Thermal stimulation: I. Determination of activation enthalpy ΔH_v for volume relaxation in polypropylene

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Volume relaxation of isotactic polypropylene was studied at the temperature region of the α-relaxation by the technique of thermal stimulation (or temperature-jump). It is shown that the interpretation of volume relaxation experiments with viscoelastic models fails unless the limiting values of the bulk compliance are assumed to be temperature dependent. Much simplification in the theory of volume relaxation follows if the rigorous formalism of viscoelasticity is adopted, particularly if the treatment by one model is intended for the interpretation of controlled experiments at a single temperature, for both volume and mechanical relaxation. With this model an experiment is designed, based on the Boltzmann superposition principle. The activation enthalpy for volume relaxation, ΔH_v, can then be determined if the Boltzmann principle is applied at an appropriate reduced time, $t/a_v(T)$, where $a_v(T)$ is the Arrhenius shift factor. For polypropylene at 40°C $\Delta H_v = 35$ kcal mol^{-1}, equal to ΔH_J the activation enthalpy for creep (at 40°C).

Keywords Thermal stimulation; activation; enthalpy; volume relaxation; polypropylene; physical ageing; viscoelasticity

INTRODUCTION

It has been known for some time that mechanical, dielectric and volume relaxation in polymeric solids are interrelated. Firstly, in the sense that whenever a polymer exhibits a mechanical (or dielectric) relaxation, a change in slope is observed in the temperature dependence of specific volume. Not all relaxations have been examined by dilatometry or other volumetric techniques, particularly at low temperatures where thermal expansion is low and therefore difficult to measure. But the accumulated evidence establishes a *prima facie* case for a working hypothesis that each polymeric relaxation has an associated knee in the V–T curve. Secondly, in many instances time effects in the specific volume are observed in the vicinity of a mechanical or dielectric relaxation. Thus when the temperature is changed instantaneously from T_0 to T, the time dependence of the specific volume $v(t)$ at T looks exceedingly like a creep experiment. The flux of molecular segments which is the basic event in mechanical and dielectric relaxation is properly thought of as the same process that occurs in volume relaxation. Indeed viscoelastic models have been commonly used in the analysis of volume relaxation[1,2]. Thirdly, physical ageing, the slow decrease in mechanical compliance that occurs after a downquench, is always accompanied by a decrease in specific volume[1,3,4]. In the related downquench–storage–upquench experiment, if the conditions lead to an increase in specific volume then the compliance also increases[4].

Of the available techniques for the study of rate processes, the T-jump experiment is of greatest precision and potential. The T-jump experiment in volume relaxation was developed in a systematic manner by Kovacs[2] some time ago. The relationship between this experiment and the more recent T-jump experiment in mechanical relaxation[5-8] is as follows. It will be of assistance to the reader to state the physics of the problem in its simplest form.

The phenomena are modelled by a mechanical Voigt element, *Figure 1a*. Generalization to include a distribution of retardation times is developed in the Appendix section. Under constant stress σ and at temperature T_0, the fully relaxed element compliance is J_0 and the element retardation time is τ_J. At equilibrium when the stress in the dashpot is zero, the relaxed strain is $\bar{\gamma} = \sigma J_0$. If γ is greater or less than $\bar{\gamma}$, then writing $J(t) = \gamma(t)/\sigma$ the differential equation is:

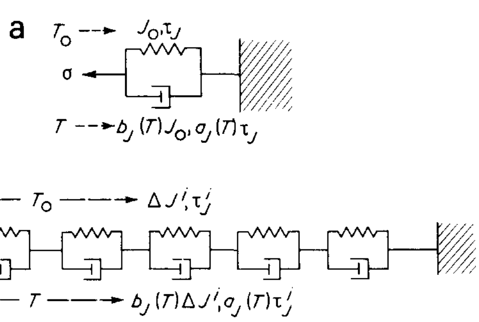

Figure 1 (a) The Voigt model analogue of volume relaxation with temperature dependent parameters. At T_0 the fully relaxed compliance is J_0 and relaxation time τ_J: at T they take the values $b_J(T)J_0$ and $a_J(T)\tau_J$. (b) Generalized Voigt elements in series with a spring: relationship between the model parameters at T_0 and T is $(\tau'_j) = a_J(T)(\tau'_j)^{T_0}$, $(\Delta J'_j)^T = b_J(T)(\Delta J'_j)^{T_0}$ and $J_U^T = c_J(T)J_U^{T_0}$. In application to volume relaxation, the analogue of specific volume is mechanical compliance

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$$\left(\frac{dJ(t)}{dt}\right)_{T_0}=\frac{1}{\tau_J}[J_0-J(t)] \qquad (1)$$

If the temperature is changed instantaneously at time t' from T_0 to T, the differential equation changes instantaneously to:

$$\left(\frac{dJ(t)}{dt}\right)_T=\frac{1}{a_J(T)\tau_J}[b_J(T)J_0-J(t)] \qquad (2)$$

in which at T the element retardation time is $a_J(T)\tau_J$, and the fully relaxed element compliance is $b_J(T)J_0$.

The two temperature parameters $a_J(T)$ and $b_J(T)$, appearing in the denominator and first term of the numerator of equation (2), cause a T-jump to generate two distinct and simultaneous effects. If $b_J(T)$ equals unity (temperature independent element compliance) we have Hopkins model[9] which yields:

$$\left(\frac{dJ(t)}{dt}\right)_T=\frac{1}{a_J(T)\tau_J}[J_0-J(t)] \qquad (3)$$

In this case the ratio of the creep rates at T and T_0 at the instant of the T-jump is exactly:

$$\frac{\dot{\gamma}_T(t')}{\dot{\gamma}_{T_0}(t')}=\frac{\dot{J}_T(t')}{\dot{J}_{T_0}(t')}=\frac{1}{a_J(T)} \qquad (4)$$

However, if $b_J(T)$ is not equal to unity but is given in the linear approximation in terms of $\Delta T=(T-T_0)$:

$$b_J(T)=1+\alpha_J\Delta T \qquad (5)$$

then at temperature T, equations (2) and (5) yield:

$$\left(dJ(t)dt\right)_T\frac{[J_0-J_{T_0}(t)]}{a_J(T)\tau_J}+\frac{\alpha_J\Delta TJ_0}{a_J(T)\tau_J} \qquad (6)$$

Thus in addition to the creep rate acceleration (equation (4)) proceeding from the first term of equation (6), there is a perturbation proportional to $\alpha_J\Delta T$. This perturbation can be considered a secondary creep experiment, initiated at t', generated by the T-jump and proceeding with time constant $a_J(T)\tau_J$: it may be observed in both mechanical and volumetric relaxation. It is indeed, in volume relaxation, the method by which relaxation is initiated in isobaric experiments.

The temperature parameter $a_J(T)$ is the shift factor which, except for α relaxations of amorphous polymers, is related to the activation energy ΔH_J through the Arrhenius equation[10]:

$$a_J(T)=\exp\left[\frac{\Delta H_J}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \qquad (7)$$

If α_J is zero, equation (4) allows us to determine ΔH_J at temperature T_0. In fact, α_J is not zero[22] and hence it is necessary to control the experimental conditions so as to eliminate as far as possible the perturbing effect of the secondary term in equation (6).

By analogy, the model can be used to rationalize the volume relaxation phenomena if we replace the parameters in equations (1) and (5) as follows:

$$J_0\rightarrow v_0$$

$$J(t)\rightarrow v(t)$$

$$\tau_J\rightarrow\tau_v$$

and, $\quad \alpha_J\rightarrow\alpha_v$

The result is:

$$\left(\frac{dv(t)}{dt}\right)_{T_0}=\frac{v_0-v(t)}{\tau_v} \qquad (8)$$

before the T-jump and at T_0 and

$$\left(\frac{dv(t)}{dt}\right)_T=\frac{v_0-v(t)}{a_v(T)\tau_v}+\frac{\alpha_v\Delta Tv_0}{a_v(T)\tau_v} \qquad (9)$$

after the T-jump. There are again two processes: a primary process which leads to an acceleration in $\dot{v}(t)$ at t',

$$\frac{\dot{v}_T(t')}{\dot{v}_{T_0}(t')}=\frac{1}{a_v(T)} \qquad (10)$$

and a secondary process proportional to $\alpha_v\Delta T$, which is initiated at time t' by the T-jump. In the volumetric

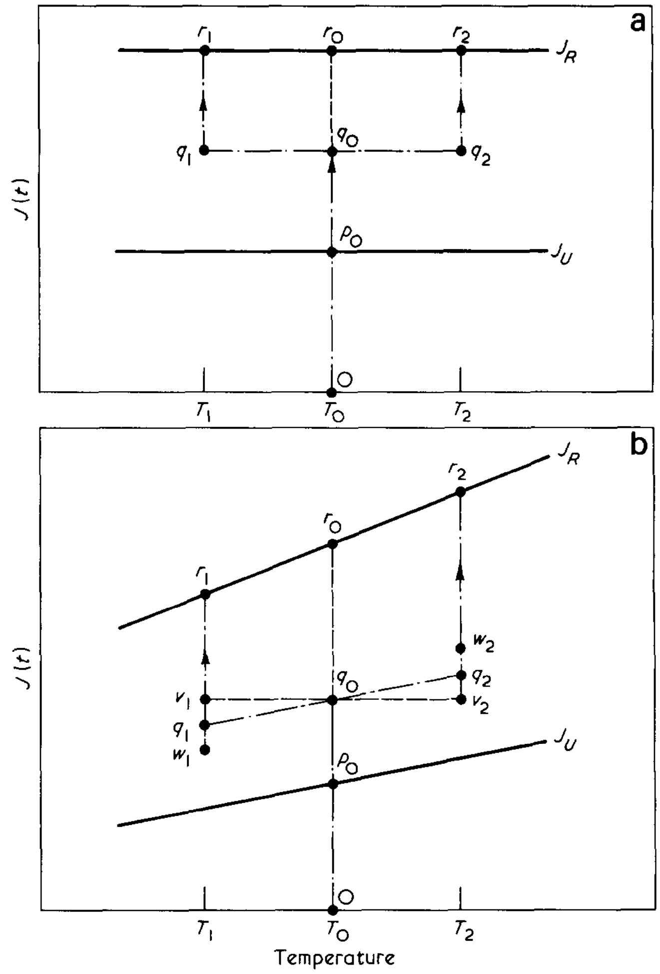

Figure 2 The origin of secondary creep process after T-jump explained from the temperature dependence of the limiting compliances (schematic). (a) The limiting compliances are assumed to be independent of temperatures: $b_J(T)=1.0$ and $c_J(T)=1.0$. (b) The limiting compliances are a function of temperature with $b_J(T)>c_J(T)>1.0$. See text for further description

experiments to be described, it is the secondary process which alone is of physical interest. The primary process, if not entirely eliminated by a judicious choice of experimental conditions, comprises a minute perturbation for which the data can be corrected. It is the other way round in mechanical experiments: the process of interest is the primary process. The experimental conditions and analysis must be chosen so as to eliminate the secondary process.

A viscoelastic model was first proposed for volume relaxation by Kovacs[2]. Since then Struik[1] has used a viscoelastic model as an analogue for the downquench–storage–upquench experiment. The analogy here is the Köhlrauch experiment[21], in which stress pulses of different magnitudes and signs are applied at different times. The analogy, however, has in the past never been pressed home. In volume relaxation the stimulus is not a change of stress but a change of temperature. It is expected that a mechanical analogue for volume relaxation will break down if the compliances of the model are temperature independent, being the assumption made by earlier workers[1,2]. In our view, much simplification follows if the rigorous formalism of viscoelasticity is adopted, particularly if the treatment by one model is intended for the interpretation of controlled experiments on a particular polymer at a single temperature, for both volume and mechanical relaxation.

We shall be concerned with volume mechanical relaxation in isotatic polypropylene at 40°C (α-relaxation). Compared to a glassy polymer near T_g, there are certain simplifications that accrue when studying a crystalline polymer. The first simplification is that the rate theory is the Arrhenius equation: equation (7) for mechanical relaxation, and for volume relaxation:

$$a_v(T)=\exp\left[\frac{\Delta H_v}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{11}$$

there being no evidence whatsoever for the use of the WLF equation in the α-region of polypropylene. There is also no evidence of an autocatalytic or self-retarding effect in crystalline polymers[4]. We shall in our volumetric experiments use the Boltzmann superposition principle, rightly regarded as the fundamental theorem of linear viscoelasticity, to seek to establish whether the linear theory with time independent (i.e. free-volume independent) relaxation times is an adequate description.*

In formulating the theory, it will not be assumed that an equilibrium state is physically acessible. In relaxation in amorphous polymers near T_g, the liquid (equilibrium) volume can be extrapolated to temperatures below T_g and can, on occasion, actually be observed in a lengthy relaxation experiment. We will, for polypropylene at 40°C, merely assume that an equilibrium (or relaxed) volume exists and its determination numerically will not be essential in any way. A comparable assumption is, of course, one of the basis postulates in the theory of viscoelastic and dielectric relaxation.

In the following paper[22] we will use a related thermal stimulation technique to determine the temperature coefficients of the limiting compliances.

THEORY

The normal method of studying viscoelastic parameters is by the application of a stress. However, for volume relaxation, the only method of stimulation is by T-jump and it is in this application that the mechanical model with temperature dependent compliances (Appendix A) is of the greatest significance, as we will now show.

Following Kovacs[2] and Struik[1], the time dependent compliance $J(t)$ models the time dependent specific volume $v(t)$. The specimen is brought to temperature T_0 and left for a long time to establish the condition described by equation (A7). Then, on T-jump from T_0 to T, the secondary volume relaxation process is given from the model, Appendix A, as:

$$\Delta v(t)=\beta_v\Delta T v_U^{T_0}+\alpha_v\Delta T(v_U^{T_0}-v_R^{T_0})\int_{-\infty}^{\infty}\mathrm{d}\ln\tau\,\varphi_v^{T_0}(\ln\tau)\times\left\{1-\exp-\left[\frac{t}{\tau a_v(T)}\right]\right\} \tag{12}$$

in which the zero time is taken at the time of the T-jump. The generalized Voigt model (with a spring in series) of *Figure 1b* is transferred to the volume phenomenon with:

$$J_U^{T_0}\rightarrow v_U^{T_0}$$
$$J_R^{T_0}\rightarrow v_R^{T_0}$$
$$a_J(T)\rightarrow a_v(T)$$

The volume distribution function, $(v_U^{T_0}-v_R^{T_0})\varphi_v^{T_0}(\ln\tau)\mathrm{d}\ln\tau$, is that portion of the specific volume which relaxes with time constant τ.† We will assume for a crystalline polymer (polypropylene) that there is no autocatalytic effect[4] and that change in temperature governs the volume spectrum according to:

$$\varphi_v^{T}(\ln\tau)=\varphi_v^{T_0}\left(\ln\frac{\tau}{a_v(T)}\right) \tag{13}$$

and that $a_v(T)$ is given by the Arrhenius equation, (equation (11): see later for further discussion). By analogy with the mechanical model (Appendix A), the temperature dependence of the limiting volumes is given by:

$$(v_U^{T}-v_R^{T})=b_v(T)(v_U^{T_0}-v_R^{T_0}) \tag{14}$$

$$v_U^{T}=c_v(T)v_U^{T_0} \tag{15}$$

As before, for values of $\Delta T=(T-T_0)$ equal to a few degrees, we assume $b_v(T)$ and $c_v(T)$ to be linear in ΔT:

$$b_v(T)=1+\alpha_v\Delta T \tag{16}$$

$$c_v(T)=1+\beta_v\Delta T \tag{17}$$

According to the model, if the volume contraction at T is interrupted at time t_1 by a return T-jump, T to T_0, then for this double T-jump experiment for $t>t_1$:

$$\Delta v(t)=\left\{\beta_v\Delta T v_U^{T_0}+\alpha_v\Delta T(v_U^{T_0}-v_R^{T_0})\int_{-\infty}^{\infty}\mathrm{d}\ln\tau\,\varphi_v^{T_0}(\ln\tau)\right.$$

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* It should be noted that the magnitude of the temperature pulse (ΔT) used in our volumetric experiments was small, $\Delta T<10$°C

† The subscript v for volume relaxation time (τ_v) is henceforth omitted for clarity

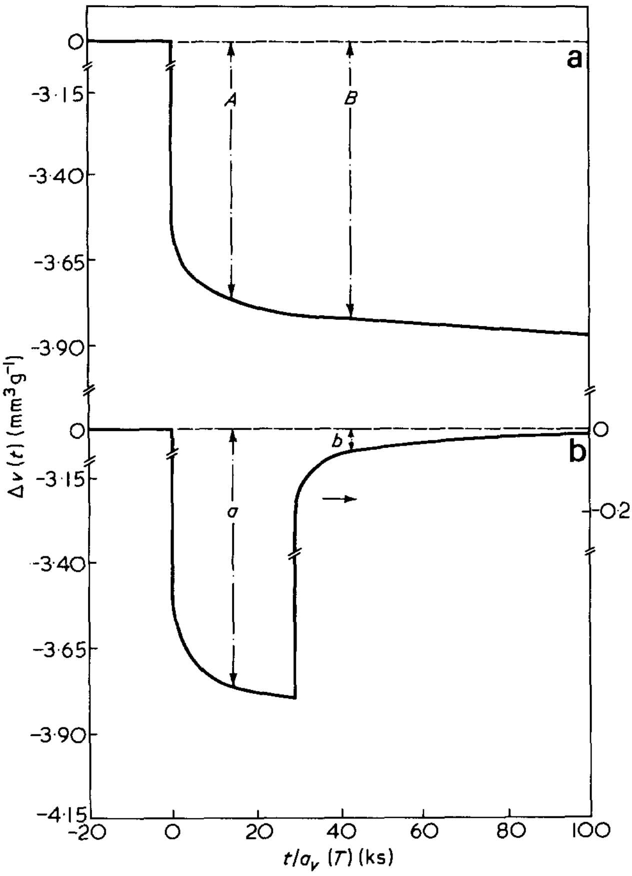

Figure 3 Model calculation: dependence of $\Delta v(t)$ on $t/a_V(T)$. (a) Single T-jump at t = 0, $T_0 \downarrow T$ with $a_V(T)$ = 4.0. (b) Double T-jump $T_0 \downarrow T$ at t = 0 and $T \uparrow T_0$ at t_1 = 115.2 ks; $a_V(T)$ = 4.0 and $a_V(T_0)$ = 1.0. Since the model we take $a_V(T)$ = 4.0 and $a_V(T_0)$ = 1.0 the data is here plotted against the correctly reduced time

$$\left[1-\exp-\frac{1}{\tau}\times\left(\frac{t_1}{a_v(T)}+t-t_1\right)\right]\Bigg\}-$$

$$\Bigg\{\beta_v\Delta T v_U^{T_0}+\alpha_v\Delta(v_U^{T_0}-v_R^{T_0})\int_{-\infty}^{\infty}\mathrm{d}\ln\tau\varphi_v^{T_0}(\ln\tau))\times$$

$$\left[1-\exp-\left(\frac{t-t_1}{\tau}\right)\right]\Bigg\} \qquad (18)$$

There are thus two secondary volume relaxation processes of equal strength, the first initiated at $t=0$ and the second at t_1 in the opposite direction. This double T-jump experiment is our prime technique in this paper.

The principle of our method for determining ΔH_v will be illustrated with a discrete relaxation time model. In this simple model it is assumed that there are a series of volume relaxation times:

$$\tau_i = 10^N \mathrm{s}$$

in which $N = -1.0, -0.75, -0.50\ldots, 5.50, 5.75$ and 6.00: the model comprises 29 Voigt elements distributed four per decade and of equal strength. To make the results fairly representative of the experiment we choose:

$$\beta_v \Delta T\, v_U^{T_0} = \pm 3.0\,\mathrm{mm}^3\,\mathrm{g}^{-1}$$

$$\alpha_v \Delta T(v_U^{T_0} - v_R^{T_0}) = \pm 0.0345\,\mathrm{mm}^3\,\mathrm{g}^{-1}$$

(negative sign for negative ΔT, plus sign for positive ΔT). Thus equation (12) for a single (negative) T-jump yields:

$$\Delta v(t) = -3.0 - 0.0345\sum_i\left[1-\exp-\frac{1}{\tau_i}\left(\frac{t}{a_v(T)}\right)\right] \qquad (19)$$

Figure 3a shows a plot of $\Delta v(t)$ against $t/a_v(T)$ for $a_v(T)=4.0$. For a negative T-jump at $t=0$ followed by a positive T-jump back to T_0 at time t_1, for $t>t_1$:

$$\Delta v(t) = -0.0345\sum_i\left[\exp-\left(\frac{t-t_1}{\tau_i}\right)-\exp-\frac{1}{\tau_i}\left(\frac{t_1}{a_v(T)}+t-t_1\right)\right] \qquad (20)$$

Figure 3b shows a plot of $\Delta v(t)$ against $t/a_v(T)$ for $a_v(T)=4.0$ and $t_1=115.2$ ks.

The method of determining ΔH_v follows at once by application of the Boltzmann superposition principle. Suppose a double T-jump experiment has been performed. The data consists of Δv as a function of laboratory time, t. Let us suppose, to start with, that $a_v(T)$ is known. It is then possible to predict what would have occurred if at time t_1, the temperature had not been returned from T to T_0, but had been left at T. The values of $\Delta v(t)$ are plotted against reduced time $t/a_v(T)$: in this example $a_v(T)=4.0$ and $a_v(T_0)=1.0$. The prediction is (see *Figure 3*)

$$A = a \qquad (21)$$

$$B = a + b \qquad (22)$$

in which A and a are the values of $\Delta v(t)$ at an arbitrary reduced time after the T-jump $T_0 \downarrow T$, b is the value of $\Delta v(t)$ at the same reduced time after the return T-jump $T \uparrow T_0$ and B is the value of $\Delta v(t)$ in the single T-jump experiment at the same reduced time (see *Figure 3*).

The prediction is illustrated in *Figure 4* in which $\Delta v(t)$ is

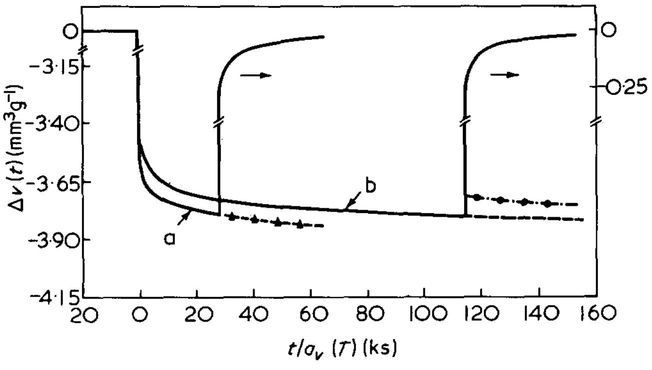

Figure 4 Model calculation showing method of prediction: $\Delta v(t)$ plotted against $t/a_V(t)$. The full lines show the calculated values of $\Delta v(t)$ in the double T-jump experiment. The closed points are the data predicted from the double T-jump experiment for a single T-jump experiment ($T_0 \downarrow T$ at t = 0) for $t > t_1$. (a) T-jump $T_0 \downarrow T$ at t = 0 and $T \uparrow T_0$ at t_1 = 115.2 ks: $a_V(T)$ = 4.0 and $a_V(T_0)$ = 1.0. Closed triangles prediction according to Boltzmann superposition principle. The prediction is exact since the data is correctly reduced. (b) As for (a) except $a_V(T)$ = 1.0 = $a_V(T_0)$; this is a plot of $\Delta v(t)$ against unreduced time. Closed circles, prediction according to Boltzmann superposition principle. The prediction fails (note mis-match at the T-jump $T \uparrow T_0$ in slope and the large step) because the time data is not correctly reduced. For both (a) and (b) the dashed line at $t > t_1$ shows the single T-jump data calculated directly from the model

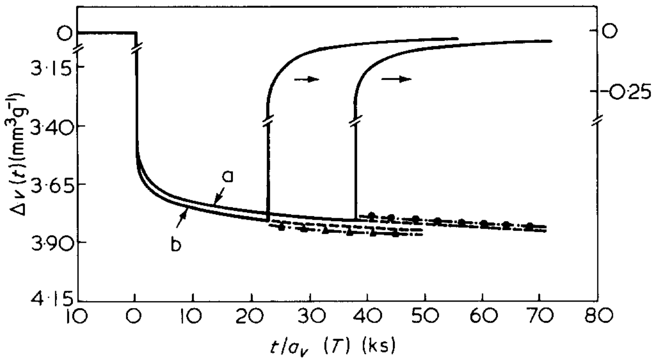

Figure 5 As for legend to *Figure 4* except that (a) $a_V(T)$ = 3.0 and $a_V(T_0)$ = 1.0, (b) $a_V(T)$ = 5.0 and $a_V(T_0)$ = 1.0. The closed points are prediction according to Boltzmann superposition principle. The prediction fails in both cases since the time data is incorrectly reduced

plotted against $t/a_v(t)$. Curve (a) shows $\Delta v(t)$ plotted against the correctly reduced time ($a_v(T) = 4.0$, $a_v(T_0) = 1.0$). The data predicted is shown by the closed triangles. The prediction is, of course, exact. Curve (b) is a plot of $\Delta v(t)$ against laboratory, or unreduced time ($a_v(T) =$ 1.0 at both T and T_0). The data predicted by equations (21) and (22) is shown by the closed circles. The prediction fails obviously and this is clear both from the mismatch in slope and in the abrupt step at the T-jump.

The value of the model lies in the estimation of sensitivity. Suppose, having generated the data using $a_v(T) = 4.0$ we elect to compute the reduced time using $a_v(T) = 3.0$. (This is equivalent to the true experimental value equalling 4.0 and a trial value for time reduction equalling 3.0.) Such erroneous reduction is shown in *Figure 5*, curve (a). The predicted data lies above the true value. *Figure 5* curve (b) shows $\Delta v(t)$ plotted against $t/a_v(T)$ for $a_v(T) = 5.0$. Again the prediction fails, the data lying below the true value.

In designing the experiment we made the reasonable *a priori* assumption that ΔH_v would at 40°C lie close to the mechanical value of 35 kcal/mol[7]. We decided also on several grounds that a value of $a_v(T)$ of order of 4 would be appropriate and we therefore imposed in all the experiments a T-jump of $\Delta T = -7.52$°C from $T_0 = 40.0$°. It was not essential to anticipate the correct value of ΔH_v since the correct value may be obtained from the experimental data by trial and error.

It will be appreciated that this technique will only be applicable if time dependent volume changes due to prior thermal history are negligible. For this reason before the initiating T-jump $T_0 \downarrow T$ the specimen was maintained for a considerable period at T_0. The elements whose relaxation is to be observed will then have essentially reached their T_0 equilibrium values.

EXPERIMENTAL

The specimen was machined from a rod of isotatic polypropylene (Propathene PXC 8830) supplied by Imperial Chemical Industries Limited. Before machining, the rod was annealed at 130°C and slow cooled to room temperature. The specimen was a thin cylindrical rod of dimensions: 6.08 mm diameter and 150.4 mm length. Its density at 23°C was 0.9065 g cm^{-3}.

The specimen was sealed into a glass dilatometer. The dilatometer construction procedures closely followed ASTM Standard D864-52. The capillary tube nominal diameter was 0.38 mm. The actual cross-sectional area of the capillary was found to be 1.1836×10^{-3} cm^2 from a determination of the length of capillary occupied by a known volume of mercury. The polypropylene specimen in the dilatometer was degassed at 130°C for 24 h under high vacuum (10^{-6} mm Hg). It was then degassed again under vacuum at 21°C for 24 h, and filled with pure mercury. The dilatometer was placed in a cavity through which deionized water at the required temperature was passed. The facility for a fast temperature jump was obtained with equipment similar to that described by Matthews and McCrum[11].

The mercury level in the capillary tube was measured using a telescope and a glass metre rule which was placed very close behind the dilatometer. The glass metre rule was silvered at the back to act as a mirror, so that accurate measurements of the mercury level were ensured when the fine scale and its image on the mirror were colinear, when viewed through the telescope. For each length measurement, the temperature inside the cavity was recorded using a very accurate Beckmann glass mercury thermometer which could be read to about ±1 m°C.

The double T-jump experiment was performed after the specimen had been at 40.0°C for 1.53 Ms. The rate of change of specific volume was then extremely small -4.59×10^{-8} mm^3 g^{-1} s^{-1}. The temperature cycle of the experiment was 40.0° ↓ 32.48° (32 h) ↑ 40.0° (8 h). Measurements of the height of the mercury column and the temperature of the water in the cavity were taken continuously.

RESULTS

The results of the double T-jump experiment are shown in *Figure 6*, in which $v(t)$ is plotted against $t/a_v(T)$ for values of $a_v(T) = 1$ and $a_v(T) = 4$. Also shown are predictions according to the Boltzmann superposition principle. It is not of course to be expected that the unreduced, raw data ($a_v(T) = 1.0$) would yield a satisfactory prediction and this

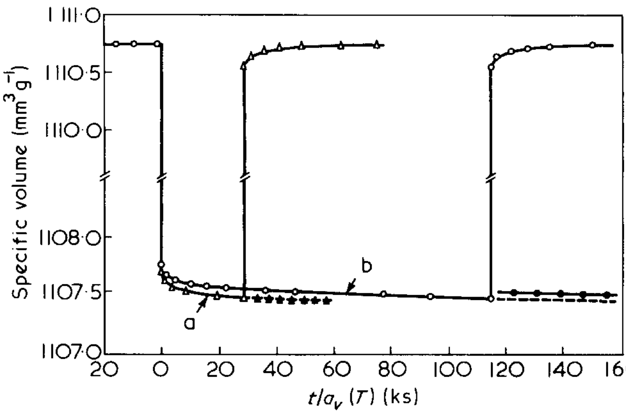

Figure 6 Experimental values of $v(t)$ plotted against $t/a_V(T)$ for the double T-jump experiment 40.0° ↓ 32.48° (32 h) ↑ 40.0° (8 h). (a) Open triangles, $a_V(T)$ = 4.0 and $a_V(T_0)$ = 1.0; closed triangles, prediction according to Boltzmann superposition principle of a single T-jump experiment for $t > t_1$. The precision of this prediction is proof that $a_V(T)$ is close to 4.0 which implies that ΔH_V is close to 35 kcal mol^{-1}. (b) Open circles, $a_V(T)$ = 1.0 = $a_V(T_0)$: this plot is therefore of $v(t)$ against laboratory (or unreduced) time. Closed circles are prediction according to Boltzmann superposition principle. The prediction fails since the data is not correctly reduced

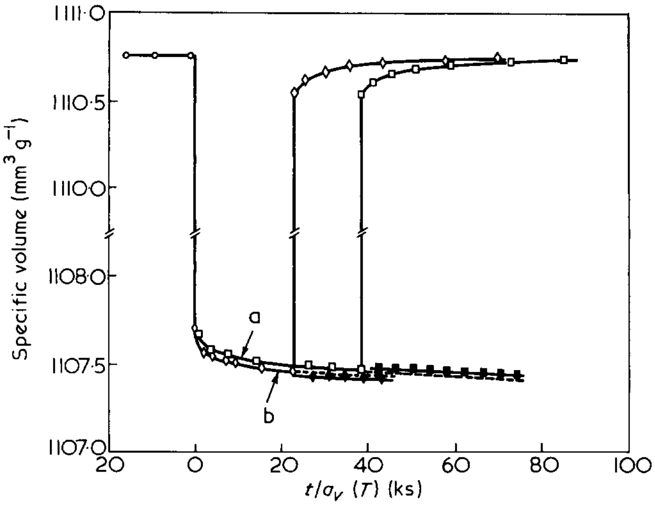

Figure 7 As for legend to *Figure 6* except that (a) $a_V(T)$ = 3.0 and $a_V(T_0)$ = 1.0, (b) $a_V(T)$ = 5.0 and $a_V(T_0)$ = 1.0. The open points are experimental data taken in the double T-jump experiment. The closed points are predictions according to the Boltzmann superposition principle. The predictions fail since the time data is not correctly reduced. The form of the failure in prediction is such as to indicate clearly that the correct $a_V(T)$ lies between 3.0 and 5.0

will be seen to be so. The curve predicted for $a_v(T) = 4.0$ is good. In order to study the sensitivity of this experiment $v(t)$ is plotted against $t/a_v(T)$ in *Figure 7* for values of $a_v(T) = 3.0$ and $a_v(T) = 5.0$. These two values of $a_v(T)$ correspond to $\Delta H_v = 28$ and 41 kcal mol^{-1}. The predictions are obviously unsatisfactory. It is clear from *Figure 7* that these values of $a_v(T)$ straddle the correct value. We take this double T-jump experiment to present *prima facie* evidence for the activation energy for volume recovery to lie between $\Delta H_v = 28$ and 41 kcal mol^{-1} and close to $\Delta H_v = 35$ kcal mol^{-1}.

The quadruple T-jump was designed after the double T-jump experiment yielded the result $\Delta H_v = 35$ kcal mol^{-1}. The specimen was held at 40.0° for 1.86 Ms at which time the time dependence of volume was negligible. The following temperature cycle was then imposed: 40.0° ↓ 32.48° (4 h) ↑ 40.0° (1 h) ↓ 32.48 (4 h) ↑ 40.0 (1 h). The dependence of specific volume on time was observed throughout the experiment. It is essential in the design of this experiment to know $a_v(T)$ since the specimen must remain at T_0 (40.0°) and T (32.48°) for equal periods of reduced time. Since our first determination of ΔH_v by double T-jump showed that for $\Delta T = -7.52°$ a value of $a_v(T) = 4.0$ was very close to the true value it will be seen that the schedule selected yielded a reduced time of 1 h at both T_0 and T. *Figure 8* shows the data (open circles) plotted against $t/a_v(T)$ for $a_v(T) = 4.0$ and $a_v(T_0) = 1.0$. The predictions of a single T-jump experiment were then made by Boltzmann superposition principle (closed circles). The predictions is:

$$A = a$$

$$B = b + a$$

$$C = c + b$$

$$D = d + c$$

in which lower case letters refer to the quadruple T-jump experiment and upper case to the predicted single T-jump experiment following the symbolic procedure illustrated in *Figure 3*.

In order to check the prediction from the quadruple T-jump experiment a single T-jump experiment was performed. The specimen was maintained at 40.0° for 1.87 Ms at which time the recovery from the preceding quadruple T-jump experiment was negligible. The following temperature cycle was then imposed: 40.0° ↓ 32.48° (16 h). It will be seen that the reduced time in this experiment was 4 h, equal to the aggregate reduced time in the quadruple T-jump experiment. The results are plotted in *Figure 8* against $t/a_v(T)$ for $a_v(T) = 4.0$ (open triangles). The directly observed and predicted single T-jump data are in good agreement. This quadruple T-jump experiment provides additional evidence that the activation energy for volume recovery in polypropylene at 40°C is $\Delta H_v = 35$ kcal mol^{-1}.

DISCUSSION

(1) We consider the relationship between the model, theory and observations of this paper with the earlier work on volume relaxation.

The model of the paper is shown in *Figure 1b* and the results which stem from it by T-jump illustrated in *Figure 9*. Before the T-jump $T_0 \downarrow T$ the specimen is relaxed for a long period of time at T_0. It is then at the point a, of a state such that shrinkage is sufficiently small to be disregarded: in the term of the theoretical section the primary relaxation rate is negligible with respect to the secondary relaxation which is to be imposed by the T-jump.

When the temperature is pulsed $T_0 \downarrow T$ the volume follows the slope of the v_U curve with coefficient β_v (a–b, *Figure 9*, equations (12) and (17)). For relaxations in general (excluding possibly the relaxation at lowest temperature) the processes which generate this instantaneous volume change are thermally activated. In the case of polypropylene at 40° the dominant process controlling β_v

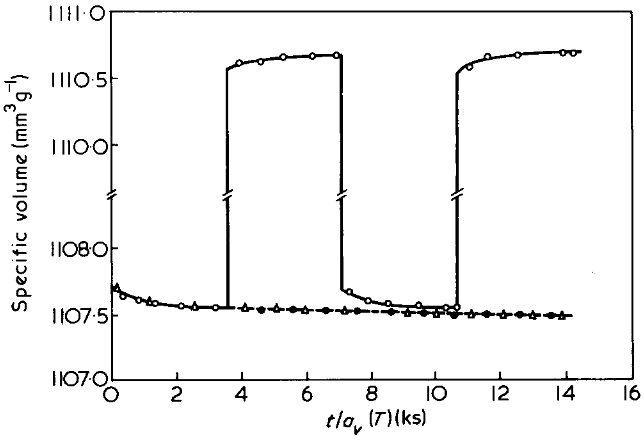

Figure 8 Time dependence of specific volume for quadruple T-jump experiment [40.0° ↓ 32.48° (4 h) ↑ 40.0° (1 h) ↓ 32.48 (4 h) ↑ 40.0 (1 h)] : ⊙, data plotted against $t/a_V(T)$ for $a_V(T_0)$ = 1.0 at 40.0° and $a_V(T)$ = 4.0 (ΔH_V = 35 kcal mol^{-1}) at 32.48°C. Predicted extrapolation of the specific volume at 32.48° is shown by the closed circles. Also plotted, △, is experimental data at 32.48° from the single T-jump experiment [40.0° ↓ 32.48° (16 h)] performed after the quadruple T-jump experiment: data plotted against $t/a_V(T)$ with $a_V(T)$ = 4.0. Note the excellent agreement between the extrapolation for $a_V(T)$ = 4.0 from the quadruple T-jump experiment and the experimental data at 32.48° with $a_V(T)$ = 4.0

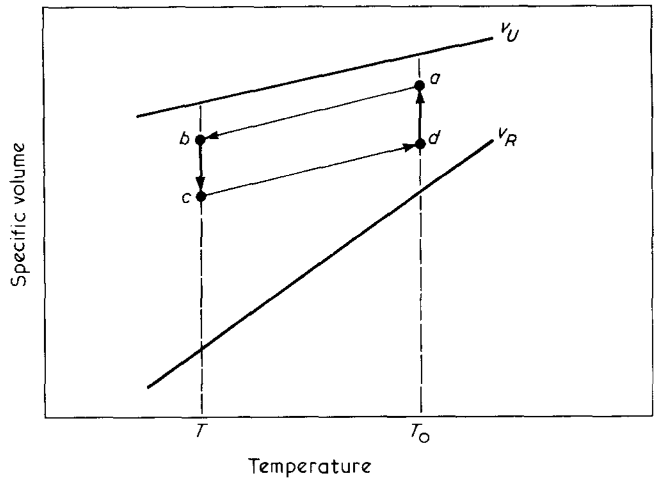

Figure 9 Schematic outline of the viscoelastic analogue of volume relaxation with temperature dependence limiting volumes (v_U and v_R): specific volume *versus* temperature, with the course of the T-jump between T_0 and T as *abcd*

is the β (glassy) relaxation at $-15°$C: the low temperature γ-relaxation ($-80°$) will also contribute. The symbol of a spring for the v_U elements (*Figure 1b*) does not imply the absence of thermal activation: merely that these elements are of time constant short compared to that of the equipment, that their time dependence is not observed in the experiment at T_0 and that they are not components of the α-relaxation.

The α-process, which is the course of the observed time dependent change indicated by *b–c* and *d–a* in *Figure 9*, from an operational point of view, consists of three packets. Packet 1 ($\tau \ll 1$ ks) comprises the short relaxation times which will be essentially in equilibrium by the time the first measurements are made. This is at approximately 0.1 ks after the T-jump since the time constant for thermal equilibration of the dilatometer is of this order. The observed time dependence is dominated by Packet 2, with τ in the region of 1 ks. Packet 3 comprises the rest of the α-process with relaxation times $\tau \gg 1$ ks. Packet 3 processes do not yield any significant time dependent volume changes at 40.0° or at 32.48° during the course of the experiment (*abcd Figure 9*). It is to be accepted therefore that the value of $\Delta H_v = 35$ kcal mol^{-1} obtained in our experiments holds for those elements of the α-relaxation in Packet 2 which at 40°C are centred in the region of 1 ks.

(2) There are two proposals for the origin of physical ageing. The original proposal of Struik[1] is that, in amorphous polymers, as ageing proceeds the distribution of relaxation times moves uniformly to longer times. This is indicated schematically in *Figure 10a*. It is now known that for crystalline polymers this does not occur. *Figure 10b* shows in outline the mechanism of Chai–McCrum for polypropylene[4,12]. The essential observation (obtained by thermal sampling) is that ageing for time t_e has no effect on relaxation times for $\tau \gg t_e$. For $\tau \sim t_e$ there are, of course, large efffects which are indicated in *Figure 10b*. Recently, this Chai–McCrum mechanism has been shown to be true even in amorphous polymers (PMMA and polycarbonate)[23].

There appears to be a one to one relationship between the volumetric and mechanical relaxation times[4]. For instance, 1 ks after quenching, when the rate of contraction is dominated by volumetric relaxation times $\tau_v \sim 1$ ks, the mechanical changes observed in ageing are seen most strongly for $\tau_J \sim 1$ ks.

An additional factor linking specific mechanical and volumetric relaxation times is the observation that for polypropylene at 40° $\Delta H_v = 35$ kcals mol^{-1}, equal to the value determined in creep, ΔH_J. The value of ΔH_J was observed in double T-jump[5,7,8] at 40°C. The mechanical elements whose ΔH_J is observed in this experiment are centred in the region $\tau_J \sim 1$ ks[4]. This equality is the more striking in that for the α-relaxation ΔH_J depends on τ, the change being 3 kcals per decade.

The observation that ΔH_J depends on τ has lead to an examination of the effect of a possible variation of ΔH_v with τ on the theory used in this paper. This was done using the discrete relaxation time model described in the theoretical section. The result[4] is that the procedures described in the theoretical section are valid. The observed ΔH_v is an average for the elements whose relaxation dominates the observed time dependence.

(3) The model of this paper throws interesting light upon the relationship between the technique of volume relaxation, as used for instance by Simha and co-workers[13–17], and the related techniques of thermal sampling[4,12,18–20]. Consider a Voigt model with temperature dependent limiting compliances, Figure 11. In thermal sampling a mechanical strain (or polarization) is frozen-in. This is achieved by applying a stress at T_1, removing it for a shorter time at the same temperature and then quenching instantaneously to T_0. Or it may be achieved by lowering the temperature slightly before removing the stress. A related method is to quench with the stress on and then remove the stress at T_0. At T_0 let the strain frozen in be γ_0 and let the relaxation time be τ_0. The specimen is now heated in a systematic manner (for instance, T or T^{-1} linear in t). Suppose the heating time schedule be:

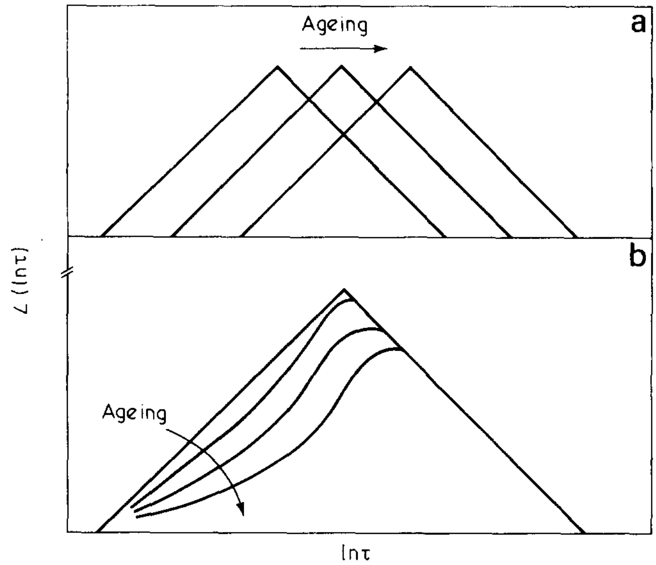

Figure 10 Schematic diagrams showing the plot of retardation times distribution, $L(\ln\tau)$ against $\ln\tau$ (a) Struiks' hypothesis of physical aging which is that the large compliance changes (during aging) are due to an isothermal shift of the retardation spectrum (without any shape change). (b) Chai–McCrum hypothesis of physical aging for semicrystalline polymers: from the thermally stimulated creep experiments, it was shown that physical aging does not change the retardation spectrum at long retardation times, for $t_e \ll \tau$. There are large changes in magnitude or temporal position (hence the shape) of the spectrum at short times which are revealed in the superposition experiments

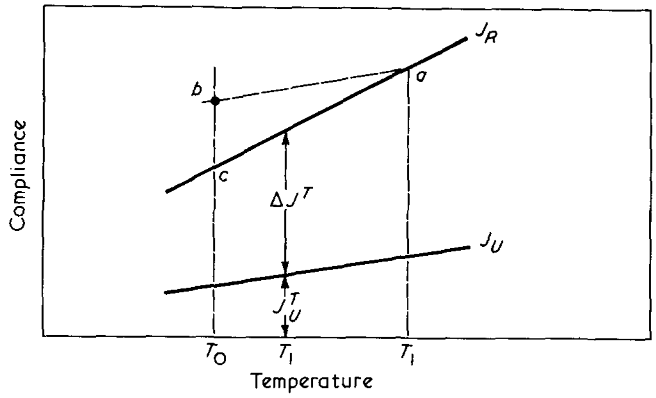

Figure 11 Schematic outline of the viscoelastic model with temperature dependence limiting compliances (J_U and J_R) for the thermal sampling technique appropriate to volume relaxation of Simha *et al.* (see text)

$$\frac{1}{T}=\frac{1}{T_0}-pt. \tag{23}$$

Since $$\tau=\tau_0\exp\frac{\Delta H}{R}\left[\frac{1}{T}-\frac{1}{T_0}\right]$$

we have $$\tau=\tau_0\exp-\left(\frac{t}{\lambda}\right) \tag{24}$$

in which $$\lambda=\frac{R}{\Delta H\,p} \tag{25}$$

The differential equation for the release of this frozen-in strain is then,

$$\frac{\mathrm{d}\gamma}{\mathrm{d}t}=-\frac{\gamma}{\tau_0\exp-(t/\lambda)} \tag{26}$$

with solution at time t for the remaining frozen-in strain[4]:

$$\gamma(t)=\gamma_0\exp\left\{(-\lambda/\tau_0)\left[\exp(t/\lambda)-1\right]\right\} \tag{27}$$

This attractive closed form solution occurs because *inter alia* the temperature dependence of the limiting compliances may be ignored since during the heating the stress is zero. This formulation may be easily extended to account for a distribution of relaxation times which is an essential step before application to experiment.

Consider next a mechanical analogue of the volumetric relaxation experiment as employed for instance by Simha and co-workers[13-17]. In a typical experiment the specimen is quenched and then heated in a systematic manner during which time the volume is observed. Take again as a model a Voigt element with temperature dependent limiting compliances, *Figure 11*. The mechanical analogue to the Simha volumetric experiment is identical to that used for thermal stimulation except that the stress is never removed.

For example, apply the stress at T_1 (relaxation time τ_1) for a time, t, $t \gg \tau_1$. Then quench to T_0. At T_1 the strain is (see *Figure 11*),

$$\gamma=\sigma[J_U^{T_1}+\Delta J^{T_1}] \tag{28}$$

whereas at T_0 the strain is

$$\gamma=\sigma[J_U^{T_0}+\Delta J^{T_0}] \tag{29}$$

so that the frozen-in strain at T_0 is,

$$\gamma_f=\sigma[\Delta J^{T_1}-\Delta J^{T_0}] \tag{30}$$

In *Figure 11* the strain frozen in is represented by *bc*. The specimen is now heated in a systematic manner. The interpretation of this heating experiment is complex because of the temperature dependence of both ΔJ and J_U. A closed form solution comparable to equation (27) for the thermal sampling experiment does not exist.

The effect is also intrinsically smaller than in the thermal sampling experiment. At temperature T_0 the frozen-in strain is:

$$\gamma_f \doteqdot \sigma\Delta J^{T_0}\alpha_J\Delta T \tag{31}$$

This is a second order quantity compared to the strains frozen-in in the thermal sampling experiment which can equal $\sigma\Delta J^{T_1}$.

(4) Our results showed that, in the α-region of polypropylene, the kinetics of volume change and their temperature dependence are the same as those of mechanical shear deformation. This finding contributes significantly to our understanding of the time dependent response of an isotropic polymer to an arbitrary 3-dimensional stress history. Similar results for other systems have been reported by other workers[21].

CONCLUSION

It is shown that the interpretation of volume relaxation experiments with viscoelastic models fails unless the limiting compliances are assumed to be temperature dependent. With this model an experiment is designed, based on the Boltzmann superposition principle, by which the activation enthalpy for volume relaxation ΔH_v is determined. For polypropylene at 40° $\Delta H_v=35$ kcal mol^{-1}, equal to ΔH_J the activation enthalpy for creep.

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APPENDIX A

Consider a generalized Voigt model in series with a spring (*Figure 1b*) with parameters whose temperature dependence is described:

$$\varphi_J^T(\ln\tau)=\varphi_J^{T_0}\left(\ln\frac{\tau}{a_J(T)}\right), \tag{A1}$$

$$(J_R^T-J_U^T)=b_J(T)(J_R^{T_0}-J_U^{T_0}), \tag{A2}$$

$$J_U^T=c_J(T)J_U^{T_0}, \tag{A3}$$

in which $\varphi_J^{T_0}(\ln\tau)$ is the normalized distribution of retardation times in creep at T_0; J_R is the relaxed compliance and J_U the unrelaxed compliance, at T or T_0 according to superscript. The parameter $a_J(T)$ is assumed to be independent of retardation time. For values of $\Delta T=(T-T_0)$ of the order of several degrees, we take $b_J(T)$ and $c_J(T)$ to be linear in ΔT and write:

$$\begin{aligned} b_J(T)&=1+\alpha_J\Delta T\\ c_J(T)&=1+\beta_J\Delta T \end{aligned} \tag{A4}$$

The temperature coefficients α_J and β_J are of order 10^{-3} $°C^{-1}$*. It follows that the parameters $b_J(T)$ and $c_J(T)$, for values of $\Delta T \sim 10°C$, differ from unity by a small quantity of the order of 10^{-2}.

Consider a constant stress applied to the model at $t=0$, at temperature T_0. At time t', the temperature is changed instantaneously to T. It then follows that the strain, $\gamma(t)$ at time t, $t<t'$ is given by[22]:

$$\frac{\gamma(t)}{\sigma}=J(t)=\left\{J_U^{T_0}+(J_R^{T_0}-J_U^{T_0})\int_{-\infty}^{\infty}\mathrm{d}\ln\tau_J\varphi_J^{T_0}(\ln\tau)\left[1-\exp-\frac{1}{\tau_J}\times\left(t'+\frac{t-t'}{a_J(T)}\right)\right]\right\}+\left\{\beta_J\Delta TJ_U^{T_0}+\alpha_J\Delta T(J_R^{T_0}-J_U^{T_0})\int_{-\infty}^{\infty}\mathrm{d}\ln\tau_J\varphi_J^{T_0}(\ln\tau)\times\left[1-\exp-\frac{1}{\tau_J}\left(\frac{t-t'}{a_J(T)}\right)\right]\right\} \tag{A5}$$

The creep described by the first bracket we term the primary process and the second bracket the secondary process.

If $\alpha_J=\beta_J=0$ (temperature independent compliances), there is no secondary process so that equation (A5) is a restatement of Hopkins result[9]. The course of such a T-jump imposed during a creep experiment is illustrated in *Figure 2a*. At the initiation of the experiment at $t=0$, $J(t)$ moves instantaneously from 0 to p_0 and then at an ever decreasing rate from p_0 towards r_0, reaching q_0 after time t'. At T-jump from $T_0 \quad T_2$ at t' causes $J(t)$ to follow the horizontal line q_0q_2 (as $\mathrm{d}J_U/\mathrm{d}T)=0$ and $q_0\ q_2=T_2-T_0)$, and thence from q_2 towards r_2. The ratio of the creep rates at T_0 and T_2, at the same time t' is:

$$\frac{\dot{\gamma}(t',T_2}{\dot{\gamma}(t',T_0)}=\frac{\dot{J}(t',T_2)}{\dot{J}(t',T_0)}=\frac{1}{a_J(T_2)} \tag{A6}$$

The creep rate is thus accelerated by the T-jump and continues at an ever decreasing rate as $J(t)$ approaches J_R at r_2. The course of a negative T-jump, $T_0 \uparrow T_1$ is also indicated in *Figure 2a*. There is, in this case, a deceleration in creep rate at t' given by equation (A6), with T_2 replaced by T_1.

If α_J and β_J are not zero (and in fact, this is always the case), a secondary process is initiated by the T-jump. At t' the compliance follows the line q_0q_2, *Figure 2b*, parallel to the J_U *versus* temperature line. There is, therefore, an instantaneous change in the compliance at t' of $\beta_J\Delta TJ_U^{T_0}$, equation (A5) (v_2q_2, *Figure 2b*). Two time dependent events described by equation (A5) then occur: (1) the normal progression of $J(t)$ towards r_2 (time dependent part of primary process), (2) the small perturbation represented by the time dependent portion of the secondary process with magnitude proportional to $\alpha_J\Delta T(J_R^{T_0}-J_U^{T_0})$. That is to say, the effect of finite α_J *and* β_J is to initiate a secondary creep experiment at time t' and temperature T_2. For a positive ΔT, the secondary process is in the direction of the primary process. But for a negative ΔT, the secondary process opposes the primary so that $J(t)$ diminishes (from q_1, towares w_1, *Figure 2b*). This transient secondary process eventually disappears and the primary process again dominates, causing $J(t)$ to proceed towards r_1, *Figure 2b*.

If t' is extremely large with respect to the largest significant retardation time present and to the time scale following the T-jump:

$$t' \gg (t-t') \tag{A7}$$

then, consideration of equation (A5) shows that the creep rate due to the primary process is essentially zero so that the secondary process may be examined in isolation. Defining, for this condition, the primary process $J_p^{T_0}(t'=\infty)$:

$$\Delta J(t)=J(t)-J_p^{T_0}(t'=\infty) \tag{A8}$$

so that from equation (A5):

$$\Delta J(t)=\beta_J\Delta TJ_U^{T_0}+\alpha_J\Delta T(J_R^{T_0}-J_U^{T_0})\int_{-\infty}^{\infty}\mathrm{d}\ln\tau_J\varphi_J^{T_0}(\ln\tau)\times\left\{1-\exp-\left[\frac{t}{t_Ja_J(T)}\right]\right\} \tag{A9}$$

in which we now (and in the rest of the paper) take our zero in time at the instant of the T-jump: if there is to be more than one T-jump the zero will be at the instant of the first T-jump. The secondary process is identical in every way to the primary process (equation (A5)) except that:

(1) the compliances are reduced to $\beta_J\Delta TJ_U^{T_0}$ (instead of $J_U^{T_0}$)and $\alpha_J\Delta T$ $(J_R^{T_0}-J_U^{T_0})$ instead of $(J_R^{T_0}-J_U^{T_0})$.

(2) the effective time is $t/a_J(T)$.

From a viscoelastic point of view the secondary process is only of interest in that it leads to determination of the two temperature coefficients, α_J and β_J. The experimental initiation of a secondary creep process by thermal jump, and the determination of these two coefficients, for polypropylene at 40°C, will be described in II.

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* These coefficients are determined by thermal stimulation in the following paper[22] which we signify henceforth by the symbol II.