The kinetics of the α and β relaxations in isotactic polypropylene

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The kinetics of the two mechanically dominant relaxations in isotactic polypropylene are studied by thermal sampling (TS). The Bucci relaxation times are corrected by the method of McCrum. The α and β relaxation processes are found to be governed by the compensation rule. For the α relaxation the isokinetic point occurs at $\tau_c = 19$ μs, $T_c = 180°C$: the β relaxation isokinetic point occurs at $\tau_c = 1.3$ ms, $T_c = 23°C$. These large values of τ_c are anomalous: they imply that the approach frequencies (τ_c^{-1}) are extremely low: 50 kHz and 0.8 kHz for the α and β relaxations respectively. The classical view of the approach frequency gives $kT/h \sim 6 \times 10^{12}$ Hz. If this anomaly is substantiated for relaxations in other polymers it will require a complete re-examination of current theories of polymer relaxation mechanisms. It is shown also that the temperature dependence of the difference between the limiting compliances, $J_R - J_U$, plays a role in thermal sampling and in thermally stimulated creep.

Keywords Polypropylene; compensation rule; viscoelastic creep; thermal sampling

INTRODUCTION

In this paper, we present a detailed description of our reformulation[1] of the technique of thermal sampling (TS)[2-5], together with experiments in which it is used to study the kinetics of the mechanically dominant relaxations in isotactic polypropylene. The most striking conclusion of the pioneering TS experiments is the proposal that within a particular distribution of relaxation times the different elements have different activation energies. Following Lacabanne et al.[3], let a distribution be represented by a set of closely spaced relaxation times τ_i: then the temperature dependence is:

$$\tau_i = \tau_c \exp \frac{\Delta H^i}{R} \left[\frac{1}{T} - \frac{1}{T_c} \right] \qquad (1)$$

T_c and τ_c are constants. Each τ_i is governed by the Arrhenius equation with a specific activation enthalpy, ΔH_i: equation (1) is empirical and is referred to as the compensation rule. At the compensation temperature T_c all relaxation times take the same value τ_c. The distribution, as T approaches T_c, thus compresses so that at T_c it appears as a single relaxation time.

The data interpretation which led to this radical conclusion was based on an analysis of TS experiments proposed by Bucci, Fieschi and Guidi (BFG plot)[6]: this plot is of unquantifiable value for polymeric relaxations unless corrected by the procedure described recently by McCrum[1]. It follows therefore that the proposal that the compensation rule holds for polymer relaxations cannot be supported by TS experiments without reappraisal of the data using the McCrum correction. A major purpose of this paper is to use this correction for TS experiments performed in the α and β regions of polypropylene. The β-relaxation is the glassy relaxation ($T_g \sim -15°C$) of the amorphous fraction and in mechanical damping at 1 Hz is

centred at about $0°C$[7]. The α-relaxation overlaps the β-process on the high temperature side: it is centred in the region of $100°C$ at 1 Hz[7]. Its origin is uncertain but is most likely an additional relaxation of the amorphous fraction triggered by the onset of molecular rotation within the crystal.

Polypropylene was selected for study for two reasons. First the compensation rule had already been established for the α-relaxation by the method of double T-jump[8]. It was obviously of paramount importance to test this result using the method of TS. Such an experiment would cross-check the two new and highly attractive techniques, double T-jump and TS. It would simultaneously provide a second test of the applicability of the compensation rule. It was clearly also desirable to examine the kinetics of the β-process in polypropylene.

EXPERIMENT

The specimen of isotactic polypropylene was the same as that used in the earlier study[8]: before machining, in order to promote stability, it had been annealed for an extended period at $130°C$ and cooled very slowly. The equipment was the same also, consisting of a torsional creep machine[9] with temperature control based on the method of Schwippert and van der Waal[10].

The machined specimen was in the form of a thin blade of dimensions $l = 60$ mm, $a = 10$ mm and $b = 1.0$ mm. It was twisted around its long axis by applying a constant current i to the torque coil. If the coil constant is k the torque is:

$$\Gamma = ki \qquad (2)$$

The angle θ through which the blade was twisted was measured by an optical lever of throw $L = 2.1$ m. The relationship between θ and the deflection of the optical

lever, *x*, from the zero point is:

$$\theta = \frac{x}{2L}$$

The maximum shear strain in the blade occurs on the surface in the centre of the face and is:

$$\gamma = \frac{\theta a}{l} = \left(\frac{a}{2Ll}\right)x \qquad (3)$$

so that the strain rate is:

$$\dot{\gamma} = \left(\frac{a}{2Ll}\right)\dot{x} \qquad (4)$$

The maximum shear stress σ occurred at the same place. This is given:

$$\gamma = J\sigma \qquad (5)$$

in which J is the compliance: σ is of course proportional to Γ and hence to i. All measurements were made at strains in the linear viscoelastic region. In this paper, discussion of stress and strain implies the maximum values of stress and strain in the blade.

Five experiments were performed in the β-region at stressing temperatures, T_σ, in the range $-16°C$ to $-27°C$. Each experiment comprised three runs, labelled σ, z and x for ease of reference. The temperature–time cycle followed in the σ-run is shown in *Figure 1*: the temperatures indicated are referred to T_σ. Thus for one of the experiments with $T_\sigma = -25°C$ the specimen was held first at 45°C for 10 min (see *Figure 1*) and then cooled to $-15°C$

and maintained at $-15°C$ for 10 min. It was then cooled at 1°C/min to $T_\sigma = -25°C$ and was held there for 43 min. In this 43 min, the specimen was 'physically aged' for the first 20 min (t_a); it was then placed under a torque for the next 20 min (t_σ): the torque was then released so that during the final 3 min (t_d) the viscoelastic strain within the specimen partially recovered. The specimen was then quenched to $-55°C$ (thus freezing-in the unrecovered viscoelastic strain) and held at that temperature for approximately 10 min. The heating run at a rate of 2°C/min then commenced, during which the frozen-in strain was slowly released: measurements of the angle through which the specimen was rotated were taken during the heating run. The heating run (i.e. data collection) was complete at $-5°C$. The σ-run was then terminated by quick heat from $-5°C$ to 45°C to promote rapid elimination of the residual frozen-in strain in preparation for the z-run.

In the z-run the specimen was taken through precisely the same temperature cycle as in the σ-run but no torque was applied at T_σ: the purpose was to determine the temperature dependence of the zero point on the heating run. This additional run was required because the specimen exhibits a small temperature induced rotation in the absence of an externally applied torque. The difference between the rotational angles in the σ and z-runs was thus known at each value of T on the heating run. The Bucci relaxation time[6] at T, τ_B^T, could then be determined since:

$$\tau_B^T = \frac{\gamma^T}{\dot{\gamma}^T} \qquad (6)$$

which from equations (3) and (4) is:

$$\tau_B^T = \frac{x}{\dot{x}} \qquad (7)$$

The BFG plot of τ_B^T for the experiment in which the stress was applied at $T_\sigma = -25°C$ is shown in *Figure 2*, circled points. The parameter required for the McCrum correction[1] is the Bucci relaxation time at 50% relaxation:

$$\tau_{B\frac{1}{2}}^T = \alpha\tau_B^T \qquad (8)$$

the correction factor α was obtained from the α-run.

In the α-run the specimen was taken through the same cycle as in the σ-run up to the point Q, *Figure 1*. At this instant (it is convenient to take Q as the zero in time, $t = 0$) the specimen was not quenched but recovery continued at T_σ. Values of $\gamma^{T_\sigma}(t)$ and $\dot{\gamma}^{T_\sigma}(t)$ were observed and used to obtain the time dependence of the isothermal Bucci relaxation time:

$$\tau_B^{T_\sigma}(t) = \frac{\gamma^{T_\sigma}(t)}{\dot{\gamma}^{T_\sigma}(t)} \qquad (9)$$

The method of calculating α^T from $\tau_B^{T_\sigma}(t)$ is described below.

In the experiments at higher temperatures in the α-relaxation region a different temperature programme was followed. Because of the possibility of premelting it was decided to keep the maximum temperature to which the specimen was to be subjected to below 90°C. Six values of T_σ were selected in the range of 36° to 68°C. The temperature programme for the σ-run in the α-region is shown in *Figure 3*: as in *Figure 1*, temperatures are
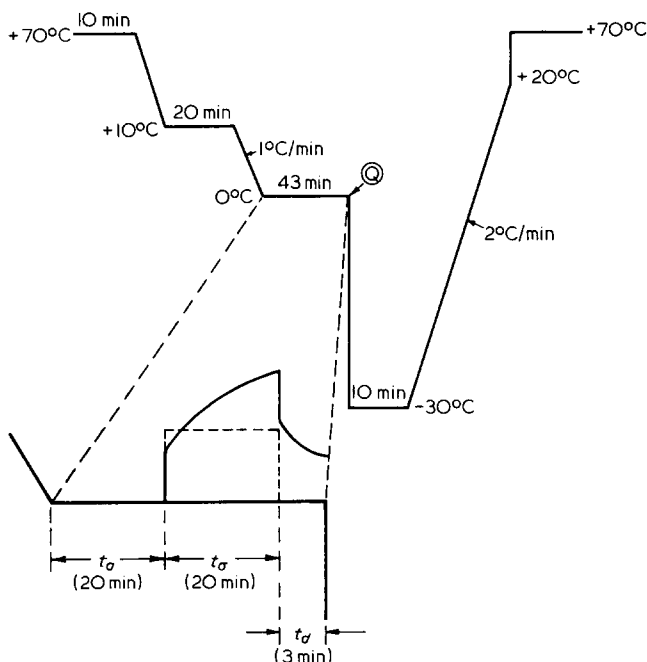

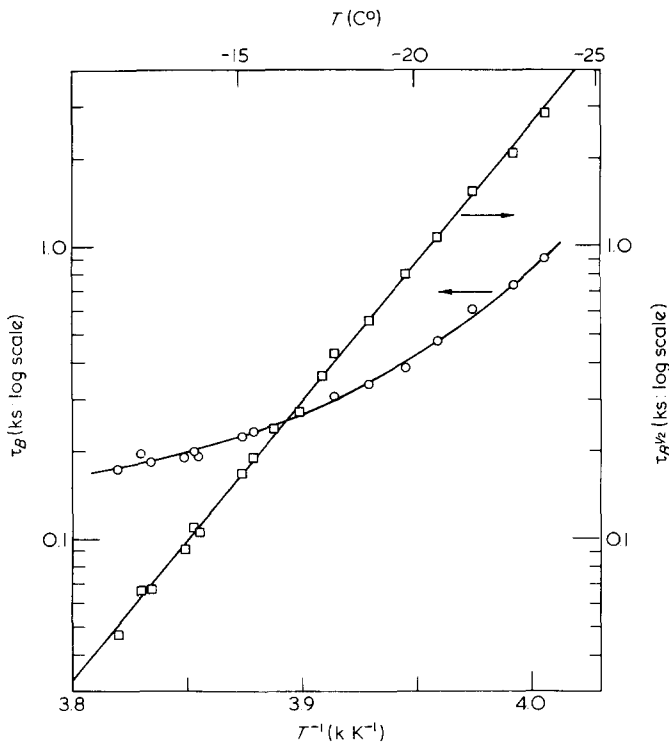*Figure 1* Temperature–time programme for σ-run in the β-region ($-16°C < T_\sigma < -27°C$): all temperatures referred to T_σ. At T_σ the specimen was held in total for 43 min: it was aged for 20 min, stressed for 20 min and then unstressed and permitted to recover for the final 3 min. It was then quenched and a heating run initiated at a heating rate of 2°/min. The heating sequence prior to T_σ is to 'clean' the specimen (remove vestigial viscoelastic strains) and to place it in a defined condition

Figure 2 BFG plot (log τ_B *versus* T^{-1}, circled points) in β-region for $T_\sigma = -25°C$: the concave-up curved line is typical of this plot. Also shown is a McCrum plot of log $\tau_{B\frac{1}{2}}$ *versus* T^{-1}, squared points: this is the τ_B data corrected by the method of reference 1: the corrected plot takes the linear Arrhenius form. Values of correction factor α (equation (8)) were obtained by theoretical computation with $q = 0.42$ (Method 1)
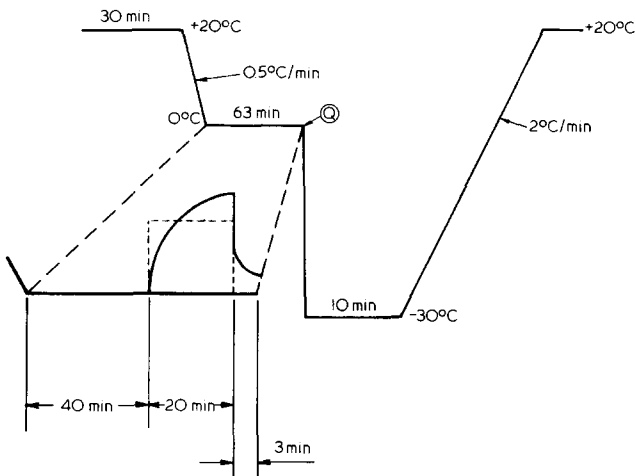

Figure 3 Temperature–time programme for σ-run in the α-region ($36°C < T_\sigma < 68°C$): temperatures referred to T_σ

referred to T_σ. Thus in the experiment with $T_\sigma = 48°C$, the specimen was heated at 68°C for 30 min and then cooled to 48°C at 0.5°C/min. It was held at 48°C for 63 min: after 40 min (t_a) at 48°C the torque was applied and then released after another 20 min (t_σ). The specimen was then permitted to recover for the final 3 min (t_d) at 48°C before it was quenched to 18°C: it was held at 18°C for approximately 10 min and then the heating run at 2°C/min was initiated during which data was collected. The run was terminated when the specimen again reached 68°C. The z-run was then performed as described above. Typical values of τ_B^T for TS experiments in the α-region are

shown in the BFG plot for $T_\sigma = 48°C$ in *Figure 4*, circled points. Finally, the α-run was performed in which the specimen, after stressing and un-stressing, was permitted to recover isothermally at $T_\sigma = 48°C$ and $\tau_B^{T_\sigma}(t)$ determined as described in the preceding paragraph.

Determination of α

The theory of the correction factor α, both its significance and method of determination, is described in ref. 1. We add here a few additional details which will be of interest to the reader.

The two most valuable methods for determining α are both based on the isothermal determination of τ_B as a function of time in the α-run at T_σ. We have used α determined by both methods to correct the data in order to ensure that the conclusions are independent of the method of determination: as will be seen, this was found to be so.

Method 1. Let the distribution consist of a series of Voigt elements closely and evenly spaced, say 20 per decade: the number per decade is of no significance providing it exceeds 3 per decade. Let the ith at T_σ be of strength J_i and relaxation time τ_i and let the distribution be of ramp form:

$$\log J_i = p + q \log \tau_i \qquad (10)$$

q may be zero (box distribution) or positive (ascending ramp) or negative (descending ramp). It follows from equation (10) that:

$$\frac{J_i}{J_0} = \left(\frac{\tau_i}{\tau_0}\right)^q \qquad (11)$$

in which J_0 and τ_0 refer to a reference relaxation element, which we take arbitrarily to be the element at 1 ks. Now for our experimental loading pattern at T_σ in the α-run, it is possible to calculate from equation (11) the dependence on time of τ_B at T_σ: the parameters of significance are
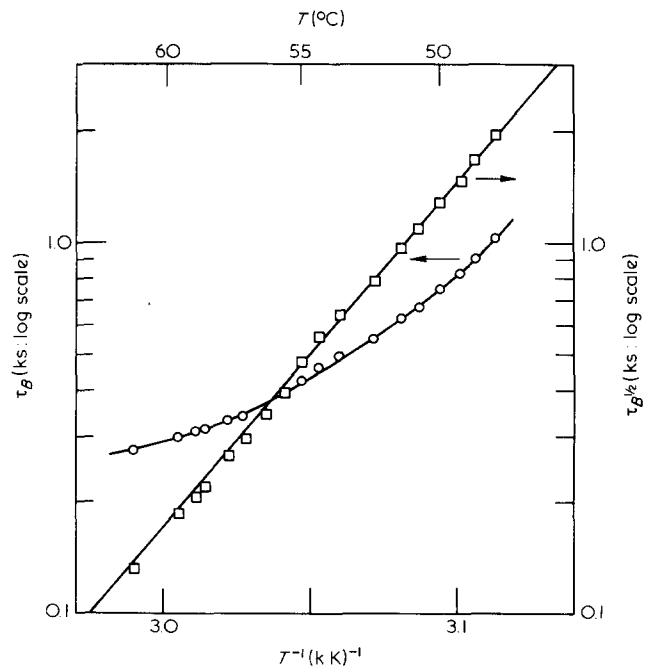

Figure 4 BFG plot (log τ_B *versus* T^{-1}, circled points) in α-region for $T_\sigma = 45°C$. Also shown is a McCrum plot, log $\tau_{B\frac{1}{2}}$ *versus* T^{-1}, squared points. Values of α (equation (8)) obtained by the empirical procedure (Method 2)

firstly, those from the experiment ($t_\sigma = 20$ min, $t_d = 3$ min) and secondly, the value of q. The dependence of τ_B on time is shown by the lines in *Figure 5* for values of q ranging from -0.5 to $+0.6$.

A simple method of finding q from experiment is to plot the isothermal values of τ_B, against log t, as shown in *Figure 5*. The experimental points can be at once compared with the theoretical predictions for different values of q. The data for a β-region experiment ($T_\sigma = -25°C$) are initially, for low t, below the $q = 0.4$ line: as t increases they pass up through it (*Figure 4*). It is clear that the value of $q = 0.4$ is a reasonable first order description of the ramp: it is of course, not to be expected that the distribution would be exactly a ramp with constant q over several decades of relaxation time. We take for this experiment with $T_\sigma = -25°C$, and for the other experiments in the β-region also, the value of $q = 0.42$ to be a reasonable estimate of the ramp slope.

For the data in the experiment at 48°C the measured points fall around the line $q = 0.2$ (*Figure 5*). For the other experiments in the α-region $q = 0.2$ is also a good first order description of the ramp slope. This substantial difference in ramp slope between the two regions, 0.2 for the α as opposed to 0.42 for the β-region, is discussed in the Discussion section. It is sufficient to note here that it is believed to be dependent on the nature of the relaxations: it is known that in polypropylene the β-relaxation is very sharp and the α-relaxation diffuse.

In practice the most useful τ_B plot is that shown in *Figure 6*. This is a plot of the calculated τ_B at time t against the calculated $\gamma(t)/\gamma(0)$ at the same value of t: $\gamma(t)/\gamma(0)$ is the ratio of the remaining strain at time t divided by the initial strain at $t = 0$. From this plot (labelled 'τ_B (method 1)' in *Figure 6*) the value of τ_B at $\gamma(t)/\gamma(0) = 0.5$ is obtained: for $q = 0.2$ it is $\tau_{B\frac{1}{2}} = 1.73$ ks. With this value of $\tau_{B\frac{1}{2}}$, α is then determined (equation (8)) and is plotted also against $\gamma(t)/\gamma(0)$ (labelled 'α (method 1)' in *Figure 6*).

Method 2. It is clear from *Figure 5* that taking q to be constant introduces a systematic error since the distribution is not precisely a ramp of constant q. Furthermore, the extent to which the distribution differs from a ramp of
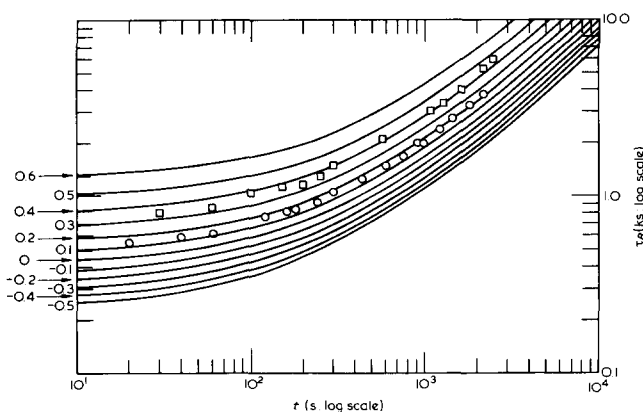

Figure 6 Calibration plot of τ_B and α as a function of $\gamma/\gamma(0)$ for the run at $T_\sigma = 48°C$. Solid lines: τ_B and α obtained by Method 1 as described in text with $q = 0.2$. Broken lines and points: τ_B and α obtained by Method 2 as described in text

constant q differs slightly from one value of T_σ to another. Method 2 is not subject to these significant errors and is considered to be the more reliable. The method is illustrated in *Figure 6* in which the experimental values of τ_B obtained in the α-run at $T_\sigma = 48°C$ are plotted by circled points against the observed values of $\gamma(t)/\gamma(0)$. From these data points a best fit line is drawn graphically, as indicated by the broken line: the value of $\tau_{B\frac{1}{2}}$ obtained from this line is 1.61 ks. Each of the values of observed τ_B are then divided by 1.61 ks (equation (8)) to give values α which are also plotted in *Figure 6*, broken line labelled 'α (method 2)'. It will be noted that the values of α shown in *Figure 6* determined by Methods 1 and 2 are in good agreement.

We turn now to describe how, from values of τ_B^T taken in the σ-run as the specimen is heated, values of $\tau_{B\frac{1}{2}}^T$ are calculated: the procedure is the same whether Method 1 or Method 2 has been used to determine α. The observables are $\gamma(0)$ (value of γ at point Q, *Figures 1* and *3*), γ^T and the derived quantity γ^T. These quantities lead to the calculation of $\gamma^T/\gamma(0)$ and to τ_B^T. From $\gamma^T/\gamma(0)$ a value of α is read off from *Figure 6* (either using Method 1 or Method 2) which is then multiplied into τ_B^T to yield $\tau_{B\frac{1}{2}}^T$ (equation (8)).

An example of the BFG plot corrected with α determined from Method 1 is shown in *Figure 2* ($q = 0.42$): a typical correction using Method 2 is shown in *Figure 4*. For the α and β relaxations in polypropylene, both corrections convert the curved BFG plot into straight lines conforming to the Arrhenius equation. As mentioned above, the more reliable correction is obtained from Method 2: in this paper Method 1 is used in a secondary role, particularly to emphasize the theoretical framework of the correction procedure. The results of the analysis—values of T_c and τ_c—vary only slightly with correction procedure as is shown in the next section.

RESULTS

Figure 7 shows values of log $\tau_{B\frac{1}{2}}$ against T^{-1} for data taken in the β-region corrected by Method 2 (*Figure 7a*) and Method 1 (*Figure 7b*). The data exhibit excellent Arrhenius lines of the form:

$$\log \tau_{B\frac{1}{2}} = a + bT^{-1} \qquad (12)$$

Visual inspection of the data shows that the lines are not parallel but are converging and this is supported quantitatively by the values of a and b determined by linear least squares analysis, which are given in *Table 1*. Also given in *Table 1* are values of ΔH. It will be seen that

Figure 5 Solid lines show the calculated isothermal dependence of τ_B on t computed from a Voigt model for values of $-0.5 < q < 0.6$ (shown on left) for $t_\sigma = 20$ min and $t_d = 3$ min. The two series of points show the values of τ_B determined isothermally by experiment in the α-region ($T_\sigma = 48°C$, circled points) and in the β-region ($T_\sigma = -25°C$, squared points). The operative value of q for the two experiments can be read off directly from this plot. Note that in both regions, as expected, the data shows the distribution not to be precisely a ramp of constant slope: this fact limits the accuracy of Method 1 determination of α
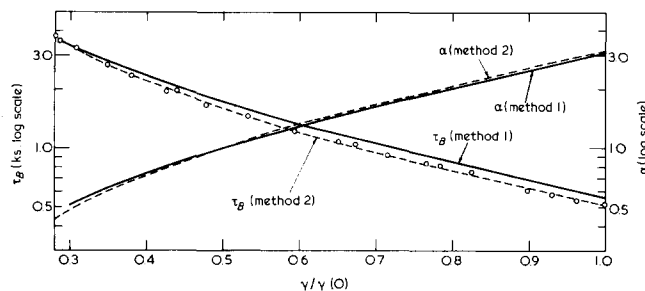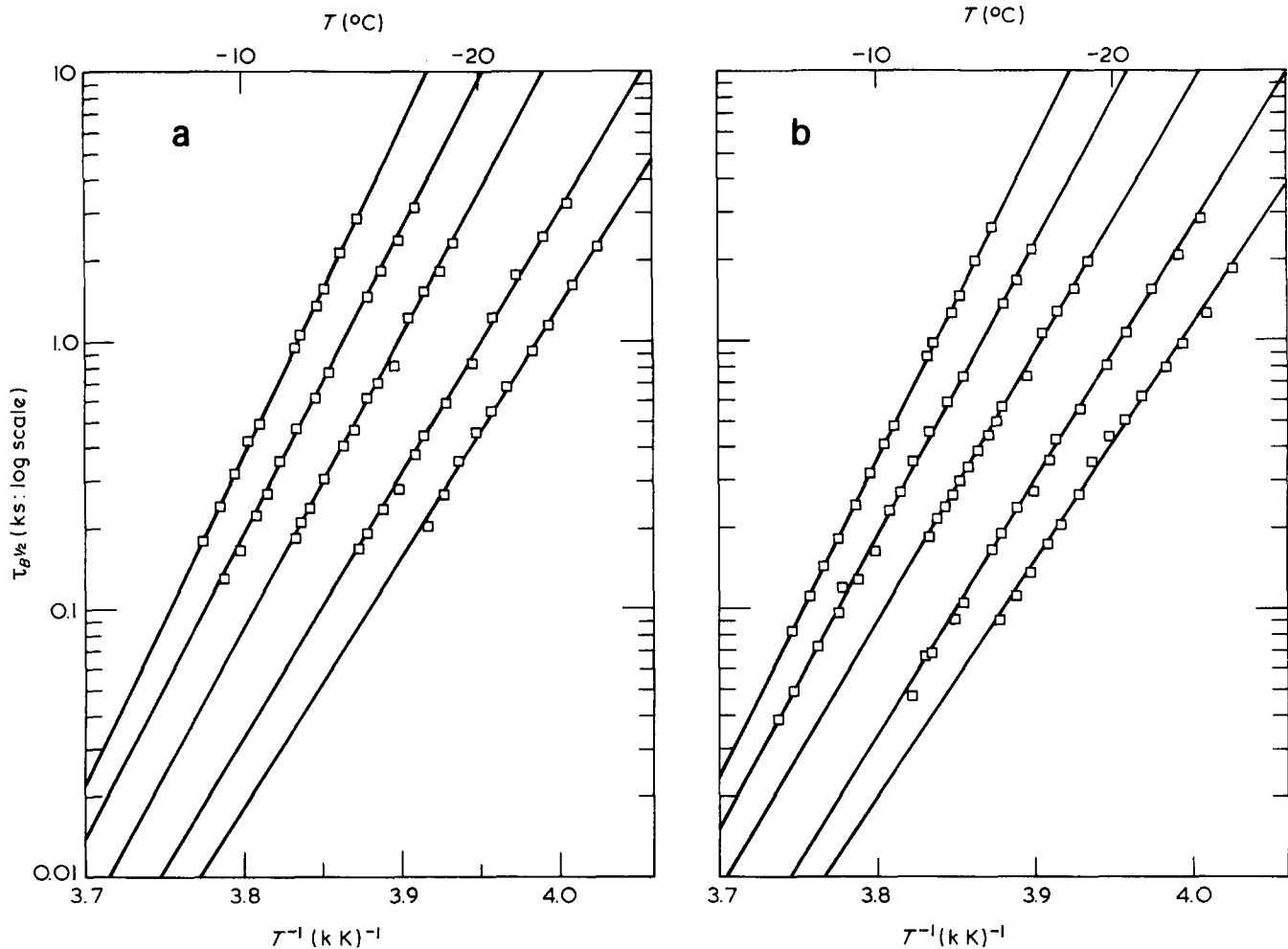
Figure 7 McCrum plot for data in β-region: (a) α computed by Method 2: (b) α computed from Method 1 with $q=0.42$

Table 1 Least squares parameters for log $\tau_{B1/2}$ versus T^{-1} plot for β-mechanism computed with values of α corrected by Methods 1 and 2: $\tau_{B_{\frac{1}{2}}}$ in ks and T^{-1} in $(kK)^{-1}$

	Method 1			Method 2		
T_σ (°C)	a	b	ΔH (k cal mol^{-1})	a	b	ΔH (k cal mol^{-1})
−16.1	−45.42	11.83	54.2	−47.24	12.31	56.4
−18.6	−42.23	10.92	50.0	−43.91	11.36	52.0
−21.9	−39.04	10.00	45.8	−42.42	10.88	49.8
−24.8	−37.58	9.499	43.5	−38.95	9.855	45.1
−27.3	−34.98	8.758	40.1	−37.16	9.319	42.7

the results of Methods 1 and 2 are in good agreement and that ΔH increases with T_σ. Figure 8 shows analogous data for the α-region. Here again the lines can be seen to converge and this is supported by the least squares parameters given in Table 2. It is clear that the double T-jump conclusions are fully supported: ΔH increases as T_σ increases. That is to say, at constant temperature, the longer the relaxation time the higher the value of ΔH.

Figure 9 shows an extended Arrhenius plot of $\tau_{B\frac{1}{2}}$ using the least squares parameters for data corrected using α computed by Method 2 for values of T^{-1} down to zero. This figure also includes at the top a histogram indicating the relative intensity of the packets of creep elements operating: the histogram represents $\gamma(0)/\sigma$ for each TS experiment: this quantity is a rough measure of the relative strength of the relaxations in the regions studied. It will be noted from Figure 9 that the Arrhenius lines

seem to converge to a point similar to the observations from double T-jump and in agreement with the compensation rule, equation (1). Values of T_c and τ_c can be estimated either visually from Figure 8 or, more reliably, by analysis of the coefficients a and b.

Suppose a series of lines of the form of equation (12) all pass through the point (log τ_c, T_c^{-1}). If the observed values of b are plotted against a and extrapolated to $b=0$ (yielding the line for which d log $\tau_{B\frac{1}{2}}/dT^{-1}=0$), then the extrapolated value of a, a_0 will be:

$$a_0 = \log \tau_c \qquad (13)$$

The value of T_c^{-1} can be obtained by plotting b^{-1} against $(-ab^{-1})$: this line when extrapolated to $b^{-1}=0$ will yield:

$$(-ab^{-1})_0 = T_c^{-1} \qquad (14)$$

These plots were obtained and yielded straight lines (*Figures 10* and *11*). The values of log τ_c and T_c^{-1} were obtained by least squares extrapolation and are given in *Table 3*. The agreement between the results of Methods 1 and 2 is excellent for the β-region but not so good for the α-region. The significance of these results is discussed in the following section.

DISCUSSION

It will be clear from the last section that in polypropylene the α and β relaxations are governed by the compensation rule. We examine first of all the way in which this conclusion fits with the current theoretical view of relaxation processes in polymeric solids.

A curious paradox in polymer science over the past twenty years has been the glaring discrepancy between the dominant working hypothesis of thermoviscoelasticity— that ΔH is the same for all components of a particular relaxation—and rational views of the origin of relaxation time distributions. The common sense view of relaxation time distribution can be quickly stated. In a polymer with several relaxations, α, β and γ, each relaxation has a specific origin due to some molecular mechanism and

each process will differ markedly from the others. But, because of the heterogeneous nature of the solid or of the molecules of which it is composed, the potential barriers controlling the relaxation rate are distributed[11-14]. Fröhlich[11] for instance assumed, for simplicity, that for a particular relaxation the potential barriers are distributed between ΔH_0 and $\Delta H_0 + v_0$: i.e.

$$\Delta H = \Delta H_0 + v \quad 0 < v < v_0 \qquad (15)$$

and that if N is the total number of relaxing elements per unit volume then:

$$\frac{dN}{N} = \frac{dv}{v_0} \qquad (16)$$

is the fraction with ΔH values in a range dv near $\Delta H_0 + v$. This simple hypothesis has been taken to its theoretical conclusion by Fröhlich[11]. It has been essentially disregarded in favour of the constant ΔH hypothesis: which is that within a particular relaxation, ΔH takes one value only and that the distribution of relaxation times exists because τ_0 is distributed. This hypothesis is easier to handle theoretically, and this is its attraction.

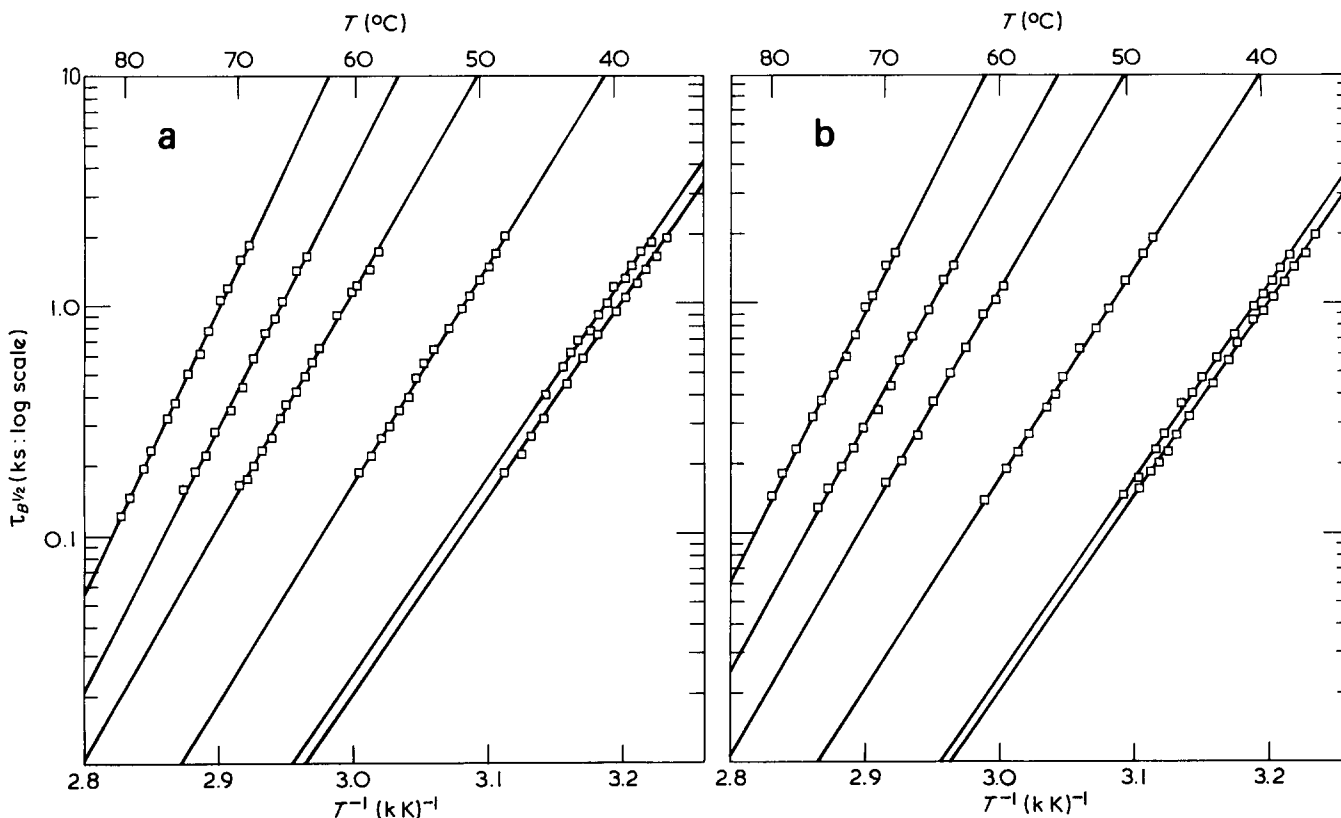There is of course, no *a priori* reason why τ_0 may not be

Figure 8 McCrum plot for data in α-region: (a) α computed from Method 2 (b) α computed from Method 1 with $q = 0.2$

Table 2 Least squares parameters for log $\tau_{B1/2}$ versus T^{-1} plot for α-mechanism: $\tau_{B1/2}$ in ks and T^{-1} in $(kK)^{-1}$

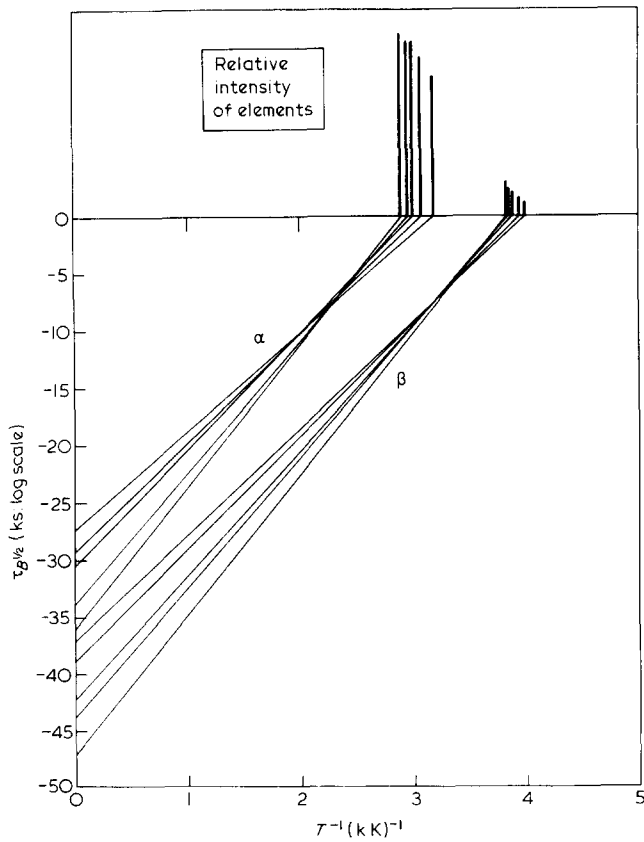|	Method 1			Method 2		
T_σ (°C)	a	b	ΔH (k cal mol^{-1})	a	b	ΔH (k cal mol^{-1})
36.1	−27.28	8.530	39.1	−27.41	8.568	39.2
37.4	−27.36	8.577	39.3	−27.43	8.603	39.4
47.8	−28.49	9.241	42.3	−29.36	9.523	43.6
58.0	−30.72	10.26	47.0	−30.53	10.19	46.7
63.2	−31.70	10.75	49.2	−33.91	11.51	52.7

Figure 9 McCrum plot for α and β relaxations in polypropylene: values of $\tau_{B\frac{1}{2}}$ obtained from Method 2. Note the convergence of the lines for both relaxations at isokinetic points given in *Table 3*
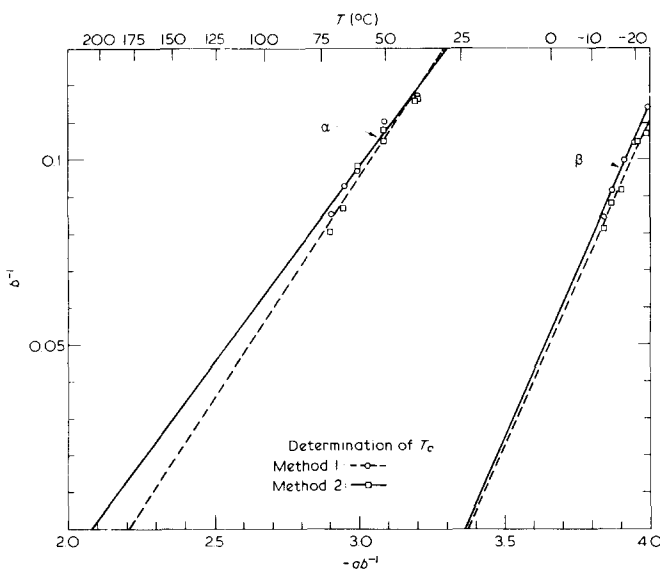

Figure 10 Least squares coefficients (*Tables 1* and *2*) plotted b^{-1} *versus* $-ab^{-1}$. The line extrapolated to $b^{-1}=0$ yields $T_c^{-1}=(-ab^{-1})_0$

relaxation is that adopted by Fröhlich. It is more likely, *a priori*, that the distribution exists because of a distribution in activation enthalpy. It follows that if dN of N relaxation elements has an activation enthalpy ΔH^i, then the activation entropy ΔS^i of these elements will be, according to the theory of Wert and Zener[16]:

$$\Delta S^i = \left(\frac{\beta}{T_m}\right)\Delta H^i \tag{17}$$

in which T_m is the melting point and β a constant of order unity. The relaxation time at temperature T, of this ith packet of relaxation elements is:

$$\tau^i = \tau_\infty \exp\left(\frac{\Delta H^i}{RT}\right) \tag{18}$$

$$\tau_\infty = v^{-1} \exp -\left(\frac{\Delta S^i}{R}\right) \tag{19}$$

in which v is the frequency at which the relaxing molecular
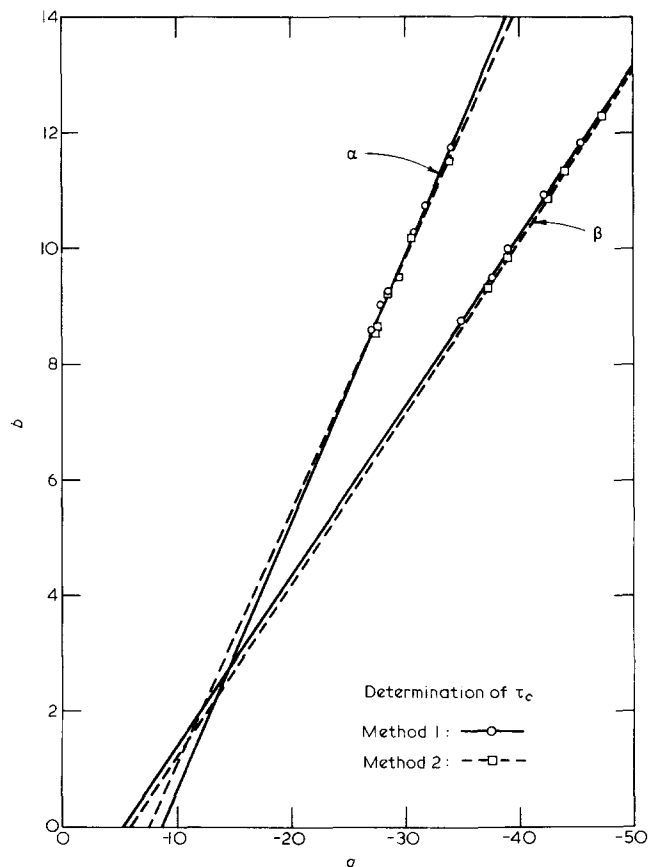

Figure 11 Least squares coefficients (*Table 1* and *2*) plotted b *versus* a. The line extrapolated to $b=0$ yields log $\tau_c=a_0$

Table 3 Values of τ_c and T_c for α and β mechanisms obtained from least squares parameters as described in the text using Methods 1 and 2 correction procedures. Earlier measurements by double T-jump for the α-mechanism yielded $T_c = 240°$C and $\tau_c = 0.12$ μs

	α-Mechanism		β-Mechanism	
	T_c	τ_c	T_c	τ_c
Method 1	207°C	1.6 μs	24°C	4.2 ms
Method 2	180°C	19 μs	23°C	1.3 ms

distributed and ΔH constant. The consolidation of soils under an imposed load is one such example: water flows out through minute pores down a pressure gradient and the soil consolidates. The Terzhagi theory[15] yields relaxation times for the consolidation which are analogous to classical heat flow solutions. These Terzhagi relaxation times are distinguished one from another in their τ_0 values and have identical values of ΔH.

But, we emphasize, the common sense view of polymer

segment approach the barrier. It follows from equations (17)–(19) that:

$$\tau^i = \nu^{-1} \exp \frac{\Delta H^i}{R} \left[\frac{1}{T} - \frac{1}{T_c} \right] \qquad (20)$$

$$T_c = \frac{T_m}{\beta}$$

Comparing the theoretical equation (20) with the empirical compensation rule, equation (1), it will be seen that the inverse of the approach frequency is identified with τ_c:

$$\tau_c \equiv \nu^{-1} \qquad (21)$$

A parallel argument[8] follows from Eby's theory[17] which yields:

$$\Delta S = 4\alpha \Delta H \qquad (22)$$

$$T_c = \frac{1}{4\alpha}$$

in which α is the isobaric coefficient of thermal volume expansion. It is thus possible to measure the approach frequency ν by determining τ_c.

In the light of these remarks the findings described above for the α and β relaxations in polypropylene are not unexpected. What is unexpected, however, is the high value of τ_c. It will be seen from *Table 3* that the τ_c values lie in the millisecond range for the β-relaxation and in the microsecond range for the α-relaxation. The latter result is in agreement with the double T-jump evidence[8] which yielded $\tau_c = 0.12$ μs for the α-process: the β-process was not studied by double T-jump. Normal considerations of rate theory, however, place $\nu^{-1} \sim 10^{-13}$ s: for example, in Eyring's formulation:

$$\nu^{-1} = \frac{h}{kT} \qquad (23)$$

which for $T = 300$ K yields:

$$\nu^{-1} = 1.6 \times 10^{-13} \text{ s}$$

Thus the values of τ_c (*Table 3*) are many orders of magnitude greater than the predictions of rate theory. If large values of τ_c found in these experiments for polypropylene are substantiated for polymers in general, then our views of relaxation processes in polymeric solids will be changed radically.

The difference between the values of τ_c for the α and β relaxations is interesting in that it explains the sharpness of the β-relaxation and the large breadth of the α-relaxation[18]. It will be interesting if study by TS of other relaxations show similar correlations: broad relaxations (for example, α-relaxations in polyethylene, polybutene-1) show values of τ_c in the μs range: sharp relaxations (for example, the α-relaxation in poly FEP)[19] show values of τ_c in the ms range.

Precision of TS technique

As explained in ref. 1, an assumption of the TS technique is that ΔH is constant for the narrow packet of relaxation times activated by the experimental parameters: the dominant experimental parameters are t_σ and t_d. Values of Z_i (the ratio of the strain in the ith element of the model at the instant of quench to the maximum possible

strain in that element, see ref. 1, equation (5)) are plotted in *Figure 10* for $t_\sigma = 20$ min, $t_d = 3$ min (the conditions of our experiments) for values of $q = -0.4, 0$ and $+0.4$. It will be seen that the half breadth of the stimulated packet varies from just below 1 decade for $q = -0.4$ to just below 2 decades for $q = +0.4$. Now we accept that in isotactic polypropylene ΔH increases with τ and it is clear therefore that the assumption of a constant ΔH involves an averaging error. This is minimized in the experiment by taking data in a restricted region:

$$0.35 < \gamma/\gamma(0) < 0.75$$

That is to say we exclude as much of the wings of the packet as is possible.

There are two additional advantages in this experimental procedure. First, we require to minimize the error involved in the correction to $\dot{\gamma}$ for zero point shift: this error can be quite substantial at temperatures low or high in the temperature run when $\dot{\gamma}$ is low. Second we require to minimize the error in γ which, due to error in the zero determination, increases as $\gamma \to 0$.

The agreement between the TS and double T-jump[8] determinations of T_c and τ_c for the α-mechanism is reasonable, *Table 3*. The double T-jump values are considered superior because of the experimental conditions, which required an ageing period of several hundred hours at the measuring temperature before experiments are initiated. Thereafter at least half a dozen experiments were performed with the specimen maintained between experiments at the measuring temperature. Now in the TS experiments this long ageing time was not possible for experimental reasons. It will be seen from *Tables 1* and *2* that the agreement between Methods 1 and 2 for the α-region is not so good as for the β-region. We believe this to be an ageing problem[20,21]: in the α-region ageing is more dominant than in the β-region and although the temperature cycles shown in *Figures 1* and *3* were rigidly adhered to with programmed automatic equipment, it is possible that the specimen at the time of the σ-run was not precisely in the same ageing state as in the α-run. The values of q are, to some extent, controlled by the ageing conditions. Higher precision could most likely be obtained in TS experiments, especially in the α-region, if the specimen was equilibrated for several hundred hours at T_σ and was maintained at T_σ throughout the experimental period, except for the necessary excursions in the experiment up and down the temperature scale.

Thermally stimulated creep recovery

In order to test the theoretically predicted pulse magnitude shown in *Figure 10* experimentally a thermally stimulated creep recovery[2] (TSCR) experiment was performed. In this experiment a stress σ was applied for 30 min at $+50°$C and the specimen was then quenched to $-60°$C without removing the stress. The specimen was equilibrated thermally at $-60°$C for several minutes and the stress then removed. In applying the stress at 50°C for 30 min the intention was to strain all the γ and β relaxation processes to complete equilibrium ($Z_i = 1$) and to take also to equilibrium the short α relaxation processes: it follows of course, that the elastic component was also strained to equilibrium. The removal of the stress at $-60°$C was followed instantly by a small recovery of

the specimen — this is the recovery of the elastic component followed rapidly by the γ component — so that the unrecovered viscoelastic strain left in the specimen at −60°C consisted of the complete β-process and the short time α-processes. The specimen was then heated at 2°C/min from −60°C to +30°C and values of γ̇ recorded. Values of (γ̇/σ) for this quenched TSCR experiment are shown in *Figure 13* by the open square points with solid line, labelled TSCR-Q. The β TSCR peak is marked at 0°C and is overlapped on the high temperature side by the α peak. Also shown in *Figure 13* are values of (γ̇/σ) for a series of five TS experiments ($t_\sigma = 20$ min, $t_d = 3$ min), also with a heating rate of 2°C/min with values of T_σ in the range 0°C to −30°C. As expected the TS data shows a series of sharp peaks.

The astonishing point about these results is the large discrepancy between the magnitudes of the values of (γ̇/σ) for the quenched TSCR and TS experiments and the predicted pulse magnitudes, *Figure 10*. The experimental TS data falls in the β-region for which $q \sim +0.4$. Reference to *Figure 12* shows that for this value of q, Z_i at the peak is of order 60% of the maximum value. Now since the heating rates are equal in the TSCR and in the TS experiments we expect the TS values to be roughly 60% of the TSCR values: this follows because in the TSCR experiments all the β-processes were strained to completion ($Z_i = 1$ for all β-processes). It will be seen from *Figure 11* that the TS peak values are considerably smaller than expected.

This anomalous result was resolved in the following way. In order to check whether or not quenching the specimen from +50°C to −60°C in the TSCR experiment caused non-equilibrium in the strengths of the viscoelastic compliances, we performed another TSCR experiment in which the specimen was not quenched, but was cooled slowly from $T_\sigma = +50$°C to −60°C at 1°C/min under constant stress. At −60°C the stress was removed and the specimen heated at 2°C/min. Thus apart from the rate of cooling under constant stress, the two TSCR experiments were identical. The values of (γ̇/σ) for this second experiment are shown in *Figure 13* (closed squares, labelled TSCR-SC). The relative magnitudes of the slow cooled TSCR values of (γ̇/σ) and the values from the TS experiment are in good agreement with the expectations derived from *Figure 12*: that is, the TS values are of order 60% of the slow cooled TSCR values.
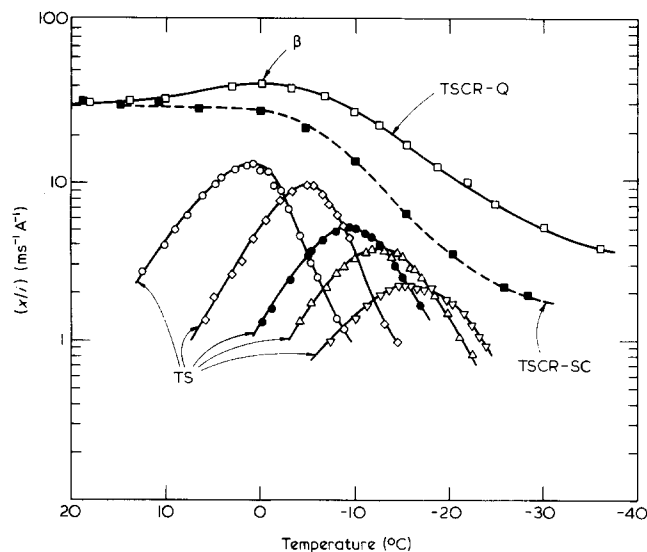
Figure 13 Temperature dependence of γ̇/σ in five TS experiments compared with γ̇/σ in a quenched and in a slow cooled TSCR experiment. The plotted experimental parameter is (ẋ/i) which is proportional to (γ̇/σ). Equations (2) and (4)

The simplest interpretation of this result is that it is due to the temperature dependence of the viscoelastic compliances, J_i, of the model (see ref. 1, Figure 3). At +50°C the J_i are larger than at lower temperatures. Measurements by Chai and McCrum[22] place the order of magnitude of the change in $(J_R - J_U)$ for polypropylene at 40°C to be 0.7% per °C. Thus a drop in temperature of 100°C would generate, if equilibrium were achieved, a reduction in $(J_R - J_U)$ of order 70%. Now when the stress is placed on the specimen at +50°C a viscoelastic strain develops which is proportional to $(J_R - J_U)$ at +50°C. When the specimen is slow cooled, under a constant stress, by 100°C and equilibrium achieved at each temperature, the viscoelastic strain will diminish on cooling by approximately 70%. Thus after releasing the stress at −50°C and heating, the (γ̇/σ) recorded will be lower than if the specimen is quenched from +50°C: in this case the quench to −50°C freezes in a larger strain, since the viscoelastic strain components are not permitted to contract on cooling. In TS (see *Figure 1*) the viscoelastic components are in equilibrium at T_σ, the specimen having been held at that temperature for some time, so that values of (γ̇/σ) taken at or just above T_σ (as in *Figure 11*) are to be compared for theoretical purposes with the TSCR-SC experiment and not with the TSCR-Q experiment.

It follows from this result that in a TS experiment, data taken at $T < T_\sigma$ will be unreliable in the sense that the J_i were equilibrated at T_σ before the quench, so that data taken on the heating run at temperatures *below* T_σ will not be easily and simply comparable with data taken for $T > T_\sigma$. Because of our restriction to ensure γ was observed only near the packet maximum, in the experiments no values of τ_B were recorded for $T < T_\sigma$.

There is a close parallel between this result and observations on thermally stimulated currents[2,23,24]. The difference is only one of sign. If an electrically charged polymer is rapidly quenched with the field on, from a high temperature T to a lower temperature T_0, then the charge at T_0 is proportional to the difference between the limiting dielectric constants, $(\varepsilon_R - \varepsilon_U)$ at T, and not to the value of $(\varepsilon_R - \varepsilon_U)$ at T_0. Now $(\varepsilon_R - \varepsilon_U)$, according for instance to the
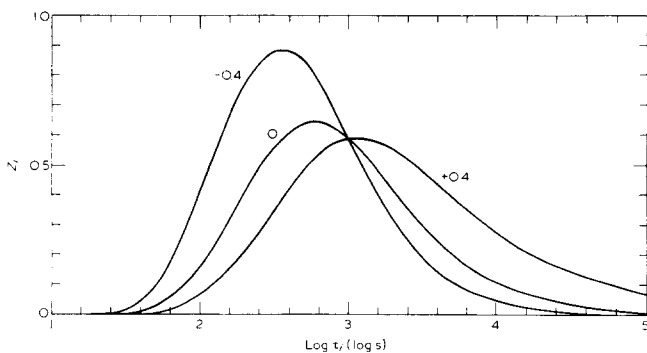

Figure 12 Model calculation of the dependence of Z_i on log τ_i for $t_\sigma = 20$ min and $t_d = 3$ min for distribution with ascending ramp ($q = +0.4$), box ($q = 0$) and descending ramp ($q = -0.4$). Z_i is the ratio of the strain in the ith element of the model at the instant of quench to the maximum possible strain in that element (see ref. 1, equation (5))

Fröhlich formulation of the theory of paraelectric dipoles, is proportional to T^{-1}. The value of $(\varepsilon_R - \varepsilon_U)$ at T_0 therefore exceeds the value of $(\varepsilon_R - \varepsilon_U)$ at the higher temperature T. Thus if the polymer is slow cooled with the field on, the charge increases as the temperature is reduced, so that at T_0 the charge exceeds the charge which would be obtained at T_0 if the polymer was quenched from T. As pointed out by Vanderschueren *et al.*[24] the change in $(\varepsilon_R - \varepsilon_U)$ can be quite large—a factor of 100%—for temperature changes used in the method of thermally stimulated currents.

FUTURE WORK

The obvious next application of TS is the study of the kinetics of the glass–rubber (α) relaxation of an amorphous polymer at temperatures above and below T_g[25]. We have completed this experiment and the results will be reported elsewhere[26]. Other experiments of equal interest concern the validity of the compensation rule for other relaxations in crystalline polymers, γ peaks in particular. These low temperature peaks have a characteristic shape, being broader, when observed say at 1 Hz, on the low temperature side than on the high[7]. Consideration of the fanning out of the relaxation times, for example in *Figure 9*, shows that the compensation rule can explain this form of asymmetry, which is seen in many polymers such as linear polyethylene, polyoxymethylene, poly(tetrafluoroethylene), the polyamides, etc. The compensation rule also explains the well known—but sparsely recorded—observation that damping peaks become sharper at higher frequencies.

It will also be necessary to examine the relevant regions close to τ_c and T_c to determine by mechanical spectroscopy if the apparent distribution narrows so that it appears as a single relaxation time. There may be experimental reasons which prevent the isokinetic point being in fact a point in the sense that melting points are never sharp: for instance (τ_c, T_c) may depend to some extent on ageing. It will also be necessary to inquire into the predictions of the compensation rule when the relaxation times shorter than τ_c are probed by high frequency experiments. In this case, because of the inversion which occurs at (τ_c, T_c), the low activation energy relaxation times are encountered first as the specimen is cooled from temperatures well above T_c: as T decreases towards T_c the activation energies increase continuously, an effect which is in some respects comparable with the predictions of the equation of Williams, Landel and Ferry. At these frequencies the peak shape would be asymmetrical, being broader on the high temperature side.

CONCLUSION

The kinetics of the α and β relaxations in isotactic polypropylene are governed by the compensation rule.

ACKNOWLEDGEMENT

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