Kinetic nature of the glass transition–II

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The recently proposed kinetic model predicts similar behaviour for the specific heat and the thermal expansivity near the glass transition and this has been verified experimentally. For a number of polymers, the thermal relaxation time constant τ and the corresponding activation energy E have been determined from specific heat measurements. The kinetic model is also extended to explain the connection between the transition observed in dynamic mechanical measurements and in thermal measurements.

INTRODUCTION

It has recently been argued[1] that the glass transition in polymers is a kinetic phenomenon and a simple model was constructed to illustrate the essential ideas of this interpretation. The basic assumptions were:

(A) The thermodynamic state of the system is determined not only by the temperature θ_a of the phonons, but also by a second 'fictive' temperature θ_b describing the excitation of other modes, presumably connected with the micro-Brownian motion of the chains.

(B) The time evolution of θ_a and θ_b is governed by

$$C_a \frac{d\theta_a}{dt} = -\gamma(\theta_a)(\theta_a - \theta_b) + P \tag{1}$$

$$C_b \frac{d\theta_b}{dt} = \gamma(\theta_a)(\theta_a - \theta_b) \tag{2}$$

where P is the external power supplied to the phonons. The heat capacities of the a and b modes, C_a and C_b, respectively, are assumed to vary slowly. Instead of γ, one may also use τ defined as

$$\tau^{-1} = \gamma(C_a^{-1} + C_b^{-1}) \tag{3}$$

which is the thermal relaxation time in the absence of external power.

(C) It was further assumed that $\tau(\theta_a)$ varies rapidly but smoothly with θ_a, e.g. around some reference temperature θ_0,

$$\tau(\theta_a) = \tau_0 \exp \frac{E}{R}\left(\frac{1}{\theta_a} - \frac{1}{\theta_0}\right) \tag{4}$$

where the activation energy E is more generally defined by

$$E = R\frac{\partial \ln \tau}{\partial(1/\theta_a)} \tag{5}$$

Under these assumptions, predictions were made: (i) the existence of a step or transition in the observed specific heat $C = P/(d\theta_a/dt)$; (ii) an increase of the transition temperature with the rate in measurement and (iii) dependence of C on the thermal history of the sample. All these features have been confirmed experimentally[1].

In this paper these ideas will be examined in greater detail. Firstly we show that assumption (A) implies a quantitative relation between C and the expansivity α of samples measured under identical conditions, and will then present experimental data to show that the predicted relationship holds. Assuming (B) (but not, however, making assumption (C) on the particular form of $\tau(\theta_a)$), we show that measurement of C at one heating rate is sufficient to give τ over a range of temperatures. Furthermore we find that τ calculated in this way is independent of heating rate, and is an intrinsic parameter important for characterizing the behaviour near glass transition.

The thermal activation energy E defined by (5) turns out to be approximately constant near the glass transition. Measurements on a number of polymers with a wide range of nominal glass transition temperatures θ_g allow the relation between E and θ_g to be examined phenomenologically.

In dynamic mechanical measurements one often refers to a mechanical relaxation time τ_m

$$\tau_m(\theta) = 2\pi/\omega_0(\theta) \tag{6}$$

where $\omega_0(\theta)$ is the angular frequency at which the loss tangent attains a maximum. By analogy one can define the mechanical activation energy E_m as

$$E_m = R\frac{\partial \ln \tau_m}{\partial(1/\theta)} \tag{7}$$

The data on a number of polymers suggest that $E \simeq E_m$ and that τ does not differ from τ_m by more than an order of magnitude.

The close relation between the glass transition as seen in dynamic mechanical measurements and in thermal properties is not previously understood. We will show that the kinetic model provides a theoretical understanding of this problem, with quantitative estimates which reasonably agree with experimental results.

EXPERIMENTAL

Samples

Three polymers have been used to test the relationship between C and α: polystyrene (PS; Styron, Dow

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Table 1 Molecular weights of polymer samples

Polymer	Number average molecular weight M_n	Weight average molecular weight M_w	M_w/M_n
Poly(dimethyl siloxane) (PDMS)	150 000	609 000	4.06
Polyisobutylene (PIB)	–	200 000	–
Poly(methyl acrylate) (PMA)	63 200	200 000	3.16
Poly(vinyl acetate) (PVAc)	47 700	195 000	4.09
Poly(vinyl chloride) (PVC)	37 400	83 500	2.23
Poly(methyl methacrylate) (PMMA)	33 200	60 600	1.83
Poly(phenylene oxide) (PPO)	32 000	244 000	7.63

Chemical), polycarbonate (PC; Macrolon, Bayer) and polyethylene terephthalate (PET, experimental sample supplied by ICI). These polymer sheets were cut into sample discs of diameter 5.5 mm and thickness 0.6 mm for C measurements and cubes of side 3.5 mm for α measurements. Additional C measurements were made on seven other polymers of widely different glass transition temperatures. These polymers were obtained from Scientific Polymer Products Inc. and are listed together with their molecular weights in *Table* 1.

All the polymers investigated are essentially amorphous. However, PET and polydimethyl siloxane (PDMS) are crystallizable, so the amorphous samples used were obtained by fast quenching. The PET sheet as received had a density of 1.337 g cm^{-3}, which implied a crystallinity of $<2\%$. The PDMS sample was quenched from room temperature to below θ_g at a rate of 40K min^{-1}, and this procedure should, according to Adachi *et al.*[2], produce an amorphous sample. Both samples were kept below $\theta_g + 20\text{K}$ during all measurements to avoid any further crystallization.

Measurements

For PS, PC and PET simultaneous measurements of C and α were made on a Perkin Elmer differential scanning calorimeter (DSC-2) and a thermomechanical analyser (TMS-2), respectively. For expansion measurements, the weight tray was loaded with sufficient mass (4.0 g) to compensate for the buoyancy of the float assembly. Thus the sample was under a true zero load when the quartz rod was brought in contact with its top surface. Helium gas was used for heat exchange between the sample and its surrounding furnace and a chromel–alumel thermocouple was placed near the sample to monitor the temperature. The output of the DSC, as displayed on a chart recorder, gives C as a function of temperature while the TMS, when combined with a first derivative computer, also gives α directly.

In all measurements the sample was first heated to about 20–30 K above θ_g and kept for 3 min. The thermal relaxation time τ at such a temperature is so short that after the above conditioning procedure we may assume that $\theta_a = \theta_b$. This is the basis for the following experiments:

(i) *Heating-rate experiments* — the sample was cooled at a constant rate of 5K min^{-1} to $\sim$30K below θ_g; then measurements were made at heating rates $q = \text{d}\theta_a/\text{d}t$ varying from 0.62–20K min^{-1}.

(ii) *Cooling-rate experiments* — the sample was first cooled to $\sim$30 K below θ_g at rates varying from 0.31–20 K min^{-1}; measurements were then made at a constant heating rate of 5K min^{-1}.

(iii) *Annealing experiments* — the sample was cooled at 5K min^{-1} to a temperature below θ_g and annealed for a specified time; then measurements were made at a heating rate of 5K min^{-1}.

Corrections

Two sources of systematic error must be dealt with before α can be compared with C. In the α measurement, thermal resistance at the gas-sample interface and heat diffusion within the sample cause the average temperature of the sample to lag behind that of the helium gas surrounding the sample by an amount $\Delta\theta_1$. Since the thermocouple of the TMS records the temperature of the helium gas, it should be corrected for this effect. To study this correction, a thermocouple junction A is inserted into a small hole drilled into the centre of a sample of PS, which is then filled with epoxy. It is reasonable to assume that junction A, secured in this manner, records the average temperature of the sample. When the entire system is heated at a rate q, the difference $\Delta\theta_1$ between the temperature at A and that of the gas is found to be:

$$\Delta\theta_1 \text{ (deg)} \simeq 0.3\, q \text{ (deg min}^{-1}\text{)}$$

Since all samples in the expansivity measurements are of similar dimensions and no significant variation is expected from polymer to polymer, this correction has been applied to all data.

A second problem, due to diffusion, is that the temperature at the centre of the sample lags behind that at the surface by $\Delta\theta_2$. This effect was investigated by attaching a thermocouple junction B into a shallow groove on the surface of the sample and directly measuring the temperature difference between junctions A and B, i.e. $\Delta\theta_2/2$. This measurement gives:

$$\Delta\theta_2 \text{ (deg)} \simeq 0.14\, q \text{ (deg min}^{-1}\text{)}$$

Because of the above effect, the measured value of α is the true value smeared over a temperature interval of of $\Delta\theta_2$, causing a broadening of all features. Correcting for this effect is not easy, and has not been carried out, so the comparison below should be judged with this in mind.

The specific heat measurements do not suffer appreciably from either of these problems because the sample is in good thermal contact with a platinum sample holder whose temperature is directly recorded, and because the very small thickness of the sample ($\simeq$0.6 mm) renders diffusivity effects negligible.

RESULTS AND DISCUSSION

Connection between specific heat and expansivity

Firstly we show how, with only assumption (A), a connection is expected between C and α. Let $U = U(\theta_a, \theta_b)$ be the internal energy of a unit mass of sample. Here θ_a is the temperature of the phonons, which is the observed temperature, sometimes simply denoted as θ, while θ_b

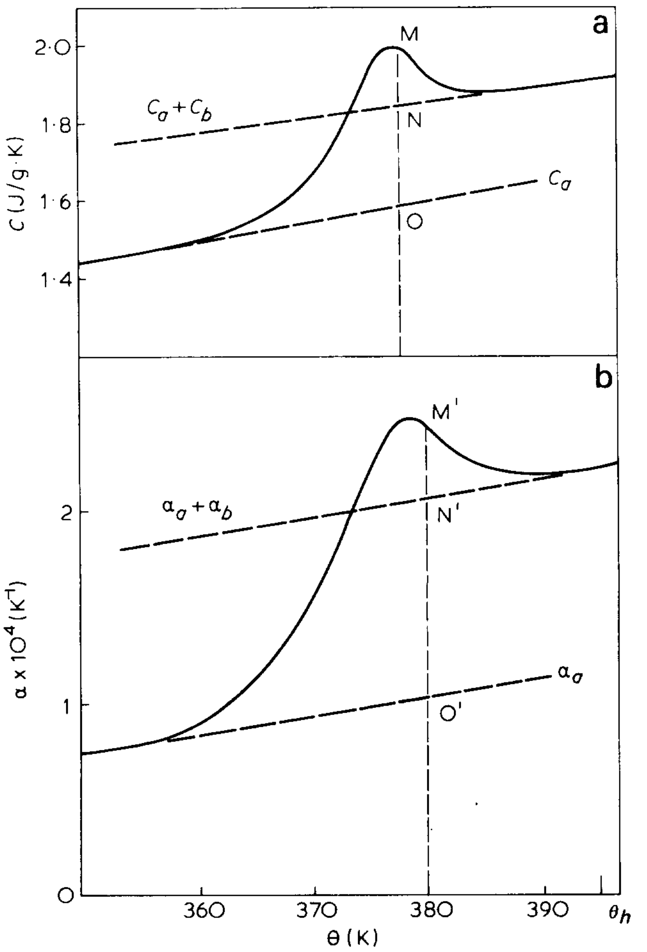

Figure 1 (a) Specific heat and (b) linear expansivity of PS, measured at a heating rate of 20K min^{-1} X_c = MO/NO; X_α = M'O'/N'O'

cannot be directly measured. When the sample is heated, the external power supplied is

$$P=\frac{dU}{dt}=\frac{\partial U}{\partial\theta_a}\frac{d\theta_a}{dt}+\frac{\partial U}{\partial\theta_b}\frac{d\theta_b}{dt}$$

$$=C_a\frac{d\theta_a}{dt}+C_b\frac{d\theta_a}{dt}$$

$$=\left(C_a+C_b\frac{d\theta_b}{d\theta_a}\right)\frac{d\theta_a}{dt} \tag{8}$$

where

$$C_{a,b}=\frac{\partial U}{\partial\theta_{a,b}} \tag{9}$$

The apparent specific heat C is the energy supplied for a unit increase in the observed temperature*

$$C=\frac{Pdt}{d\theta_a}=C_a+C_b\frac{d\theta_b}{d\theta_a} \tag{10}$$

In the kinetic point of view there are no sudden changes in the thermodynamic variables C_a, C_b, so the appearance of a transition is caused entirely by the behaviour of $d\theta_b/d\theta_a$. At low temperatures the a and b modes are decoupled, so $d\theta_b/d\theta_a=0$ and $C=C_a$, whereas at high temperatures the modes are closely coupled, so $d\theta_b/d\theta_a=1$ and $C=C_a+C_b$, resulting in a step in C.

Similarly, the length L of a sample is a function of both θ_a and θ_b, i.e. $L=L(\theta_a, \theta_b)$, therefore the observed linear expansivity α is

$$\alpha=\frac{1}{L}\frac{dL}{d\theta_a}=\alpha_a+\alpha_b\frac{d\theta_b}{d\theta_a} \tag{11}$$

where

$$\alpha_{a,b}=\frac{1}{L}\frac{\partial L}{\partial\theta_{a,b}} \tag{12}$$

are assumed to be varying slowly. A step in α is expected because of the previously described behaviour of $d\theta_b/d\theta_a$. This suggests that C and α should be related closely for samples having the same history under the same measurement conditions.

Figure 1 shows typical data on C and α, in this case for PS measured at a heating rate of 20K min^{-1}. For a quantitative comparison we define (see *Figure* 1 for illustration)

$$X_c=(C-C_a)/C_b \tag{13}$$

$$X_\alpha=(\alpha-\alpha_a)/\alpha_b \tag{14}$$

From (10) and (11), both X_c and X_α should be equal to $d\theta_b/d\theta_a$ and to each other. *Figures* 2–4 show representative data for testing this equality illustrating the effect of different heating rates, cooling rates and annealing respectively. The quantitative agreement between corresponding X_c and X_α is satisfactory.

As assumption (A) only was used in the above analysis, the validity of the relation $X_c=X_\alpha$ demonstrates that the thermal state of the polymer can be summarized by one 'fictive' temperature θ_b apart from the measured temperature θ_a. If U and L depend on more than one 'fictive' temperature, e.g. $U=U(\theta_a; \theta_b, \theta_b', \ldots)$, $L=L(\theta_a; \theta_b, \theta_b', \ldots)$ then no such relation between X_c and X_α can be expected to hold.

Relaxation time and activation energy

In this section (B) is assumed and we show that τ can be determined from the measurement at one heating rate. Since specific heat and expansivity measurements yield the same information, namely $X(=X_c=X_\alpha)=d\theta_b/d\theta_a$, it is sufficient to consider any one of the two. Specific heat determinations can be made at fairly high heating rates without serious thermal lag corrections, and with better sensitivity. Expansivity measurements also suffer from the inconvenience that above the glass transition, the sample becomes so soft that the slightest non-zero pressure from the quartz rod, coupling it to the linear differential transformer, would cause a substantial error. Therefore all subsequent results are derived from data on C.

Consider a single measurement of C, as in *Figure* 1a. From this we determine $X=d\theta_b/d\theta_a$. Then θ_b for each θ_a can be calculated from

$$\theta_b=\int^{\theta_a} X d\theta_a+C_1 \tag{15}$$

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* See Ref 1 for a slightly different derivation. The present derivation is meant to emphasize the similarity with the expansivity.

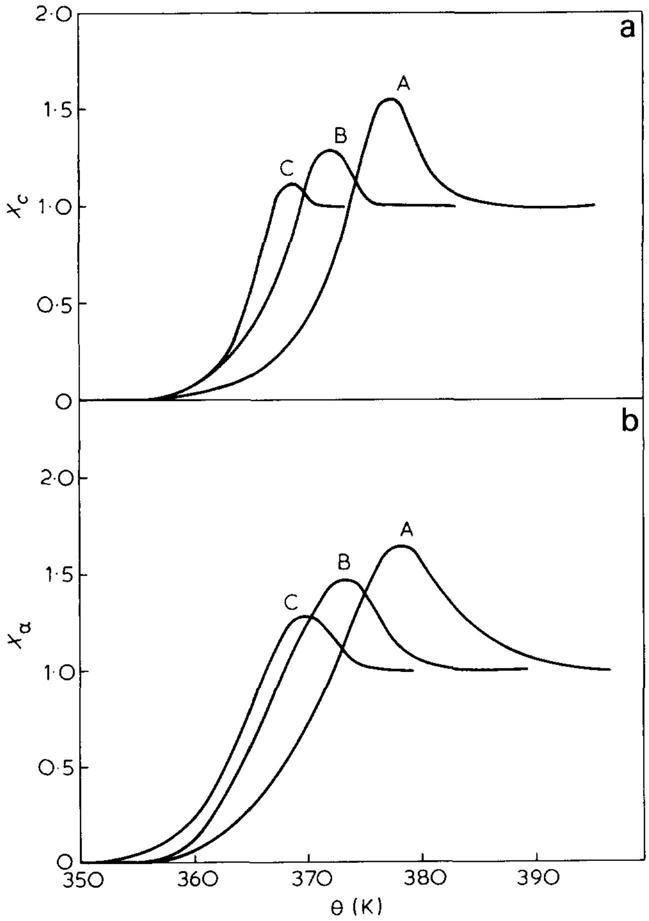

Figure 2 Effect of different heating rates on (a) X_c and (b) X_α for PS. Heating rate is A, 20K min^{-1}; B, 5K min^{-1}; C, 1.25K min^{-1}

The constant C_1 can be determined since above the transition, at high temperature θ_h (*Figure* 1*a*), the relaxation time τ must be so short that θ_b and θ_a are equal, i.e. $\theta_b = \theta_h$ when $\theta_a = \theta_h$. Hence using this final condition,

$$\theta_b = \theta_h - \int_{\theta_a}^{\theta_h} X \mathrm{d}\theta_a \qquad (16)$$

Note that (16) is insensitive to the precise choice of θ_h, since $X(\theta_h) = 1$. From (2), we see that

$$\gamma = C_b \frac{\mathrm{d}\theta_b}{\mathrm{d}t} (\theta_a - \theta_b)^{-1}$$

$$= C_b X q (\theta_a - \theta_b)^{-1} \qquad (17)$$

which allows γ, and hence τ to be determined. The fractional error in τ could be substantial at the lower end of the transition, where $X \simeq 0$ and at the upper end of the transition, where $\theta_a - \theta_b \simeq 0$. In effect, this procedure gives τ in the middle of the transition range — a range of 5–10 degrees. From the temperature dependence of τ, the activation energy $E = \partial(\ln \tau)/\partial(1/\theta)$ can also be determined. Technical details of this calculation are discussed in the Appendix.

The present method of determining the activation energy has several advantages over techniques based on comparing the shift of the transition with rate of measurement.

(i) Only one measurement is needed, which avoids systematic errors due to difference in heating rate. The most significant of these is the instrumental thermal lag, which causes an extra shift of the measured transition with heating rate indistinguishable from the intrinsic shift. If not corrected for, this effect would lead to too low an activation energy. In our case, any instrumental lag would cause a horizontal shift of the curves in *Figure* 5 with negligible effect on the slope.

(ii) Previous work[3] usually starts from some assumed form for the temperature dependence of τ (e.g. equation (4)) and in some mathematical approximation relates the observed shift of the transition to the activation energy. Our method does not require any assumption on the form of $\tau(\theta)$ and avoids the ambiguity of having to define a shift between curves of different shapes (*Figure* 2).

It is suggested that this is a useful technique for the thermal analysis of glass transitions.

Comparison of different heating rates

Although τ can be obtained from a single heating rate, it is nevertheless instructive to compare the values obtained from different heating rates, each of which being analysed independently. *Figure* 5 shows such a comparison for PS. With the exception of data taken at the highest heating rate of 20K min^{-1}, the results for τ agree with one another within experimental error. The 20K min^{-1} curve has essentially the same slope but is shifted

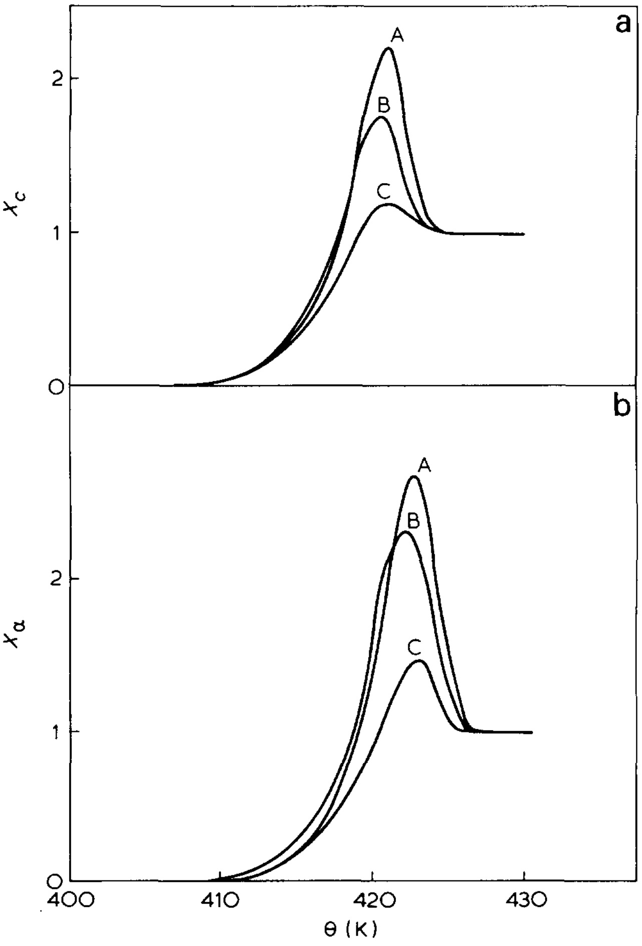

Figure 3 Effect of different cooling rates on (a) X_c and (b) X_α for PC. Cooling rate is A, 0.31K min^{-1}; B, 1.25K min^{-1}; C, 20 K min^{-1}

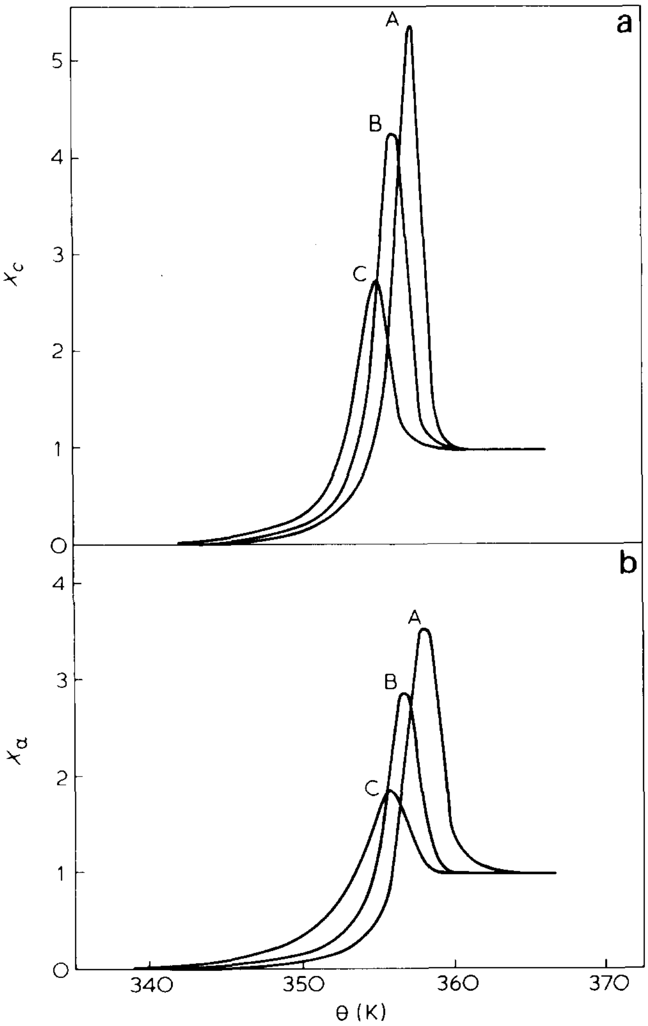

Figure 4 Effect of annealing time on (a) X_c and (b) X_α for PET. The sample has been annealed at 340K for A, 16 h; B, 4 h; C, 1 h

by one to two degrees towards higher temperatures. This small residual shift is consistent with being an instrumental thermal lag, which is expected to be proportional to the heating rate q and significant only for the largest q. Such an interpretation is justified by the mutual consistency among lower heating rates.

The excellent agreement among the results obtained at different heating rates shows that we have extracted an intrinsic parameter of the system, which is of greater interest than the apparent specific heat itself, and that assumption (B) is correct. Data taken after annealing the sample (e.g. *Figure* 4) or after cooling the sample at a slow rate (e.g. *Figure* 3), give less satisfactory results. This is not surprising — annealing or slow cooling leads to a relatively large value of $\theta_a - \theta_b$ in the transition range (see *Figure* 4 in ref. 1) so that the linear approximation for the heat exchange term in equations (1) and (2) is no longer valid. Therefore the subsequent discussion is based on data taken only from the heating rate experiments.

Several features of τ are worthy of comment. In terms of τ, there is no transition whatsoever, i.e. τ varies smoothly. An apparent transition (in C or α, say) is observed at a temperature θ if the experimental time scale t is such that $t \simeq \tau(\theta)$, so it is impossible to define a unique and meaningful glass transition temperature θ_g. Conventionally one uses the slowest measurements (e.g. a time scale of 10^2 s) to define θ_g. However, such an arbitrary choice of time scale, and hence of θ_g, is more a statement about the time scales convenient for experiments than a statement about the polymer itself.

Within experimental error, the activation energy is constant over the range of temperatures considered. *Table* 2 gives the activation energy E for PS determined for each heating rate. The spread is indicative of the accuracy which can be expected from this method.

With all heating rates taken together, this technique measures τ over a temperature interval of some 20 degrees, corresponding to τ in the range 1 s to 10^2 s. The analysis of thermal relaxation times complements dynamic mechanical measurements, which for practical reasons usually cover time scales below 1 s.

Study of different polymers

Since ln τ is linear in $1/\theta$, the result for each polymer can be specified by two quantities: θ_g (defined to be the temperature at which $\tau = 100\text{s}^*$) and the activation energy E. The values of these quantities are given in *Table* 3. It is estimated that θ_g is accurate to one degree and E to 10%.

There is clearly a correlation between E and θ_g. *Figure* 6

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* We have used a time scale of 10^2 s instead of a more conventional choice of say 10^3 s in order to avoid the need to extrapolate our data.

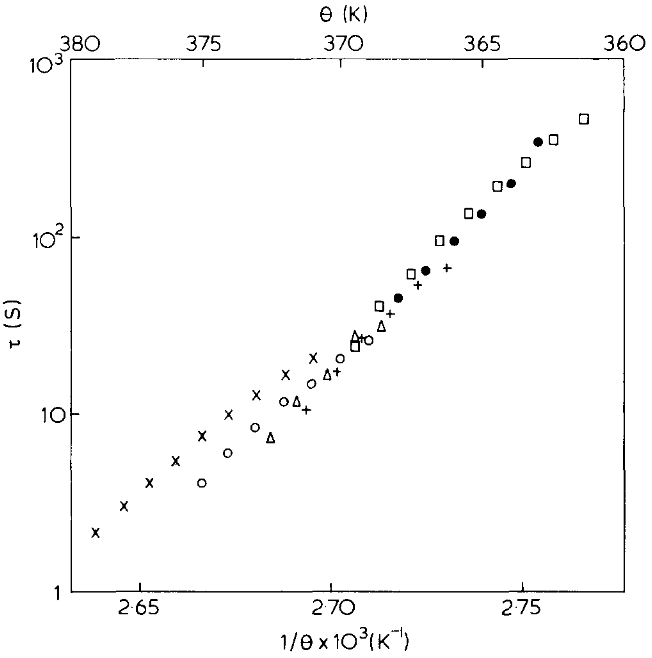

Figure 5 τ *versus* 1/θ for PS, determined from different heating rate experiments: x, 20K min; ○, 10K min; △, 5K min; +, 2.5K min; ●, 1.25K min; □, 0.625K min

Table 2 Thermal activation energy E of PS independently determined for each heating rate q

q (K min^{-1})	E (kcal mol^{-1})
20	81
10	83
5	93
2.5	103
1.25	101
0.625	97
Average	93

Table 3 Activation energies for various polymers

		Thermal	Mechanical[b]		Dielectric[b]		
Polymer	$\theta_g{}^a$ (K)	E (kcal mol^{-1})	Frequency (Hz)	E_m (kcal mol^{-1})	Frequency (Hz)	E_d (kcal mol^{-1})	τ/τ_m
Poly(phenylene oxide)	488	210			10^2–10^4	150^c	–
Polycarbonate	416	138			1–10^4	130^d	1.7^d
Poly(methyl methacrylate)	379	66			10^{-2}–1	110^e	2.8^e
Polystyrene	366	93	10–10^4	86^f	10^{-2}–1	125^e	0.6^e
Poly(vinyl chloride)	354	92	10^{-2}–1	165^g	10^{-2}–1	185^h	$0.6^g, 4.6^h$
			10–10^4	77^f			
Poly(ethylene terephthalate)	350	117	10^{-2}–1	180^i	10^{-2}–1	170^e	$1.4^i, 3.5^e$
Poly(vinyl acetate)	307	44			10^{-2}–1	80^e	8.0^e
Poly(methyl acrylate)	270	30			10–10^4	57^j	–
Polyisobutylene	207	31	10^{-2}–1	29^k			–
Poly(dimethyl siloxane)	149	46			10^2–10^5	38^l	–
					10^2–10^5	24^m	
					10^2–10^5	18^n	

[a] θ_g is the temperature at which the thermal relaxation time is 100 s
[b] These activation energies have been extracted from data in literature and have an accuracy of 10–20%
[c–m] Refs 6–16
[n] Ref 2

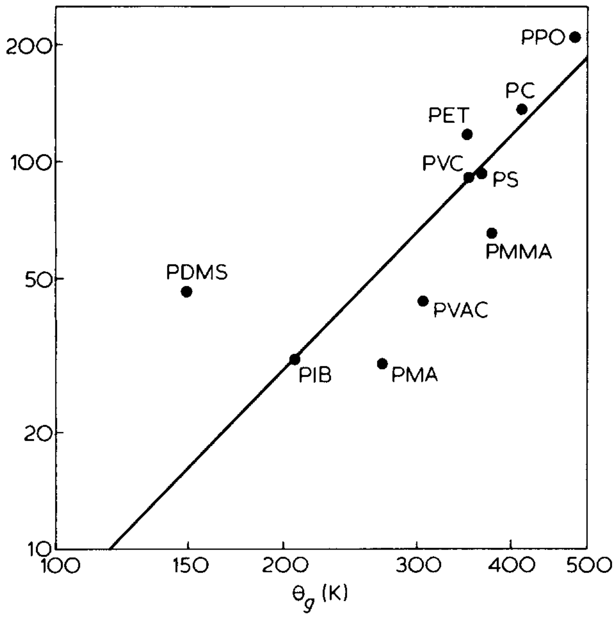

Figure 6 *E versus* θ_g. The straight line corresponds to $E \propto \theta_g^2$

shows that E is roughly proportional to θ_g^2, which is consistent with the WLF equation[4] with universal coefficients.

In *Table* 3 we have also listed the mechanical activation energy E_m (or its dielectric counterpart E_d). In general E_m varies with frequency, but may be regarded as constant within a limited frequency range. There is probably a 20% error in E_m (estimated from the consistency between different experiments). Therefore $E \simeq E_m$.

The above relation implies that the plot of $\ln \tau$ and $\ln \tau_m$ against $1/\theta$ are approximately parallel straight lines, the separation of which may be specified by τ/τ_m, say at $\theta = \theta_g$. From *Table* 3 we see that $\tau \sim \tau_m$, i.e. the thermal and mechanical relaxation times are comparable.

This is the first systematic study of the thermal relaxation time and the corresponding activation energy of polymers at the glass transition to our knowledge. The result supports, but does not explain, the folklore that the thermal and mechanical transitions are 'the same'. The next section supplies an explanation.

CONNECTION BETWEEN MECHANICAL AND THERMAL RELAXATIONS — A MODEL

General comments

Dynamic mechanical and thermal measurements are usually said to exhibit 'the same' glass transition, which means (i) the transitions are observed at roughly the same temperature and (ii) both techniques show that the transition shifts to higher temperature with decreasing time scale of measurement. These properties can be stated more precisely as (i) $\tau(\theta) \sim \tau_m(\theta)$, (ii) $E \sim E_m$. In mechanical measurements, the sample is set into vibration at a low frequency, say 10^{-2} Hz, and the vibration may be thought of as phonons of this frequency. Since the transition shifts up by ~ 5 degrees for each decade increase in frequency, it might be thought that thermal properties, dependent on phonons of say 10^{13} Hz, would have a transition at a temperature ~ 75 degrees higher. The fact that thermal and mechanical properties exhibit transitions at essentially the same temperature is puzzling.

In mechanical experiments, the polymer at temperature θ absorbs phonons of frequency ω with an 'absorption coefficient' equal to the loss tangent $\Delta(\theta, \omega)$, which peaks at a frequency $\omega_0(\theta)$. In thermal experiments, the heat exchange between thermal phonons and the macromolecular modes (b modes) is described by (1) where γ plays the role of an 'effective absorption coefficient' for the entire phonon spectrum. Thus γ or τ^{-1} must be the thermal average of Δ, and we now derive this relation.

Basic equation

Both the damping of mechanical vibrations and the heat exchange between the thermal phonons and the b modes can be described in terms of the time evolution of the number of phonons $n(\omega)$ in a particular mode, which may be written as

$$\frac{\mathrm{d}n(\omega)}{\mathrm{d}t} = -\beta[n(\omega) - n_{\mathrm{eq}}(\theta, \omega)] \tag{18}$$

where $n_{\mathrm{eq}}(\theta, \omega)$ is the equilibrium distribution. In dynamic mechanical measurement, $n(\omega)$ for one specific ω is excited to well over equilibrium values, so that the first term in

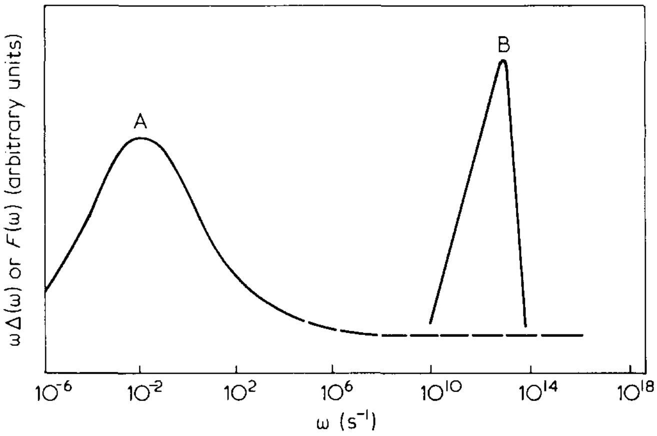

Figure 7 Schematic diagram illustrating the factors whose overlap integral determines γ. A, $\omega\Delta(\omega)$; B, $F(\omega)$

(18) dominates and

$$\Delta=\frac{1}{2\pi}\text{(fractional energy loss per cycle)}$$

$$=\beta/\omega \tag{19}$$

Since (18) represents the interaction with b-modes, θ in (18) should refer to θ_b. Hence we get

$$\frac{\mathrm{d}n(\omega)}{\mathrm{d}t}=-\omega\Delta(\theta_b,\ \omega)[n(\omega)-n_{\mathrm{eq}}(\theta_b,\ \omega)] \tag{20}$$

Thus with mechanical data (i.e. Δ) as input, the behaviour of the phonon spectrum is completely determined by (20).

Application to thermal relaxation

For thermal relaxation, $n(\omega)$ is given by an equilibrium distribution $n_{\mathrm{eq}}(\theta_a,\ \omega)$ at a temperature θ_a, in general different from θ_b, so (20) becomes

$$\frac{\mathrm{d}n(\omega)}{\mathrm{d}t}=-\omega\Delta(\theta_b,\ \omega)[n_{\mathrm{eq}}(\theta_a,\ \omega)-n_{\mathrm{eq}}(\theta_b,\ \omega)]$$

$$=-\omega\Delta(\theta,\ \omega)\frac{\partial n_{\mathrm{eq}}}{\partial\theta}(\theta_a-\theta_b) \tag{21}$$

to first order in the temperature difference. The rate of loss of energy, $\mathscr{L}$, from the phonon system as a whole is then

$$\mathscr{L}=-\int\frac{\mathrm{d}n(\omega)}{\mathrm{d}t}\hbar\omega D(\omega)\mathrm{d}\omega$$

$$=\int\omega\Delta(\theta,\ \omega)\frac{\partial n_{\mathrm{eq}}}{\partial\theta}(\theta_a-\theta_b)\hbar\omega D(\omega)\mathrm{d}\omega \tag{22}$$

D being the density of states. But in the absence of external power, $\mathscr{L}$ is also given by

$$\mathscr{L}=-C_a\frac{\mathrm{d}\theta_a}{\mathrm{d}t}=\gamma(\theta_a-\theta_b) \tag{23}$$

Equating (22) with (23) and expressing the result in terms of τ we have

$$\tau^{-1}(\theta)=\frac{1+\eta^{-1}}{C_a}\int\omega\Delta(\theta,\ \omega)\frac{\partial n_{\mathrm{eq}}}{\partial\theta}\hbar\omega D(\omega)\mathrm{d}\omega \tag{24}$$

where $\eta=C_b/C_a$ is the fractional jump of the specific heat at the glass transition.

While in principle τ can be calculated directly from (24), a much simpler expression is possible. The phonon contribution to the specific heat is

$$C_a=\int\frac{\partial n_{\mathrm{eq}}}{\partial\theta}\hbar\omega D(\omega)\mathrm{d}\omega\equiv\int F(\omega)\mathrm{d}\omega \tag{25}$$

so in terms of $F(\omega)$:

$$\tau^{-1}(\theta)=\frac{1+\eta^{-1}}{C_a}\int\omega\Delta(\theta,\ \omega)F(\omega)\mathrm{d}\omega$$

$$\simeq\frac{1+\eta^{-1}}{C_a}\omega_\theta\Delta(\theta,\ \omega_\theta)\int F(\omega)\mathrm{d}\omega$$

$$=(1+\eta^{-1})\omega_\theta\Delta(\theta,\ \omega_\theta) \tag{26}$$

using the fact that the integral comes mainly from the contribution near the peak of $F(\omega)$, namely at $\omega_\theta\simeq4k\theta/\hbar$ $10^{13}\ \mathrm{s}^{-1}$ (*Figure* 7).

Under the assumption of time–temperature equivalence Δ may be written as

$$\Delta(\theta,\ \omega)=\bar{\Delta}[\omega/\omega_0(\theta)] \tag{27}$$

So,

$$\tau^{-1}(\theta)=(1+\eta^{-1})\omega_\theta\bar{\Delta}[\omega_\theta/\omega_0(\theta)] \tag{28}$$

Note that $\omega_\theta/\omega_0(\theta)\sim10^{13}\ \mathrm{s}^{-1}/10^{-2}\ \mathrm{s}^{-1}\gg1$, so we need to know the behaviour of $\bar{\Delta}(\omega/\omega_0)$ for very large ω/ω_0. Assume that for $\omega/\omega_0\gg1$,

$$\bar{\Delta}\simeq\bar{\Delta}_0(\omega/\omega_0)^{-l} \tag{29}$$

where $\bar{\Delta}_0$ is a constant. Substituting (29) into (28) gives

$$\tau^{-1}(\theta)=(1+\eta^{-1})\bar{\Delta}_0\omega_\theta^{1-l}\omega_0(\theta)^l \tag{30}$$

The thermal activation energy E is therefore:

$$E=R\frac{\partial\ln\tau}{\partial(1/\theta)}\simeq-lR\frac{\partial\ln\omega_0(\theta)}{\partial(1/\theta)} \tag{31}$$

since only $\omega_0(\theta)$ is strongly (i.e. exponentially) dependent on θ. Comparing with (6) and (7) gives

$$E=lE_m \tag{32}$$

Determination of l and $\bar{\Delta}_0$

Generalizing from a Maxwell element, one may write the complex modulus $G=G_1+\mathrm{i}G_2$ as[5]

$$G_1(\omega)=G_r+\int\frac{H(\sigma)\omega^2\sigma^2}{1+\omega^2\sigma^2}\mathrm{d}\ln\sigma$$

$$\approx\int H(\sigma)\mathrm{d}\ \ln\sigma \tag{33}$$

$$G_2(\omega)=\int\frac{H(\sigma)\omega\sigma}{1+\omega^2\sigma^2}\mathrm{d}\ \ln\sigma$$

$$\approx\frac{1}{\omega}\int\frac{H(\sigma)}{\sigma}\mathrm{d}\ \ln\sigma \tag{34}$$

the latter forms being valid at large ω. If we define the mean relaxation time σ_0 by

$$\frac{1}{\sigma_0}=\int\frac{H(\sigma)}{\sigma}\mathrm{d}\ln\sigma\Big/\int H(\sigma)\,\mathrm{d}\ln\sigma \tag{35}$$

then

$$\Delta=G_2/G_1=\frac{1}{\sigma_0\omega} \tag{36}$$

Comparing with (29) gives $l=1$ and

$$\bar{\Delta}_0=[\sigma_0(\theta)\omega_0(\theta)]^{-1} \tag{37}$$

We therefore conclude from (32) that the thermal and mechanical activation energies are equal, in agreement with experimental observation. Also, (30) implies that the ratio of thermal and mechanical relaxation times is given by

$$\frac{\tau(\theta)}{\tau_m(\theta)}=[2\pi(1+\eta^{-1})\bar{\Delta}_0]^{-1} \tag{38}$$

Since the mean relaxation time σ_0 is roughly the reciprocal of the frequency ω_0 at the absorption maximum, we expect from (37) that $\bar{\Delta}_0\simeq 1$. This implies τ/τ_m is unity to within an order of magnitude, in agreement with the experiment results of $\tau/\tau_m\simeq 0.6$–8 listed in *Table* 3.

To be able to predict $\tau(\theta)/\tau_m(\theta)$ even to within an order of magnitude is not a trivial result. If θ is the nominal glass transition temperature determined mechanically, then Δ at this temperature peaks at $\omega_0(\theta)\sim 10^{-2}\ \mathrm{s}^{-1}$. But $\tau(\theta)$, for the same θ, depends on phonons of frequency $\omega_\theta\sim 10^{13}\ \mathrm{s}^{-1}$. The present calculation is a theoretical framework for making this tremendous extrapolation of 15 orders of magnitude*.

CONCLUSION

The present study has placed the kinetic model on a firm footing by demonstrating that

(i) There is a second temperature θ_b which determines the state of the polymer.

(ii) The relaxation of θ_b is given by a single time constant τ.

(iii) τ and the associated activation energy E are phenomenologically related to their mechanical counterparts which can be understood.

The conceptual understanding of the glass transition has been advanced by the success of the kinetic model, and in particular we have been able to relate the behaviour of the dynamic modulus, the specific heat and the expansivity. However, these relations are all based on the concept of the b modes, treated as a 'black box'. The next challenge would obviously be the unravelling of this 'black box', i.e. the attempt to understand the nature and properties of the b modes microscopically.

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APPENDIX

Here we discuss a technical problem encountered in the calculation of τ from the apparent specific heat C. In principle, the procedure, as discussed in the text, is to choose two linear functions to represent C_a and C_a+C_b (*Figure* 1) from which $X=(C-C_a)/C_b$ is calculated and θ_b is found.

However, two related problems occur. Firstly we expect (e.g. from computer simulations[1]) that the experimental value of C should first dip below C_a and have a cross-over at some temperature θ_x (*Figure* 8). The physical reason can be readily understood if we plot θ_a and θ_b *versus* time (*Figure* 9) and notice that θ_b will always relax towards θ_a. So during heating, θ_b should initially decrease, $X=\mathrm{d}\theta_b/\mathrm{d}\theta_a<0$ and $C<C_a$. For this reason, one should *not* take C_a to be a line asymptotic to the low temperature

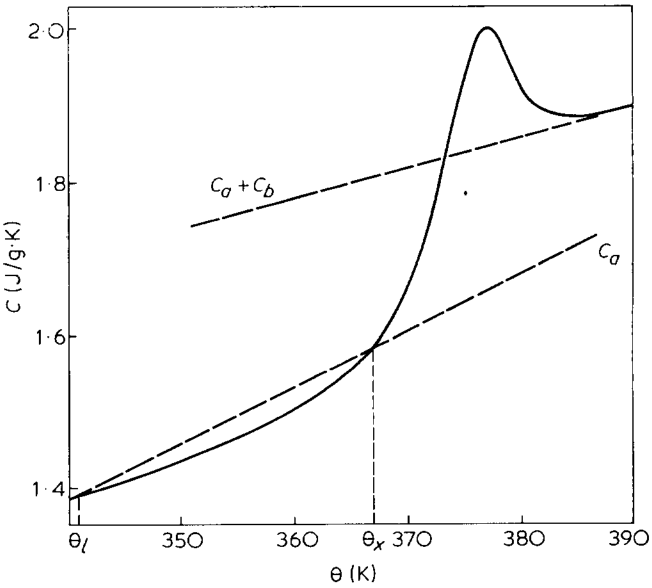

Figure 8 Choice of slope for C_a, illustrated by data on PS measured at 20K min. C crosses C_a at θ_x

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* Note that in general equation (38) for τ/τ_m should have an extra factor of $(\omega_\theta/\omega_0)^{l-1}$, so that if the effective l is different from 1 by as little as 0.1, there would be an error of $(10^{15})^{0.1}\sim 30$.

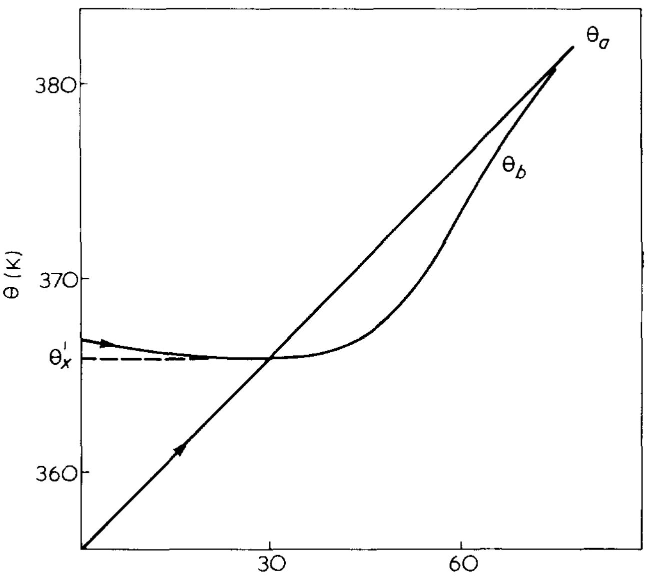

Figure 9 θ_a and θ_b *versus* time, illustrating the initial decrease of θ_b. This graph is obtained from the raw data of *Figure 8*. θ_a and θ_b cross at θ'_x

part of C. We may take the value of C_a at a low temperature point θ_l to be fixed by the experimental value of C and must look for a method to determine the slope of C_a[*]. From the above discussion and equation (10), we see that θ_x (as given in *Figure* 8) has the property that $d\theta_b/d\theta_a = 0$ when $\theta_a = \theta_x$.

Secondly, suppose the slope of C_a is known and θ_b has been determined from θ_a. There will be a temperature, say θ'_x at which $\theta_b - \theta_a = 0$ (*Figure* 9). But our model of thermal relaxation requires

$$\frac{d\theta_b}{d\theta_a} \propto \frac{d\theta_b}{dt} \propto -(\theta_b - \theta_a)$$

which shows that θ_x and θ'_x must be identical. If unequal values of θ_x and θ'_x were used, then

$$\frac{1}{\tau} \propto \gamma \propto \frac{d\theta_b/d\theta_a}{\theta_a - \theta_b}$$

would have the numerator and denominator vanishing at different points, leading to erroneous zero and infinity for τ.

Both of these problems can be simultaneously solved by the following procedure. (i) We choose an arbitrary slope for C_a. This determines θ_x in *Figure* 8. (ii) θ_b is found by integrating X, as described in the text. The point θ'_x is then determined. (iii) In general $\theta_x \neq \theta'_x$, so we vary the slope for C_a until equality is achieved. This method, by ensuring the absence of extraneous zeros and poles in τ, naturally gives more reliable results. Nevertheless, at the cross-over point $\theta_x = \theta'_x$, τ is given by 0/0, so that it is obvious that τ can only be accurately determined above θ_x.

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[*] The slope of C_a and α_a have been chosen arbitrarily to calculate X_c and X_α in *Figures* 2–4, so that both X_c and X_α as shown there are wrong by a linear function. However this does not affect the comparison between the two.