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Frequency–temperature relationships for relaxations in polymers [1]

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Abstract

Two classes of relaxations have been found in which the relationship between the frequency and the temperature can be defined in terms of a single adjustable parameter. In the first class, the activation entropy is close to zero and

$$f = \frac{kT}{2\pi h} e^{-\Delta H^{\neq}}$$

where $\Delta H^{\neq}$ is the activation enthalpy. The second class of internal motions occurs close to absolute zero. These relaxations have frequencies proportional to the absolute temperature and are attributed to quantum mechanical tunneling. Relaxations such as gas transitions which have very large apparent activation energies are believed to reflect a distribution of internal motions which is sampled differently at different temperatures.

The increase in the frequency of a relaxation with temperature can be expressed by the Arrhenius equation

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

or the Eyring expression

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

Both of these relationships require two experimental parameters. Other equations, such as the WLF and Vogel–Fulcher expressions, require at least three constants. There are, however, two classes of relaxations which require only one experimental constant.

The relationship between the Arrhenius activation energy E_a and the Eyring activation enthalpy $\Delta H^{\neq}$ is

$$\Delta H^{\neq} = E_a - RT \tag{3}$$

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The activation free energy $\Delta F^{\neq}$ can be written by rearranging eqn. (2)

$$\Delta F^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} = RT[\ln(k/2\pi h) + \ln(T/f)] \tag{4}$$

We have found a class of simple, non-cooperative relaxations for which the activation entropy $\Delta S^{\neq}$ is essentially zero [1-3]. In this case, $\Delta F^{\neq}$ is independent of temperature. If T' is defined as the temperature of a relaxation at a frequency of 1 Hz, we obtain for this class the following relationship between E_a and T' by combining eqns. (3) and (4)

$$E_a = RT'[1 + \ln(k/2\pi h) + \ln T'] \tag{5}$$

The extent to which the measured activation energy exceeds this value is $T'\Delta S^{\neq}$. For nearly all relaxations, $\Delta S^{\neq}$ is zero or positive. This is illustrated in Fig. 1.

Relaxations for which $\Delta S^{\neq} = 0$ include those attributed to the motion of side groups, e.g. ester or alkyl groups, and several kinds of internal motions in crystals. The common feature seems to be small structural units moving independently of each other.

The distribution of relaxation times of a log frequency scale can be approximated by

$$\Phi(1/\omega) = \frac{2}{\pi}\frac{E''(\omega)}{(E_u - E_r)} \tag{6}$$

where E'' is the loss modulus, and E_u and E_r are the unrelaxed and relaxed moduli for the relaxation. An analogous expression for the dielectric

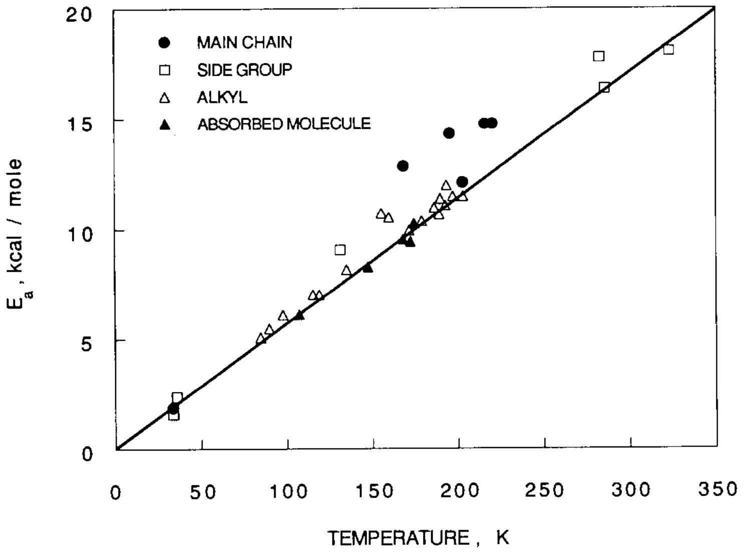

Fig. 1. Activation energy vs. the temperature at 1 Hz for several kinds of secondary relaxations in polymers.

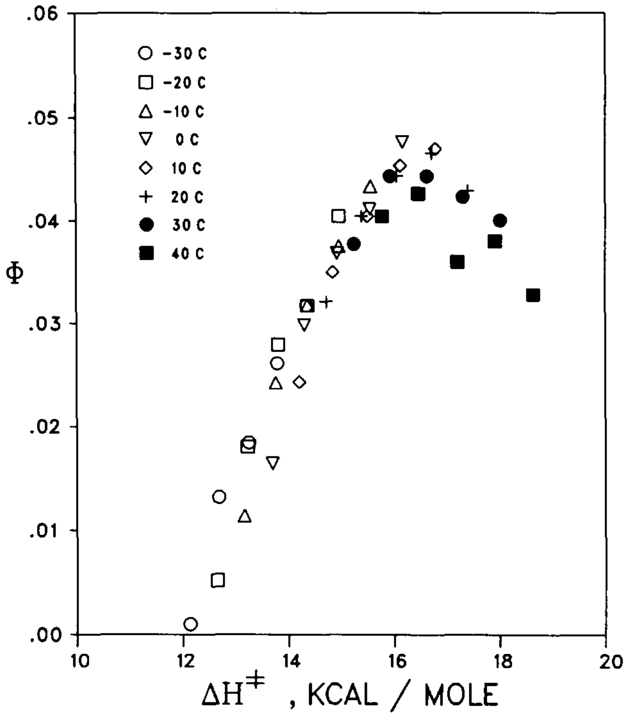

Fig. 2. Distribution of activation enthalpies for the β-relaxation in polymethyl methacrylate.

permittivity can also be used. When the distribution is plotted in terms of $\Delta F^{\neq}$, data taken at different temperatures will follow the same relationship as shown in Fig. 2 for the β-relaxation in polymethyl methacrylate, provided that $\Delta S^{\neq} = 0$ [4]. If not, $\Delta S^{\neq}$ can be determined by shifting along the $\Delta F^{\neq}$ axis.

The second class of relaxations is attributed to quantum mechanical tunneling, and is observed dielectrically only within a few degrees of absolute zero [5–7]. In this case, the activation enthalpy $\Delta H^{\neq}$ is zero, and it can be seen from eqn. (4) that both $\Delta F^{\neq}$ and f will be proportional to T, the absolute temperature. It has also been found that polyethylene, polypropylene, and Irganox® 1010, a stabilizer, have such a relaxation between 0 and 4 K, as shown in Fig. 3. For all three materials, the proportionality constant between f and T is 1 kHz K^{-1}. This relaxation may be due to the reorientation of hydroxyl groups on either the stabilizer or the polymer.

There are two classes of relaxations involving motions of the main chain of polymer segments in the amorphous regions. Local-mode or γ-relaxations which occur at relatively low temperatures, are associated with short aliphatic segments of four or more chain atoms. Glass transitions are believed to involve much larger segments, perhaps about 100 chain atoms.

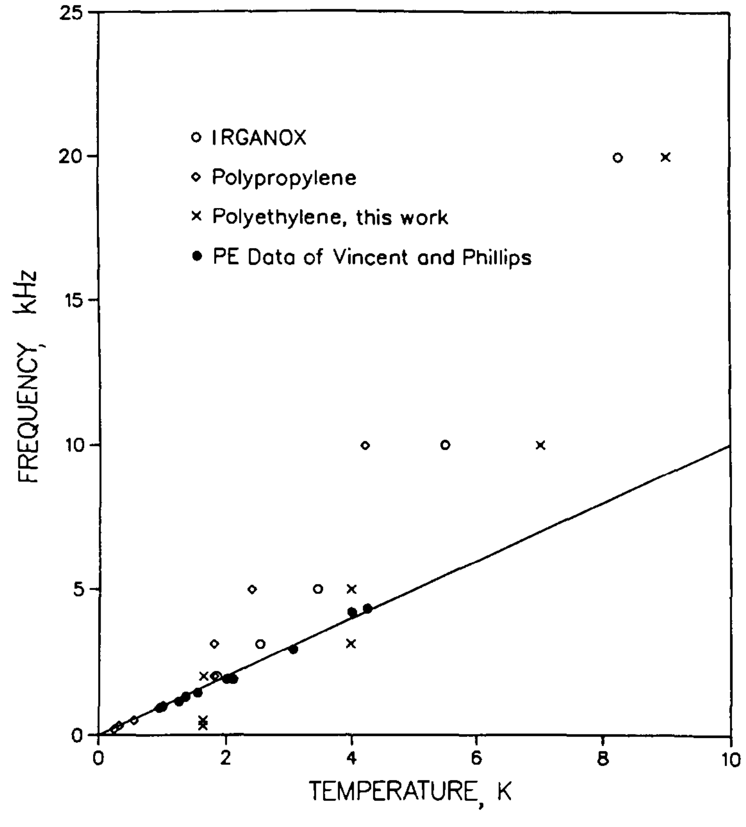

Fig. 3. Frequency–temperature relationships for ultra-low-temperature relaxations.

At the glass transition the modulus may decrease by a factor as large as 1000.

Both of these relaxations involve a transition with a large positive activation entropy between limiting low and high temperature states having activation entropies close to zero [2–4, 8] The activation free energy from eqn. (4) is always less than the strength of a chemical bond (about 50 kcal mol^{-1}). Therefore, if $\Delta H^{\neq}$ is large, $\Delta S^{\neq}$ must also be large. The same applies to A and E_a in the Arrhenius equation (eqn. (1)). An activation entropy of zero corresponds to an Arrhenius pre-exponential factor A of $9.0 \times 10^{9} T$ or about 2.7×10^{12} Hz at room temperature. This is in the range of molecular vibrational frequencies. Much larger frequencies are unphysical.

When we calculate an activation energy, enthalpy, or entropy, we make the tacit assumption that the same process is being observed over a range of temperature. It seems probable that large apparent activation parameters reflect a distribution of internal motions which is sampled differently at different temperatures [1, 3].

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