation in polyethylene since both involve short polymethylene segments. It is thought that hydrogen bonds immobilize the amide groups at low temperatures and restrict the spectrum of main-chain motions. Recent dielectric studies[16] have shown that the γ relaxation in nylon is only slightly broader than for a Debye model, especially in samples containing moisture. It is thought that water forms mechanically stable bridges between amide groups at low temperatures and that this largely restricts the motions to single segments of four or six methylene units.

The γ relaxation in polyethylene is reported to contain as many as three components.[17–19] The lowest temperature component, known as γ_{III}, was reported by Illers[17] to occur near 110 K at a frequency of 1 Hz with an activation energy of 5 kcal/mol. Others have reported an activation energy of 8–9 kcal/mol.[18] Illers' value is close to the line for a zero activation entropy. The γ_{III} relaxation has been attributed to intracrystalline motion[17] and is reported to be intensified by annealing ultradrawn polyethylene.[19]

The γ relaxation in poly(chlorotrifluoroethylene) is thought to be composed of crystalline and amorphous contributions. As shown in Figure 3, they have activation entropies near 0 and 10 eu, respectively. Apparently, the amorphous activated state is more complex than the crystalline one. It is believed that the motions of short chain segments of this polymer are cooperative in the amorphous regions but independent in the crystals. In all three cases where the activation entropy of a local mode main-chain relaxation is close to zero, the moving segment appears to be limited by either crystallinity or hydrogen bonding. Hoffman, Williams, and Passaglia[20] have given models for γ_c relaxations associated with short chain segments in the crystals for which the activation entropy is very small.

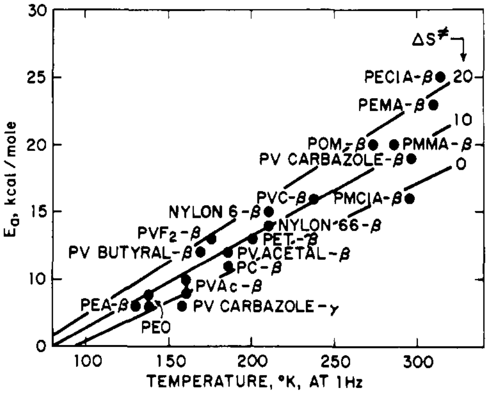

Figure 4. Polar group relaxations.

Polar Group Relaxations

Secondary relaxations involving the motion of polar groups are plotted in Figure 4. A few of these phenomena have activation entropies close to zero, but for many others $\Delta S^{\ddagger}$ is from 10 to 20 eu. In most instances, the reasons for these differences are unclear. It is probable, however, that they reflect variations in the degree to which motions of a given group involve sympathetic motions of its neighbors.

The relaxation in poly(ethylene oxide) (PEO) is probably a local mode main-chain relaxation. Its properties are in marked contrast with those of the γ relaxation in poly(oxymethylene) (POM) shown in Figure 3. Presumably, the oxygen links can move more independently in PEO. It has been suggested[11] that this relaxation involves both the amorphous regions and crystal defects.

In poly(vinylcarbazole), the γ relaxation has a small, possibly negative activation entropy while the β relaxation has a larger, positive activation entropy. It seems likely that the γ relaxation involves the motion of single polar side groups, and the β relaxation is due to the cooperative motion of larger molecular segments. The β relaxation in poly(vinyl acetate) appears to resemble the γ relaxation in poly(vinylcarbazole) while the β relaxations in poly(vinylacetal) and poly(vinylbutyral) have substantial activation entropies. It is understandable that their ring structures and the presence of residual hydroxyl or ester groups would lead to more complex motions.

The β relaxations in polycarbonate (PC) and poly(ethylene terephthalate) (PET) are superficially very similar, but the activation entropy is significantly larger for PET. This may reflect more cooperative motion of the ester groups. The substantial activation entropies for the β relaxations in nylons 66 and 6 are consistent with the dielectric data,[16] which point to highly cooperative motions, in contrast with the γ relaxation discussed earlier.

In most acrylic polymers, the β relaxations, which are assigned to the motion of ester groups, have fairly large activation entropies, in contrast with the alkyl group relaxations, which occur at lower temperatures. An exception is poly(methyl chloroacrylate) (PMClA). The ester groups of adjacent monomer units are very close together,

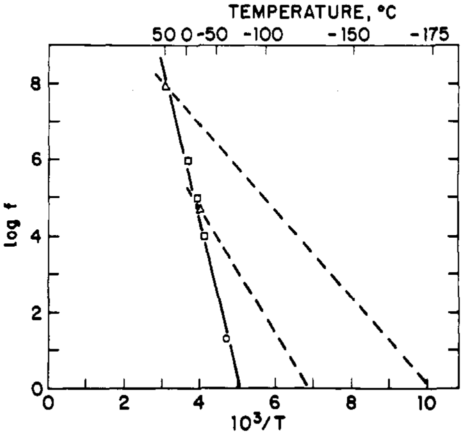

Figure 5. Relaxation map for the glass transition of an ethylene–propylene copolymer: (○) mechanical; (□) dielectric; (△) NMR. Solid line, overall complex relaxation; dashed lines, component simple relaxations from T_1 and $T_{1\rho}$.

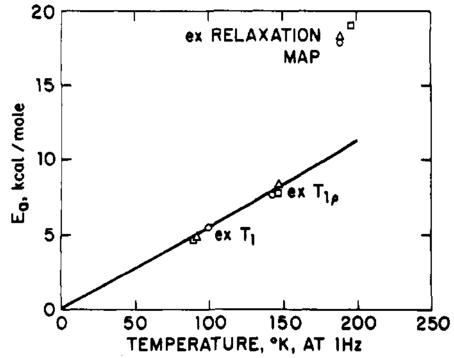

Figure 6. Activation energies for the glass transition in ethylene–propylene copolymers: (○) E/P mole ratio 1.3 (vanadium-based catalyst); (□) E/P mole ratio 1.3 (titanium-based catalyst); (△) E/P mole ratio 2.0 (2.5 mol % 1,4-hexadiene). Line: $\Delta S^{‡} = 0$.

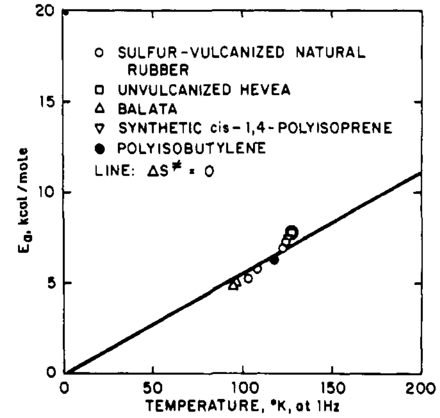

Figure 7. Activation energies for the glass transitions in various rubber samples based on NMR data.

and it is to be expected that they would undergo highly cooperative motions.

Glass Transitions

Glass transitions have large activation energies and activation entropies and are clearly highly complex relaxations. Nevertheless, there is evidence that they may consist of a distribution of simple component relaxations. An Arrhenius plot for the glass transition of an ethylene–propylene copolymer is shown in Figure 5. This copolymer was made with a vanadium-based catalyst and had an ethylene/propylene mole ratio of 1.3. A number of its properties have been reported in an earlier paper.[21] Data obtained by dynamic mechanical, dielectric, and NMR methods correlate very well and indicate an activation energy of 18 kcal/mol and an activation entropy of 40 cal deg^{-1} mol^{-1}. These values are based on the straight line shown in the figure. The curvature, if any, is much less than is usually observed for glass transitions.

It is also possible to calculate activation energies from the dependence of the NMR spin–lattice relaxation times, T_1 and $T_{1\rho}$, on temperature. These activation energies are frequently much smaller than those calculated from Arrhenius plots such as the one in Figure 5. The difference may be attributed to the sensitivity of NMR to relatively short-range effects. These smaller activation energies, derived from the data on the high-temperature side of the T_g minima in Figure 7 of ref 21, are indicated by dashed lines in the figure.

The relationship between the activation energy and the temperature at a frequency of 1 Hz based on these calculations is shown in Figure 6 for three ethylene–propylene copolymers. The points near the top of the figure for the overall relaxation are based on the solid line in Figure 5 while those near the line for a zero activation entropy are based on the dashed lines in the previous figure. For each polymer, the activation entropy was about 40 eu for the overall relaxation and near zero for the component relaxations, as calculated from the dependence of T_1 and $T_{1\rho}$ on temperature. Measurements of T_1 for the various primary, secondary, and tertiary carbons in one of these copolymers have also been made by ^{13}C NMR.[21] The dependence of both the proton and carbon-13 T_1 values for the longer polymethylene sequences gave activation energies of 5–6 kcal/mol and activation entropies near zero. Since the proton measurements were on undiluted polymer and those based on carbon-13 were on 25–50% solutions in $CDCl_3$, these observations support the view that this component relaxation involves a simple, noninteracting motion of polymer chain segments.

Similar results have been obtained from a number of other elastomers. Gutowsky and co-workers[22] measured the variation of T_1 with temperature for a number of samples of sulfur-vulcanized natural rubber as well as uncured samples of Hevea, balata, and synthetic *cis*-1,4-polyisoprene. From the resonance frequencies, the temperatures of the T_1 minima, and the activation energies from the NMR data, the temperatures at a frequency of 1 Hz and the activation entropies were calculated. As shown in Figure 7, all of these component relaxations have activation entropies close to zero. The activation energies from NMR data are 5–8 kcal/mol while that from an Arrhenius plot of dielectric and dynamic mechanical data is about 30 kcal/mol.[22]

The spin–lattice relaxation time of polyisobutylene was studied by Powles and Luszczynski,[23] who reported a minimum in T_1 at 50 °C for a resonance frequency of 21.5 MHz. The temperature dependence of T_1 corresponds to an activation energy of 6.2 kcal/mol. Extrapolation gives a temperature of 118 K at a frequency of 1 Hz. As shown in Figure 7, the activation entropy is close to zero. While this component relaxation is not far from the alkyl group relaxation at 95 K and 1 Hz shown in Figure 2, they do seem to be distinguishable processes. It is well-known that the two relaxations in polyisobutylene approach each other at higher temperatures and frequencies.[12,13]

Conclusions

Use of the theory of absolute reaction rates brings out a major difference between chemical reactions and viscoelastic relaxations. Many reaction rate constants have very small preexponential factors corresponding to negative activation entropies. This indicates that the activated complex is more ordered than the reactants. In contrast with this, viscoelastic relaxations tend to have positive activation entropies which are frequently very large. In these cases, the activated state must be more disordered than the ground state, and the relaxations are believed to involve complex cooperative interactions among neighboring groups.

An activation entropy close to zero is a limiting value, and relaxations in this class generally involve relatively simple motions of small molecular subgroups.

There is evidence that some complex relaxations may consist of a spectrum of simple relaxations involving different amounts of material and having different activation energies. As the frequency is increased, the absorption of energy is dominated by components having progressively smaller activation energies. This results in an apparent activation energy which is larger than that of the simple, component relaxations and a large, positive apparent activation entropy.

The glass transition has been treated by many different approaches. For example, Williams[24] has compared the Arrhenius model, transition state theory, free volume theories, and dipole diffusion. The free volume approach has been especially effective in treating the curvature of Arrhenius plots.[25,26] Of special relevance to the present discussion are the relationships among the enthalpy, entropy, and volume of activation.[27,28]

Many phenomena have been treated in terms of a distribution of relaxation times from which may be inferred a distribution of activation energies, activation entropies, or both. This possibility complicates the application of eq 2 to the analysis of experimental data. If a relaxation is governed by a nonexponential decay function,[29-31] the necessity to invoke a distribution of relaxation times may be avoided. However, these functions may have the effect of stretching the frequency scale, thereby increasing the apparent activation energy and entropy.[32]

The examples given here suggest that in at least some cases, the glass transition may be treated in terms of a special kind of distribution of relaxation times characterized by activation entropies close to zero and small-to-moderate activation energies.

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Brillouin Scattering from Polyepoxide Solutions and Gels

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ABSTRACT: The Brillouin splitting and line width are measured for the system consisting of the solvent Cellosolve Acetate and a polyepoxide formed from glycerol and bisphenol-A with epoxide end groups. Gels were formed by end-linking the chains in solution with a low molecular weight poly(propylene glycol) with amine end groups. Addition of polymer does lead to increased hypersonic attenuation and a greater Brillouin splitting, but cross-linking the chains has no measurable effect at constant concentration.

Introduction and Theory

Brillouin scattering probes the high-frequency mechanical properties of fluids.[1] The velocity and attenuation of hypersonic waves can be determined from the Brillouin frequency shift and line width. The longitudinal Brillouin splitting is given by

$$\pm\Delta\omega_l = qV_l(q) \qquad (1)$$

where $q = (4\pi n/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector for light of vacuum wavelength λ traveling in a medium of refractive index n which is scattered

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