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Frequency–Temperature Relationships for the Glass Transition

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ABSTRACT: Glass transitions are characterized by large apparent activation energies and entropies. However, at sufficiently high temperatures, the activation entropy decreases to zero. This is a characteristic of noncooperative internal motions. The frequency–temperature relationship can be fitted by an equation which combines the Vogel–Fulcher and Eyring formulations with only two adjustable parameters.

Introduction

One way to express the relationship between the frequency and temperature of a viscoelastic relaxation is derived from the Eyring theory of absolution reaction rates.

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

where k is Boltzmann's constant, h is Planck's constant, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the activation enthalpy and entropy. This equation can be rearranged in terms of the activation free energy, $\Delta F^{\ddagger}$.

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

The activation enthalpy is related to the Arrhenius activation energy, E_a, the following expression.

$$E_a = -R[\mathrm{d}\ln f/\mathrm{d}(1/T)] = \Delta H^{\ddagger} + RT \qquad (3)$$

Combining eqs 2 and 3,

$$E_a = RT[1 + \ln(k/2\pi h) + \ln(T/f)] + T\Delta S^{\ddagger} \qquad (4)$$

We have found that for many secondary relaxations the activation entropy is close to zero.[1-3] This is especially true for motions assigned to side groups or to dislocations in a crystalline phase. An activation entropy of zero can be recognized either by applying eq 4 or by finding that the activation free energy from eq 2 is independent of temperature.

For motions involving the main chain, the situation is more complex. Consider local motions frequently known as γ-relaxations. When frequency–temperature shift factors were determined separately for the high and low temperature sides of the dynamic mechanical loss peaks, the data from the low-temperature side corresponded closely to a zero activation entropy, but those from the high-temperature side did not.[3,4] When the distribution of relaxation times was converted to the corresponding distribution of activation free energies, the data from different temperatures coincided only on the low-temperature side of the maxima.[3,4]

With dielectric data which are generally taken at higher frequencies, the situation is strikingly different as exemplified by a study on a copolymer of ethylene and vinyl alcohol.[5] In that case, the distributions of activation free energies for different temperatures superposed only on the high-temperature side of the maximum.

From these observations we conclude that the local mode relaxation comprises a spectrum of internal motions, probably involving chain segments of different lengths. This distribution has well-defined lower and upper limits, each of which is characterized by an activation entropy close to zero. At intermediate temperatures, a variety of segments are active, and the apparent activation entropy is positive.

Through the study of thermally stimulated currents following charging in a narrow temperature interval, it is possible to determine the activation energy as a function of temperature even in regions remote from any relaxation.[6] The activation energy remains close to the values from eq 4 with $\Delta S^{\ddagger} = 0$ except in the region of the glass transition where E_a exhibits a large maximum. This is illustrated in ref 6 for poly(ether ether ketone) and ref 3 for polycarbonate. It is clear that the apparent activation energy decreases at temperatures above T_g. However, it is difficult to determine exact relationships in polymers having high glass temperatures by the method of thermally stimulated currents because of the complicating effect of ionic conductivity.

Activation Energy for the Glass Transition at High Temperatures and Frequencies

For the glass transition, the relationship between the frequency and temperature is frequently expressed in terms of the equation of Williams, Landel, and Ferry.[7] However, the applicability of that equation is questionable at temperatures far above the usually reported T_g values. Equation 2 is particularly useful, because an activation free energy can be calculated for each combination of temperature and frequency without recourse to differentiation. If a region is found in which $\Delta F^{\ddagger}$ is independent of temperature, $\Delta S^{\ddagger}$ is zero, and the cooperative qualities which characterize the main body of the glass transition no longer apply.

The upper part of Figure 1 is a relaxation map of the dielectric data of Vaselovskii and Slusker for the α-relaxation in poly(vinyl acetate).[8] In the lower part of the figure, the same data are plotted as $\Delta F^{\ddagger}$ vs T. At 390–403 K, $\Delta F^{\ddagger}$ has reached a constant value of 9.3 kcal/mol (39 kJ/mol). Figure 2 is a similar treatment of the data of Mikhailov and co-workers for poly(ethyl acrylate).[9] In this case, $\Delta F^{\ddagger}$ levels off at 5.8 ± 0.1 kcal/mol (24.3 ± 0.4 kJ/mol) at 385–419 K.

Another example comes from the data of Connor, Read, and Williams on poly(ethylene oxide) of molecular weight 2.8×10^5.[10] In this case (Figure 3), $\Delta F^{\ddagger}$ reaches a value of 4.85 ± 0.06 kcal/mol (20.3 ± 0.25 kJ/mol) at 279–315 K. In all of these cases, the studies extended to very high frequencies and thus to temperatures far above the usually quoted glass transitions (e.g., 305 K for poly(vinyl acetate), 249 K for poly(ethyl acrylate), and 203 K for poly(ethylene oxide).[11]

A particularly interesting case is the γ-relaxation in poly(oxymethylene). It is generally considered to be a local mode relaxation of chain segments in the amorphous regions, yet a relaxation map of log frequency vs $10^3/T$ (K) for dielectric data has the curvature usually associated

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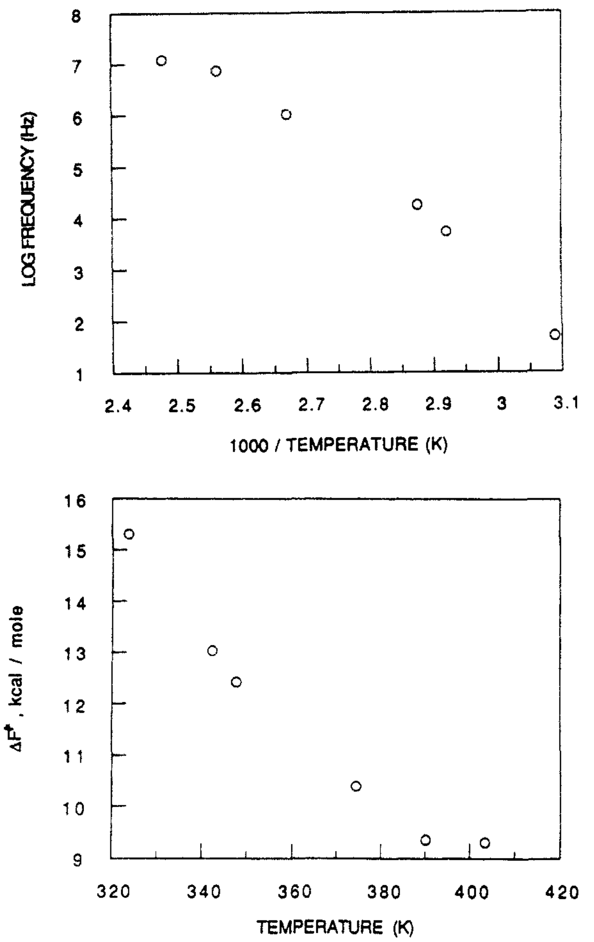

Figure 1. Poly(vinyl acetate): α-Relaxation.

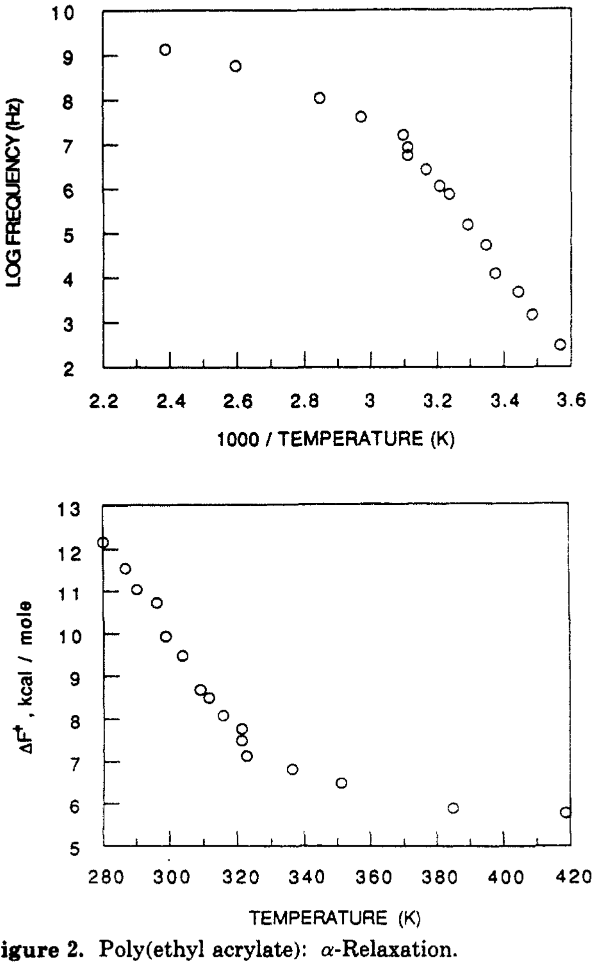

Figure 2. Poly(ethyl acrylate): α-Relaxation.

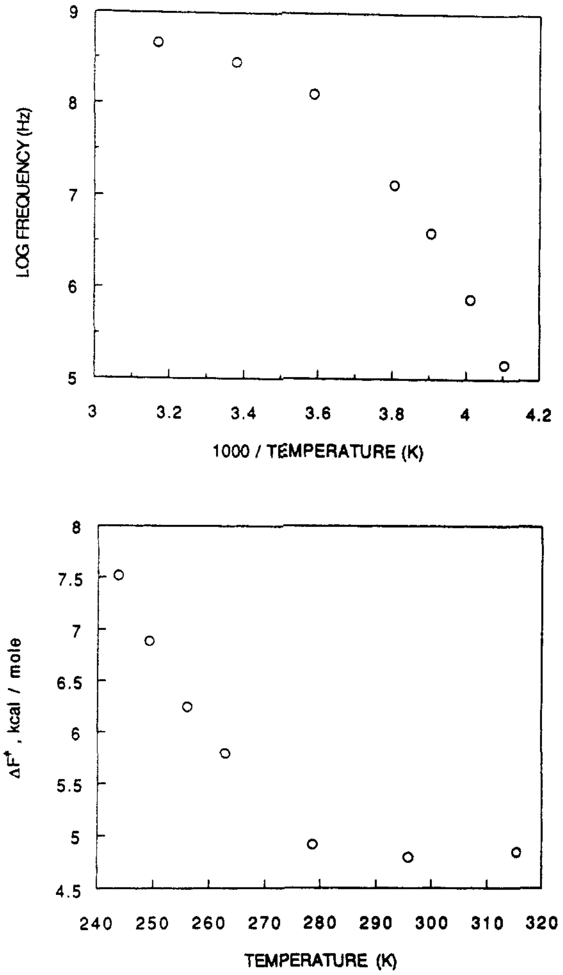

Figure 3. Poly(ethylene oxide): α-Relaxation.

with glass transitions. The plot in the upper part of Figure 4 was adapted from one given by McCrum, Read, and Williams.[12] The original data are from refs 13–16. The designations (f and T) refer to maxima in isothermal frequency scans and isochronal temperature scans, respectively. At temperatures from 292 to 383 K, the value of $\Delta F^{\ddagger}$ is 4.90 ± 0.14 kcal/mol (20.5 + 0.6 kJ/mol). Poly(oxymethylene) is a highly crystalline polymer, and the location of its glass temperature is uncertain.[17] Values from 188 to 263 K have been suggested.[11] This range encompasses both the γ- and β-relaxations.

A Modified Vogel–Fulcher Equation

The relationship between the frequency and the temperature for many glass transitions as well as other phenomena can be fitted very well by the Vogel–Fulcher equation[18,19] which we will express as follows:

$$f = A e^{-E/R(T-T_0)} \qquad (5)$$

If $T_0 = 0$, this reduces to the Arrhenius equation with $E = E_a$. The values for the three adjustable parameters, A, E, and T_0, are shown in Table I for the glass transitions of several polymers. We note that the energy terms, E, are quite small, and the preexponential factors, A, are clustered around the order of magnitude of molecular vibrations. In all cases, the correlation coefficients, r^2, are greater than 0.98.

We now combine the forms of the Vogel–Fulcher and Eyring equations, i.e., eqs 1 and 5, with $\Delta S^{\ddagger} = 0$.

$$f = \frac{kT}{2\pi h} e^{-H/R(T-T_0')} \qquad (6)$$

This approach is related to that of Macedo and Litovitz.[26] If $T_0' = 0$, this reduces to eq 1 with $H = \Delta H^{\ddagger}$ and $\Delta S^{\ddagger} =$

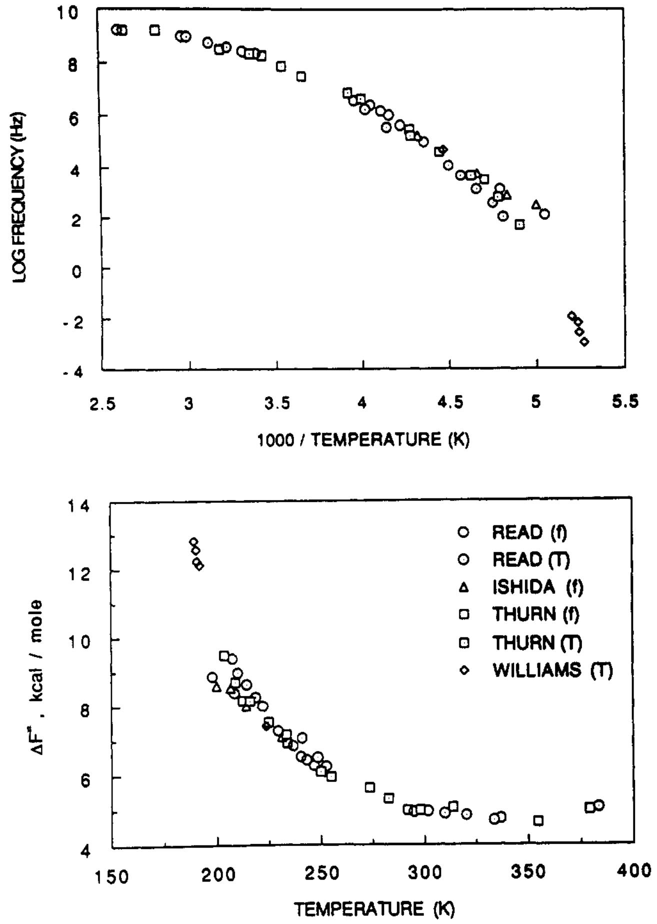

Figure 4. Poly(oxymethylene): γ-Relaxation.

0. There are now only two adjustable parameters, H and T_0'. In Table II, the parameters are shown based on the same data that were used in Table I. It turns out that eq 6 fits the data as well as or better than eq 5, even though it has one less adjustable parameter. The energy terms, H, are the right order of magnitude for barriers to rotation. In at least two cases, they are smaller when there are oxygen links in the chain.

Discussion

Matsuoka has given an extensive treatment in which the size of units which must relax cooperatively increases as the temperature is reduced toward the glass transition.[27,28] The activation energy for the rotation of individual bonds is 3.1–3.5 kcal/mol (13.0–14.6 kJ/mol) with a relaxation time of about 10^{-10} s. At a temperature T^*, which he states is about 500 °C, the fractional free volume is about 0.5, and the conformers can relax independently with a frequency of about 3×10^{10} Hz. As the temperature is decreased, the free volume decreases and increasing numbers of conformers must relax cooperatively. This causes the apparent activation energy to increase, reaching about 200 kcal/mol at T_g where the number of conformers in the relaxing units is thought to be 7–10. At a temperature T_0, which is about 50 °C below T_g, the size of the relaxing units becomes infinite and all but the most local kinds of internal motion stop. Matsuoka's model leads to relationships which are similar to the Adam–Gibbs and Vogel–Fulcher formulations.

The present discussion has several points in common with that of Matsuoka. The attainment of a zero activation entropy is considered to be a signature of a noncooperative relaxation. We have shown that, in some cases, this situation can be reached at temperatures well below 500 °C. The Vogel–Fulcher energies in Table I are similar to those given by Matsuoka on p 49 of ref 28. We have found that an additional simplification can be made by combining elements of the Vogel–Fulcher and Eyring relationships. The ratio of the apparent activation energy or enthalpy from eq 1 or eq 3 to the value obtained by setting the activation entropy, $\Delta S^{\ddagger}$, in eq 4 equal to zero may be taken as an indicator of the size of the units which must relax cooperatively.

Conclusions

The scope of noncooperative internal motions having activation entropies close to zero is larger than previously considered. In addition to very local motions mostly found at low temperatures, this class includes main-chain motions at temperatures far above the usually reported glass

Table I. Vogel–Fulcher Parameters for the Glass Transitions of Several Polymers

polymer	ref	T_0 (K)	E kcal/mol	E kJ/mol	log A	r^2
poly(vinyl acetate)	8	248	3.76	15.7	12.47	0.9980
poly(methyl acrylate)	20	236	3.60	15.1	13.71	0.9921
poly(ethyl acrylate)	9	234	2.07	8.7	11.85	0.9844
isotactic poly(methyl methacrylate)	21	318	0.74	3.1	7.88	0.9941
poly(vinylidene fluoride)	22	229	0.76	3.2	9.05	0.9977
natural rubber	23	147	3.99	16.7	14.79	0.9979
poly(ethylene oxide)	10	215	0.67	2.8	10.23	0.9946
poly(propylene oxide)	24	175	1.64	6.9	11.23	0.9998
polyacetaldehyde	25	220	1.46	6.1	9.06	0.9982
poly(oxymethylene) (γ-relaxation, f-scans only)	12–15	126	3.58	15.0	12.67	0.9940

Table II. Parameters for the Modified Vogel–Fulcher Equation

polymer	T_0' (K)	H kcal/mol	H kJ/mol	r^2
poly(vinyl acetate)	252	3.42	14.3	0.9999
poly(methyl acrylate)	253	2.30	9.6	0.9975
poly(ethyl acrylate)	230	2.24	9.4	0.9984
isotactic poly(methyl methacrylate)	273	3.30	13.8	0.9990
poly(vinylidene fluoride)	190	2.63	11.0	0.9989
natural rubber	164	2.28	9.5	0.9994
poly(ethylene oxide)	185	1.78	7.4	0.9983
poly(propylene oxide)	172	1.47	6.2	0.9999
polyacetaldehyde	204	2.91	12.2	0.9990
poly(oxymethylene) (γ-relaxation, f-scans only)	135	2.89	12.1	0.9991

transition. Even the main body of the glass transition can be incorporated in this picture by introducing the Eyring preexponential term into the Vogel–Fulcher equation.

If we apply eq 3 to eq 6, we obtain the following expression for the apparent Arrhenius activation energy.

$$E_a = H\left(\frac{T}{T - T_0'}\right)^2 + RT \tag{7}$$

In a similar manner, we can obtain the following expressions for the apparent Eyring activation enthalpy and entropy by combining eq 6 with eqs 1 and 2

$$\Delta H^{\ddagger} = H\left(\frac{T}{T - T_0'}\right)^2 \tag{8}$$

$$\Delta S^{\ddagger} = H\frac{T_0'}{(T - T_0')^2} \tag{9}$$

Thus, it is seen that the apparent values of E_a, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ all blow up as the temperature is decreased toward T_0'. This is clearly consistent with the ideas of Matsuoka.

The value of the activation free energy as defined by eq 2 is always moderate as illustrated in Figures 1–4. Therefore, a large value for the apparent $\Delta H^{\ddagger}$ is always coupled with a large positive value for the apparent $\Delta S^{\ddagger}$. In the same sense, a large value of the Arrhenius activation energy, E_a, is always coupled with a large value of the preexponential factor. Values of that factor larger than the frequencies of molecular vibrations are certainly unphysical. The usual calculations of these parameters are based on the assumption that the same relaxation process is active over a range of temperatures. If the degree of cooperativity is temperature dependent, that is responsible for the decrease in $\Delta F^{\ddagger}$ with increasing temperature, and the true value of $\Delta S^{\ddagger}$ is close to zero as it is for the low-temperature relaxation discussed earlier.

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