

# The freezing-in of non-equilibrium values of the limiting compliances as a mechanism of physical ageing

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The theory of a new method for measuring the temperature dependence of the limiting compliances,  $J_R$  and  $J_U$ , is described. The method is based on the observation of secondary creep; this is a small effect generated in a stressed specimen by a  $T$ -jump. In the experiment, the specimen is maintained isothermally under a constant stress until the primary creep rate is negligible. A  $T$ -jump of several degrees, positive or negative, is then imposed and this generates the secondary creep. If  $J_R$  and  $J_U$  are independent of temperature there is no secondary creep. The secondary creep has the same time dependence as primary creep. A comparison of the magnitudes of secondary and primary creep – at equivalent reduced times – leads by means of the theory of thermoviscoelasticity to the determination of  $\alpha$  and  $\beta$ , the temperature coefficients of  $(J_R - J_U)$  and  $J_U$ . For isotactic polypropylene in the  $\alpha$ -region at 40°C both coefficients are positive:  $\alpha = 0.7 \times 10^{-2}$  and  $\beta = 0.1 \times 10^{-2} \text{ } ^\circ\text{C}^{-1}$ . It is clear from the positive sign for the coefficient of  $(J_R - J_U)$  that the  $\alpha$ -relaxation is of the type in which stress increases the entropy. The magnitudes of the coefficients support the conclusion that the use of un-normalized time-temperature superposition to determine activation energy in polypropylene will be highly erroneous. The magnitude of the coefficient of  $(J_R - J_U)$  is sufficiently large to account partially for physical ageing in crystalline polymers. Quenching from  $T$  down to  $T_0$  will freeze in a non-equilibrium value of  $(J_R - J_U)$ , considerably in excess of the equilibrium value at  $T_0$ . Storage at  $T_0$  permits the equilibrium value to be slowly attained, so that with increasing ageing time the polymer becomes stiffer and exhibits lower creep rates.

**Keywords** Creep; ageing; limiting compliances; polypropylene

## INTRODUCTION

In this paper we describe a determination of the temperature dependence of the limiting compliances  $J_R$  and  $J_U$  which, until now, has been an essentially unsolved experimental problem. The complexity introduced by distributed relaxation times and partially superposed relaxations of diverse origin means that in polymers, unlike metals, the opportunity to find a temperature range in which  $J_U$  and  $J_R$  can be observed directly by isochronal measurement is severely restricted if not eliminated, other than at the lowest temperatures. This is particularly true in crystalline polymers: for example in polypropylene, starting at  $-150^\circ\text{C}$  the  $\gamma$ ,  $\beta$  and  $\alpha$  processes<sup>1</sup> occur in succession and overlap so that at no temperature is it possible to obtain the temperature coefficient of either limiting compliance: for the  $\alpha$ -process, indeed, melting intervenes before relaxation is complete. The relaxation effects completely mask the much smaller changes in limiting compliance.

The temperature coefficients of the limiting compliances are also of practical interest in that they constitute a major perturbation to the application of time-temperature superposition for long time creep prediction and the determination of activation energy. It has been shown that this perturbation incurs an error of

the order of 50% in the determination of activation energy  $\Delta H$  for the  $\beta$ -relaxation in poly(methyl methacrylate)<sup>2</sup>. McCrum *et al.*<sup>2</sup> introduced the temperature parameters  $b_T$  and  $c_T$  for the study of temperature dependence of the limiting compliances:

$$(J_R^T - J_U^T) = b_T (J_R^{T_0} - J_U^{T_0}) \quad (1)$$

$$J_U^T = c_T J_U^{T_0} \quad (2)$$

For small values of  $\Delta T$  ( $= T - T_0$ ), we take

$$b_T = 1 + \alpha \Delta T \quad (3)$$

$$c_T = 1 + \beta \Delta T \quad (4)$$

where  $\alpha$  and  $\beta$  are the temperature coefficients of  $(J_R - J_U)$  and  $J_U$  respectively.

For an entropy driven relaxation, such as the glass-rubber relaxation in amorphous crosslinked polymers<sup>3</sup> and the Snoek relaxation in metals<sup>4-6</sup> the relaxed compliance  $J_R$  decreases with temperature  $T$ , *Figure 1a*: the mechanical stress creates order and so decreases the entropy. However, it is a fact that observations on other relaxations in polymeric solids suggest a tendency for  $J_R$  to increase with temperature, *Figure 1b*. To mention a few of such observations: there are the extensive works of Heijboer<sup>7</sup> on the secondary loss peaks of cycloalkyl and substituted cycloalkyl methacrylate

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polymers, and the dynamic and static mechanical measurements by Miki *et al.*<sup>8</sup> and Gray<sup>9</sup> on the  $\alpha$ -relaxation of polyoxymethylene. Saito<sup>10</sup> has reported on the dielectric behaviour in poly(vinylidene chloride) where below  $T_g$ , the magnitude of dielectric dispersion,  $\Delta\epsilon (= \epsilon_R - \epsilon_U)$ , decreases with decreasing temperature (i.e.  $d\Delta\epsilon/dT$  is positive: compare with Figure 1a). This implies that the entropy is increased by the electric field or—in the viscoelastic case—by the mechanical stress. Thus, if this evidence is accepted at face value, it must be concluded (as proposed by Saito) that whatever the detailed molecular origin, a general feature of these relaxation processes is that mechanical stress (or external electric field) creates disorder. This would, of course, comprise most valuable information. Unfortunately, due to the difficulties of observation mentioned earlier, no rigorous observation of the temperature dependence of  $J_R$  or of  $(J_R - J_U)$  has been obtained prior to the studies we are about to describe.

It was anticipated that a determination of the temperature dependence of  $\alpha$  and  $\beta$  would yield quantitative information to test the Chai-McCrum<sup>11</sup> hypothesis of physical ageing in crystalline polymers. This postulates

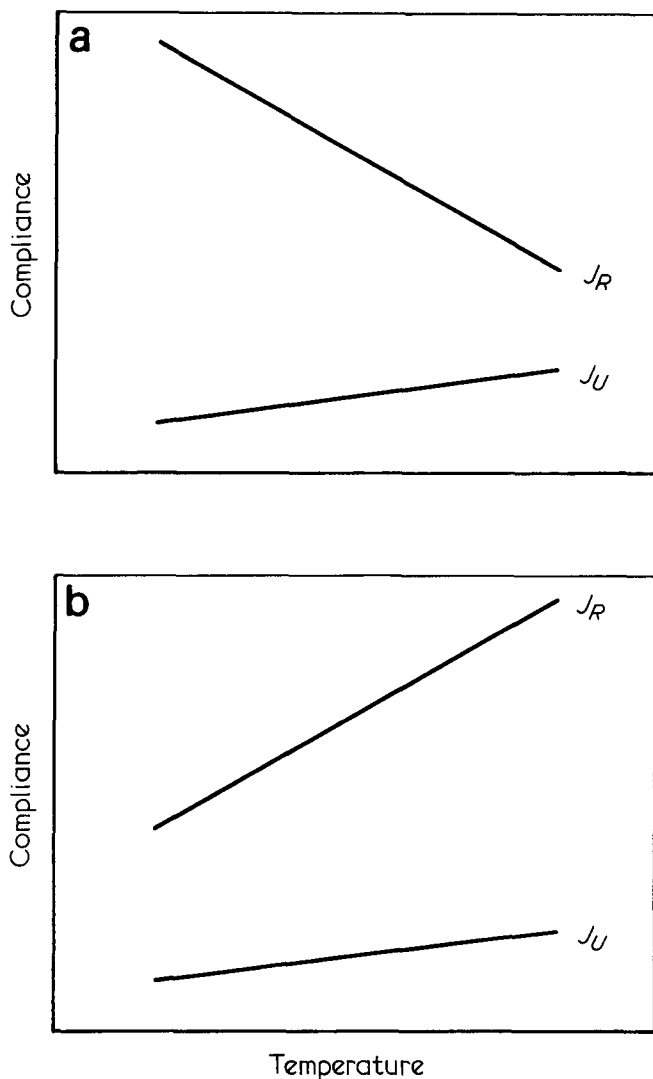


Figure 1 Schematic plot of the temperature dependence of the limiting creep compliances ( $J_U$  and  $J_R$ ): (a) for entropy driven relaxation,  $J_R$  is found to decrease with increasing temperatures; (b) for other relaxations,  $J_R$  increases with increasing temperatures

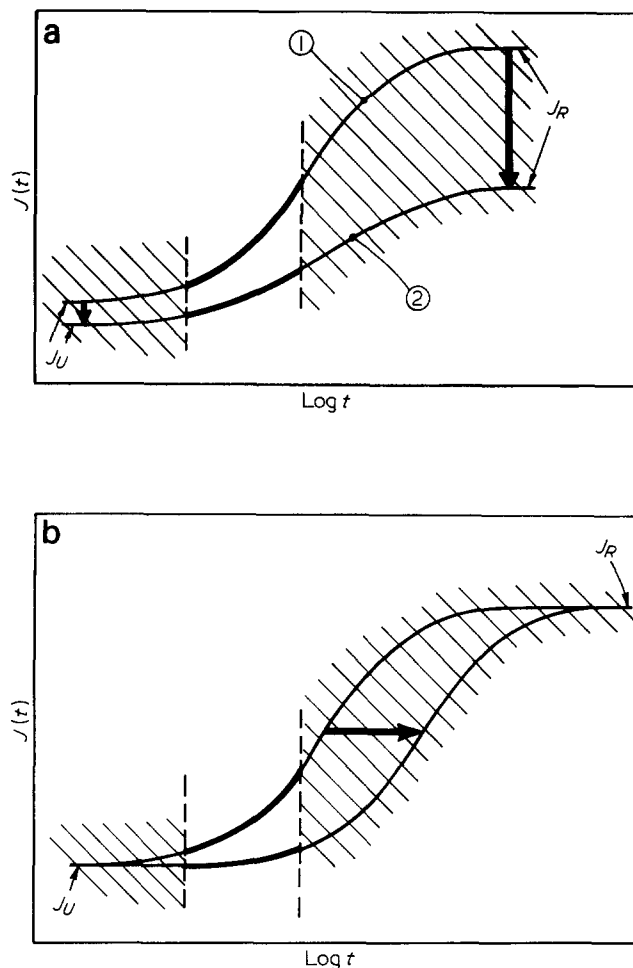


Figure 2 Two isothermal mechanisms of physical ageing in a crystalline polymer which has been rapidly quenched from  $T$  to  $T_0$ : (a) ageing proceeds at  $T_0$  by a diminution of  $J_U$  and  $(J_R - J_U)$  from the large values specific to  $T$  which were frozen-in by the quench to  $T_0$ : note from the arrows  $J_R$  diminishes more than  $J_U$ . (b) Ageing proceeds by a shift of the distribution of relaxation times, with no change in  $J_R$  or  $J_U$ . Both effects could, and probably do, occur simultaneously in crystalline polymers. The experimentally accessible region in creep is shown unshaded

that a principal factor in physical ageing is the diminution of relaxation magnitude ( $J_R - J_U$ ) with elapsed time at the ageing temperatures following the quench. The mechanism is illustrated in Figure 2a. Curve 1 is the plot of specimen compliance against  $\log t$  immediately after quenching: curve 2 is the plot of compliance when considerable ageing has taken place. The changes brought about by ageing occur in the limiting compliances:  $J_R$  decreased more than  $J_U$ , so that  $(J_R - J_U)$  decreases. The observation window is illustrated schematically by the unshaded portion of the curves. Another mechanism of physical ageing is that of Struik which is shown in Figure 2b. Ageing shifts the distribution of relaxation times to longer times so that the inflection in the compliance *versus*  $\log t$  curve occurs at longer and longer times as ageing proceeds:  $J_U$  and  $J_R$  do not change with ageing.

The difference between these two mechanisms would be easily detected if the complete curves could be observed, particularly at extremely short and extremely long times: it is the latter which imposes the main experimental problem. Unfortunately, as the diagram illustrates, it is not possible to judge from the observation window which mechanism is dominant. As can be seen from Struik's

detailed study<sup>12</sup>, and elsewhere<sup>11</sup>, the available creep data could fit either mechanism.

The connection between  $\alpha$  and the Chai-McCrum hypothesis is as follows. It is known that in polypropylene a quench from say 80° to 40°C, for instance, yields a volume which at 40°C shows time dependence<sup>13</sup>. There is a large reduction in volume which occurs rapidly at the instant of quench but on storage at 40°C the volume slowly contracts further; the equilibrium volume at 40°C is not reached for an exceedingly long time. Now suppose that  $(J_R - J_U)$  behaves similarly: suppose that on quenching from 80° to 40°C the equilibrium value of  $(J_R - J_U)$  specific to 40°C takes a long time to be established? One way of testing this hypothesis is to measure the temperature dependence of  $(J_R - J_U)$  to observe whether or not it is of the correct sign and of sufficient magnitude to explain the large ageing effects which are observed.

The observed ageing effects call for a coefficient of temperature change of  $(J_R - J_U)$  considerably in excess of the volume coefficient, which is  $\sim 6 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ . For a coefficient of the latter magnitude, a quench from 80° to 40°C could produce, at most, an ageing effect of 2.4%, which is quite insufficient to explain the observations. In polypropylene such a quench yields an ageing effect—a diminution of compliance between ageing times of 0.18 and 191 ks—of more than 25%<sup>11</sup>. It is clear therefore that  $\alpha$  must be positive and must exceed by an order of magnitude at least the coefficient of volume expansion.

The principle of the new method can be outlined in a simple way. Consider a specimen to be modelled by a series of Voigt elements of total compliance  $(J_R^T - J_U^T)$  in series with a spring of compliance  $J_U^T$  (Figure 3b). Let a constant stress,  $\sigma$ , be applied at  $T_0$  for a time of sufficient length to cause complete relaxation: the strain is then  $\sigma J_R^T$ . Now pulse the temperature from  $T_0$  to  $T$  instantaneously. At  $T$  the equilibrium relaxed strain is  $\sigma J_R^T$ . The stress acting on the specimen will then cause the specimen to creep to the new equilibrium at  $T$ . There will be an instantaneous change of strain of magnitude:

$$\sigma(J_U^T - J_U^{T_0}) = \sigma J_U^{T_0}(c_T - 1) = \sigma \beta \Delta T J_U^{T_0}$$

and a time dependent change of strain of total magnitude:

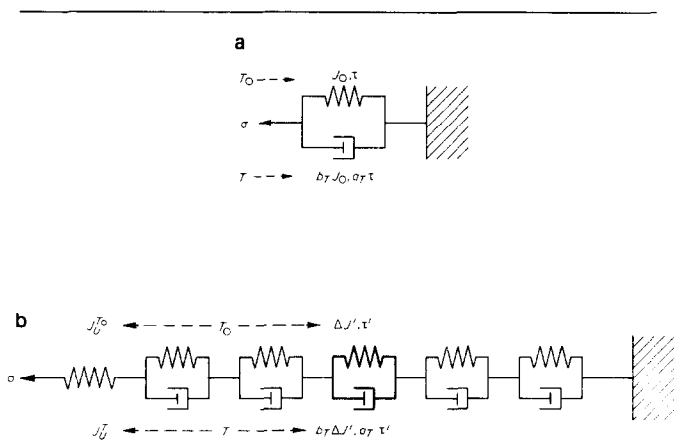


Figure 3 (a) Voigt model with temperature dependent parameters. At  $T_0$  the fully relaxed compliance is  $J_0$ , the relaxation time  $\tau$ ; at  $T$  they take the values  $b_T J_0$  and  $a_T \tau$ . (b) Generalised Voigt elements in series with a spring; relationship  $(\Delta J^T)^T = b_T (\Delta J^T)^{T_0}$  and  $J_U^T = c_T J_U^{T_0}$

$$\begin{aligned} \sigma[(J_R^T - J_U^T) - (J_R^{T_0} - J_U^{T_0})] &= \sigma(J_R^{T_0} - J_U^{T_0})[b_T - 1] \\ &= \sigma \alpha \Delta T (J_R^{T_0} - J_U^{T_0}) \end{aligned} \quad (5)$$

Now a normal, isothermal creep experiment at  $T_0$  triggered by stress  $\sigma$  would yield an instantaneous change of strain  $\sigma J_U^{T_0}$  and a time dependent change of strain of total magnitude  $\sigma(J_R^{T_0} - J_U^{T_0})$ . Thus the strain ratios of the two creep experiments (i.e. strain generated by  $T$ -jump on the previously stressed specimen divided by the strain in the normal creep experiment generated by the application of stress  $\sigma$ ) comprise:

- instantaneous component ratio =  $\beta \Delta T$  and,
- total time dependent component ratio =  $\alpha \Delta T$ .

Hence by performing these two creep experiments it is possible to determine both  $\beta$  and  $\alpha$ .

It can be objected that awaiting complete relaxation is too time consuming or impossible, since another relaxation will intervene sooner or later. We will show, however, in the theoretical section, that it is unnecessary to do this. Rather than perturb the system at equilibrium with a  $T$ -jump, the equivalent data may be obtained by perturbing the system at any point in its approach to equilibrium. It will be noted that  $\beta \Delta T$  and  $\alpha \Delta T$  constitute a driving force for the generation of a thermally triggered secondary creep process as the temperature of the specimen is  $T$ -jumped from  $T_0$  to  $T$ . This secondary creep has been discussed before<sup>13,15</sup>, since it is the main perturbation in the determination of  $\Delta H$  by the single and double  $T$ -jump techniques. The theoretical consideration of this secondary creep phenomenon and its role on the determination of  $\alpha$  and  $\beta$  will be described in the next section.

## THEORY

### Single retardation time model

The phenomenon of the thermally triggered secondary creep process in a viscoelastic solid can best be modelled, in its simplest form, by a single mechanical Voigt element, under a constant stress,  $\sigma$ , Figure 3a. Generalization to include a distribution of retardation times is developed in the next section. Assume the fully relaxed element compliance, at temperature  $T_0$ , to be  $J_0$  and the element retardation time,  $\tau (= \eta J_0)$ , where  $\eta$  is the dashpot coefficient and  $J_0^{-1}$  is the stiffness of the spring). If  $\gamma$  is the strain, then the stress in the spring is  $\gamma/J_0$ : the stress in the dashpot is  $\eta \dot{\gamma}$ . The resultant stress is the sum of the two separate stresses:

$$\sigma = \frac{\gamma(t)}{J_0} + \eta \frac{d\gamma(t)}{dt} \quad (6)$$

At equilibrium when the stress in the dashpot is zero, the relaxed strain is  $\bar{\gamma} = \sigma J_0$ . Equation (6) can be written, defining here  $J(t) = \gamma(t)/\sigma$ :

$$\left( \frac{dJ(t)}{dt} \right)_{T_0} = \frac{1}{\tau} [J_0 - J(t)] \quad (7)$$

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

$$\left( \frac{dJ(t)}{dt} \right)_T = \frac{1}{a_T \tau} [b_T J_0 - J(t)] \quad (8)$$

in which at  $T$  the element retardation time is  $a_T\tau$ . For a crystalline polymer<sup>1</sup>:

$$a_T = \exp \frac{\Delta H}{R} \left[ \frac{1}{T} - \frac{1}{T_0} \right] \quad (9)$$

$\Delta H$  is the activation enthalpy for creep and  $R$  the gas constant.

The two temperature parameters  $a_T$  and  $b_T$ , appearing in the denominator and first term of the numerator of equation (8), cause a  $T$ -jump to generate two distinct and simultaneous effects. If  $b_T$  is not equal to unity but is given in the linear approximation in terms of  $\Delta T$  (equation (3)) then at temperature  $T$  equation (8) becomes:

$$\left( \frac{dJ(t)}{dt} \right)_T = \frac{[J_0 - J(t)]}{a_T\tau} + \frac{\alpha\Delta TJ_0}{a_T\tau} \quad (10)$$

Thus in addition to the creep rate acceleration proceeding from the first term in equation (10), there is a perturbation proportional to  $\alpha\Delta T$ . This perturbation can be considered a secondary creep experiment, generated by the  $T$ -jump and proceeding with time constant  $a_T\tau$ .

*Generalization to a distribution of retardation times*

The single retardation time model shows that the secondary creep process generated by the  $T$ -jump is due to the temperature dependence of the limiting compliances. To extend the model for a distribution of retardation times, let us consider a generalized Voigt model in series with a spring (Figure 3b) with parameters whose temperature dependence is described by equations (3), (4) and:

$$\phi^T(\ln \tau) = \phi^{T_0} \left( \ln \frac{\tau}{a_T} \right) \quad (11)$$

$\phi^T(\ln \tau)$  and  $\phi^{T_0}(\ln \tau)$  are the normalized distributions of retardation times in creep at  $T$  and  $T_0$ <sup>1</sup>.

The method of this paper necessitates knowledge of the activation enthalpy for creep in order to obtain  $a_T$ , equations (9) and (11). The experiments are conducted at temperatures close to 40°C. In this temperature region the activation enthalpy for polypropylene is known for the portion of the retardation spectrum activated in the experiments<sup>14,15</sup>. In formulating the theory it will be assumed that we are probing this portion of the relaxation spectrum, and that the effective  $\Delta H = 34.5$  kcal mol<sup>-1</sup>.

At temperature  $T_0$ , consider a constant stress applied to the model at  $t=0$ . At time  $t'$ , the temperature is changed instantaneously to  $T$ . Then, according to the Boltzmann principle of superposition, the creep  $J^T(t)$  at any time  $t$  (after  $t'$ ) can be written as:

$$\begin{aligned} J^T(t) = & c_T J_{T_0}^{T_0} + (J_R^{T_0} - J_{T_0}^{T_0}) \int_{-\infty}^{\infty} \phi^{T_0}(\ln \tau) \\ & \times \exp - \left( \frac{t-t'}{a_T\tau} \right) \left[ 1 - \exp \left( - \frac{t'}{\tau} \right) \right] d(\ln \tau) \\ & + b_T (J_R^T - J_{T_0}^{T_0}) \int_{-\infty}^{\infty} \phi^{T_0}(\ln \tau) \\ & \times \left[ 1 - \exp - \left( \frac{t-t'}{a_T\tau} \right) \right] d(\ln \tau) \quad (12) \end{aligned}$$

For values of  $\Delta T = (T - T_0)$  of the order of several degrees, we can approximate  $b_T$  and  $c_T$  to be linear in  $\Delta T$ , equations (3) and (4). Then equation (12) becomes:

$$\begin{aligned} J^T(t) = & \left\{ J_{T_0}^{T_0} + (J_R^{T_0} - J_{T_0}^{T_0}) \int_{-\infty}^{\infty} d(\ln \tau) \phi^{T_0}(\ln \tau) \right. \\ & \times \left. \left[ 1 - \exp - \frac{1}{\tau} \left( t' + \frac{t-t'}{a_T} \right) \right] \right\} \\ & + \left\{ \beta\Delta TJ_{T_0}^{T_0} + \alpha\Delta T (J_R^T - J_{T_0}^{T_0}) \int_{-\infty}^{\infty} d(\ln \tau) \phi^{T_0}(\ln \tau) \right. \\ & \times \left. \left[ 1 - \exp - \frac{1}{\tau} \left( \frac{t-t'}{a_T} \right) \right] \right\} \quad (13) \end{aligned}$$

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

If  $t'$  is extremely large with respect to the time scale following the  $T$ -jump,  $t' \gg (t-t')$  then, consideration of equation (13) shows that the creep rate due to the primary process is essentially zero, so that the secondary process may be examined in isolation. Experimentally this is easily accomplished: the specimen is stressed isothermally for a long time until the creep rate is essentially zero: the  $T$ -jump, up or down, is imposed and the specimen then begins to creep again: this is the secondary creep process. Defining, for this condition, the secondary process to be  $\Delta J(t)$  from equation (13), we obtain

$$\begin{aligned} \Delta J(t) = & \Delta T \left\{ \beta J_{T_0}^{T_0} + \alpha (J_R^T - J_{T_0}^{T_0}) \int_{-\infty}^{\infty} d(\ln \tau) \phi^{T_0} \right. \\ & \times \left. \left[ 1 - \exp - \left( \frac{t/a_T}{\tau} \right) \right] \right\} \quad (14) \end{aligned}$$

in which we now (and in the rest of the paper) take our zero in time at the instant of the  $T$ -jump. The secondary process is identical in every way to the primary process (equation (13)) except that:

(i) the compliances are reduced to  $\beta\Delta TJ_{T_0}^{T_0}$  (instead of  $J_{T_0}^{T_0}$ ) and to  $\alpha\Delta T (J_R^T - J_{T_0}^{T_0})$  instead of  $(J_R^T - J_{T_0}^{T_0})$ .

(ii) the effective time is  $(t/a_T)$  instead of  $t$ .

From a viscoelastic point of view, the secondary process is of interest in that it leads to determination of the two temperature coefficients,  $\alpha$  and  $\beta$ . The experimental initiation of a secondary creep process by temperature jump, and the determination of these two coefficients, for polypropylene at 40°C, will be the major purpose of this paper.

*Methods of determination of  $\alpha$  and  $\beta$*

It will be noted that, for constant  $(t/a_T)$ , equation (14) is linear in  $\Delta T$ . Thus a series of experiments from  $T_0$  to different values of  $T$ , should yield values of  $\Delta J$ , which if plotted against  $\Delta T$  for constant  $t/a_T$  will yield a straight line relationship. This experiment is entirely satisfactory in testing the linearity of the system—as shown in Figure 5—but does not afford a quantitative measure of either  $\alpha$  or  $\beta$ .

The quantitative method of measuring  $\alpha$  and  $\beta$  involves an analysis of two experiments: in the first,  $\Delta J(t)$  is determined following a  $T$ -jump from  $T_0$  to  $T$ : in the second the compliance is determined in a (normal) stress triggered, isothermal creep experiment. For the latter at  $T_0$  and at time  $(t/a_T)$

$$J^{T_0}(t/a_T) = J_{T_0}^{T_0} + (J_R^{T_0} - J_{T_0}^{T_0}) \int_{-\infty}^{\infty} d(\ln \tau) \phi^{T_0} \times \left[ 1 - \exp\left(-\frac{t/a_T}{\tau}\right) \right] \quad (15)$$

It follows from equations (14) and (15) that

$$J^{T_0}(t/a_T) = J_{T_0}^{T_0} \left[ 1 - \frac{\beta}{\alpha} \right] + \frac{\Delta J^T(t)}{\alpha \Delta T} \quad (16)$$

The application of equation (16) for the determination of  $\alpha$  and  $\beta$  is as follows.

A constant stress is applied to the specimen at temperature  $T_0$  for a length of time such that the primary creep rate is essentially negligible. Then a  $T$ -jump triggered creep experiment is performed by jumping the temperature abruptly from  $T_0$  to  $T$  and the secondary creep,  $\Delta J^T(t)$ , thus generated measured as a function of  $t$ . The stress is removed and the specimen allowed to recover. This is followed by a normal isothermal stress triggered creep experiment which is performed at  $T_0$  and the creep compliance  $J^{T_0}(t)$  determined. From this latter creep data, the corresponding creep compliances at reduced time  $(t/a_T)$ ,  $J^{T_0}(t/a_T)$ , may be computed:  $a_T$  is the value of shift factor computed for the previous  $T$ -jump experiment. These values of  $J^{T_0}(t/a_T)$  are then plotted against  $\Delta J^T(t)$ : for instance for  $a_T = 10$  and  $t = 100$  s, the value of  $\Delta J$  observed at 100 s is plotted against the value of  $J^{T_0}$  observed at 10 s. This plot should yield a straight line, according to equation (16), of slope  $(\alpha \Delta T)^{-1}$  and with intercept  $J_{T_0}^{T_0} [1 - \beta/\alpha]$ . It follows that both  $\alpha$  and  $\beta$  can be determined if  $J_{T_0}^{T_0}$  is known. It is necessary for the thermal history of the specimen before the start of the two experiments ( $T$ -jump and stress triggered) to be the same, in order to minimize the effect of physical ageing on the results.

In the above experiment there is the possibility of an intrinsic physical ageing perturbation. The stress-triggered experiment is at  $T_0$ : the temperature-triggered experiment is at  $T$  and is initiated with a  $T$ -jump from  $T_0$  to  $T$ . For low values of  $(T - T_0)$  the perturbation will be small: its significance can, nevertheless, be detected since we have a second method of determining both  $\alpha$  and  $\beta$  which is not subject to perturbation due to physical ageing. As before, there are two experiments, one stress-triggered and the other temperature-triggered, but both take place at  $T$ . In the temperature-triggered experiment the specimen is equilibrated under constant stress at  $T_0$ , an imposed  $T$ -jump then brings the temperature to  $T$  and the temperature-triggered creep then occurs which, in this case, it is convenient to write:

$$\Delta J^T(t) = \beta \Delta T J_{T_0}^{T_0} + \alpha \Delta T (J_R^{T_0} - J_{T_0}^{T_0}) \times \int_{-\infty}^{\infty} d(\ln \tau) \phi^T(\ln \tau) [1 - \exp(-t/\tau)] \quad (17)$$

In the stress-triggered experiment the unstressed specimen is equilibrated at  $T_0$  for a time equal to that in the temperature-triggered experiment: the temperature is then  $T$ -jumped from  $T_0$  to  $T$  and at that instant a stress applied. For this experiment it is convenient to write the compliance at  $T$ :

$$J^T(t) = c_T J_{T_0}^{T_0} + b_T (J_R^{T_0} - J_{T_0}^{T_0}) \times \int_{-\infty}^{\infty} d(\ln \tau) \phi^T(\ln \tau) [1 - \exp(-t/\tau)] \quad (18)$$

It follows from equations (3), (4), (17) and (18) that:

$$J^T(t) = J_{T_0}^{T_0} \left[ 1 - \frac{\beta}{\alpha} \right] + \Delta J^T(t) \left[ 1 + \frac{1}{\alpha \Delta T} \right] \quad (19)$$

Taking  $t$  to be the laboratory time in both experiments, after performing several such pairs of experiments we plot  $J^T(t)$  against  $\Delta J^T(t)$ . The slope is then equal to  $[1 + (\alpha \Delta T)^{-1}]$  and the intercept  $J_{T_0}^{T_0} [1 - \beta/\alpha]$ . Thus, again, both  $\alpha$  and  $\beta$  may be obtained if  $J_{T_0}^{T_0}$  is known.

In summary, the method consists in comparing two creep experiments. One of these is a normal creep experiment, stress triggered, performed at  $T_0$ , or immediately after a  $T$ -jump from  $T_0$  to  $T$ . The other creep experiment is temperature triggered: the specimen is maintained under constant stress at  $T_0$  and then a  $T$ -jump is performed. The  $T$ -jump generates a secondary creep component, much smaller than the primary creep in the normal stress-triggered experiment. The two observations are then analysed using equation (16) or equation (19) to derive  $\alpha$  and  $\beta$ . The validity of this theoretical analysis was established in experiments on isotactic polypropylene at  $T_0 = 40^\circ\text{C}$  ( $\alpha$ -relaxation) which are described in the following section.

## EXPERIMENTAL

The specimen used in the experiments was machined from a rod of isotactic polypropylene (Propathene PXC 8830) supplied by Imperial Chemical Industries Limited. Before machining, the rod was annealed at  $130^\circ\text{C}$  and slow cooled to room temperature. The specimen was a thin-walled tube of dimensions: length 60 mm, internal radius 3.94 mm, wall thickness 0.23 mm; its density at  $23^\circ\text{C}$  was  $0.9065 \text{ g cm}^{-3}$ . It was mounted in a torsional creep machine and surrounded by a cavity through which deionized water at the required temperature was passed. The facility for a fast temperature jump was obtained with equipment previously described<sup>16</sup>.

The specimen was annealed at  $80^\circ\text{C}$  for 20 hours to erase previous history and then slow cooled to  $T_0 = 40^\circ\text{C}$ . All experiments described below were conducted with this thermal prehistory and from this value of  $T_0 = 40^\circ\text{C}$ .

### *T-jump triggered creep experiments*

In this experiment the specimen was held initially at  $40^\circ\text{C}$  for 1.7 Ms. A stress of  $1.20 \text{ MNm}^{-2}$  was then applied at  $40^\circ\text{C}$  and held constant for a further 1.89 Ms. At this time the (primary) creep rate was extremely low,  $\dot{\gamma} \sim 10^{-10} \text{ s}^{-1}$ . The first secondary creep process was then triggered by a  $\Delta T = +7.5^\circ\text{C}$  and the strain measured as a function of time  $t$ , to a maximum  $t = 500$  s. For poly-

propylene at  $T_0 = 40^\circ\text{C}$ , the dominant activation energy is  $\Delta H = 34.5 \text{ kcal mol}^{-1}$  (refs. 14, 15) which for  $\Delta T = +7.5^\circ\text{C}$  yields  $a_T = 0.273$ . The maximum value of reduced time was therefore equal to  $(500/0.273) \text{ s} \sim$  half an hour. The specimen was then cooled to  $T_0 = 40^\circ\text{C}$  and allowed to equilibrate (with the stress still on). The procedure was then repeated for three additional  $T$ -jumps of  $\Delta T = +4.0^\circ\text{C}$  ( $a_T = 0.497$ ),  $-4.0^\circ\text{C}$  ( $a_T = 2.049$ ) and  $+12.0^\circ\text{C}$  ( $a_T = 0.128$ ). For each  $T$ -jump the specimen was allowed to creep for a reduced time of half an hour at  $T$  before the temperature was brought back to  $T_0 = 40^\circ\text{C}$ . The stress was constant at  $1.20 \text{ MNm}^{-2}$  throughout the entire sequence of experiments.

Two small corrections were applied to the data. First, a correction for the continuation of primary creep. Second, a correction for a temperature induced rotation. Because of the inhomogeneous nature of polymeric specimens, minute thermoelastic stresses are generated by a change of temperature in the absence of applied stress. The thermoelastic rotation was measured from a separate set of  $T$ -jump experiments conducted from  $T_0 = 40^\circ\text{C}$  in the absence of stress. These two corrections were of magnitude 1% (correction for continuation of primary creep) and 13% (correction for thermoelastic effect). The thermoelastic rotation may be distinguished from a  $T$ -jump triggered creep experiment in that the rotation is in one direction for a positive  $\Delta T$  and in the opposite direction for a negative  $\Delta T$ . In a  $T$ -jump triggered creep experiment the rotation depends on the direction of the torque as well as the sign of  $\Delta T$ .

#### Stress triggered creep experiments

*Isothermally at  $T_0 = 40^\circ\text{C}$ .* In this experiment the thermal history of the specimen was identical to the  $\Delta T = +7.5^\circ\text{C}$  run of the  $T$ -jump triggered creep experiments. Specifically the specimen was heated at  $80^\circ\text{C}$  for 20 h then cooled to  $T_0 = 40^\circ\text{C}$ , and left at this temperature for 3.6 Ms (in the  $T$ -jump triggered creep experiment, the specimen had been aged at  $40^\circ\text{C}$  for 3.6 Ms before the secondary creep experiment was triggered by the  $T$ -jump with  $\Delta T = +7.5^\circ\text{C}$ ). A stress of  $1.20 \text{ MNm}^{-2}$  was then applied to the specimen and the strain was measured as a function of time at  $40^\circ\text{C}$  and  $J^{T_0}(t)$  thus obtained.

*Isothermally at  $T = 47.5^\circ\text{C}$ .* In this experiment the prior thermal history was identical to that of the previous experiment. After the 3.6 Ms ageing at  $40^\circ\text{C}$  a  $T$ -jump of  $\Delta T = +7.5^\circ\text{C}$  was applied and at the same time a stress of  $1.20 \text{ MNm}^{-2}$  was initiated. The creep compliance  $J^T(t)$  was then observed at  $T = 47.5^\circ\text{C}$ , taking  $t = 0$  at the time of the  $T$ -jump. In order to observe the reproducibility of this unusual experiment it was repeated to obtain another set of data.

## RESULTS

Figure 4 shows a plot of  $\Delta J(t)$  against reduced time  $t/a_T$  for the four values of  $\Delta T$  applied in the  $T$ -jump triggered (secondary) creep experiments. The reader is reminded that  $\Delta J(t)$  is the change in compliance of the stressed specimen at  $t$  seconds after the imposition of the  $T$ -jump (it is equal to the  $T$ -jump generated change in strain, divided by the constant stress applied). All the secondary creep compliances  $\Delta J$ , have been corrected for the errors due to the thermoelastic strains and the continuation of the primary creep. The curves are strikingly similar to

primary creep curves. Note that for a positive  $\Delta T$  the derived  $\Delta J$  is positive: the  $T$ -jump generates additional creep strain. For negative  $\Delta T$ ,  $\Delta J$  is negative, which means the specimen exhibits creep recovery.

Figure 5 is a plot of  $\Delta J$  against  $\Delta T$  for values of reduced time  $t/a_T = 50, 100$  and  $150$  s. The straight lines are in agreement with equation (14).

The dependence of the compliance on time (logarithmic scale) for the two stress-triggered creep experiments are shown in Figure 6: curve (A) is the isothermal compliance at  $40^\circ\text{C}$ ; curve (B) is the isothermal compliance at  $47.5^\circ\text{C}$  determined in the experiment in which the stress and the  $T$ -jump from  $40^\circ\text{C}$  are applied simultaneously. It will be noted that, for the latter experiment, good reproducibility is observed between the first and the repeat experiment.

The predictions of the theory of thermoviscoelasticity embodied in equations (16) and (19) are examined in the two plots in Figure 7. This shows  $\Delta J$  generated at time  $t$  at  $47.5^\circ\text{C}$  by a  $T$ -jump from  $40^\circ\text{C}$  plotted against the compliance obtained in two ways: plot (B) shows the compliance obtained at  $47.5^\circ\text{C}$  at time  $t$ ; plot (A) shows

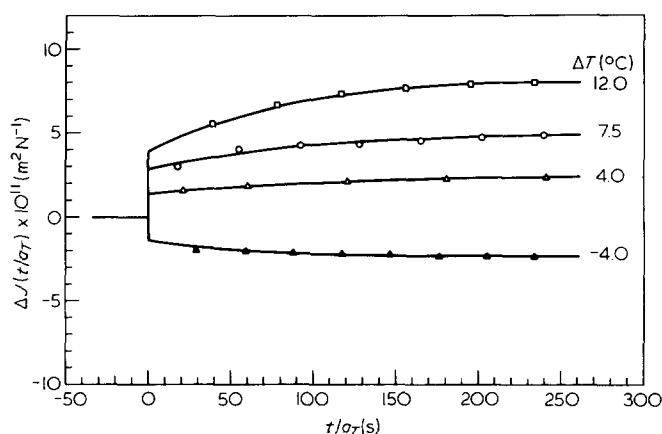


Figure 4 Dependence of the experimental secondary creep compliance,  $\Delta J(t)$ , initiated by  $T$ -jump at  $T_0 = 40.0^\circ\text{C}$ , on the reduced time ( $t/a_T$ ) for four values of  $\Delta T$ :  $\blacktriangle$ ,  $a_T = 2.049$ ;  $\circ$ ,  $a_T = 0.497$ ;  $\square$ ,  $a_T = 0.128$ ; all the values of  $a_T$  are calculated from the Arrhenius equation assuming  $\Delta H = 34.5 \text{ kcal mol}^{-1}$  for polypropylene at  $40^\circ\text{C}$

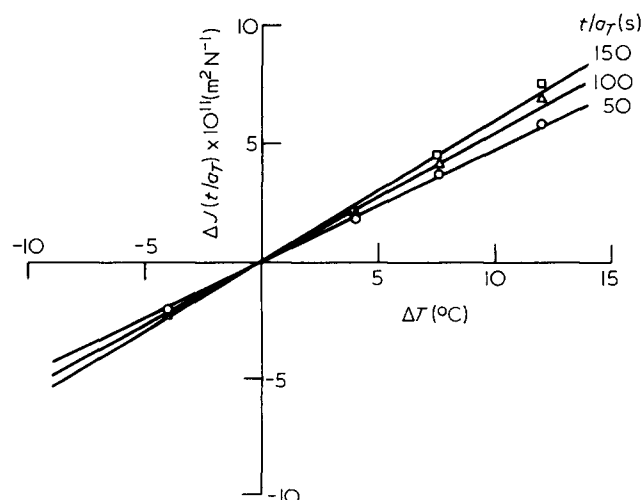


Figure 5 Isochronal (reduced time) dependence of the secondary creep compliance,  $\Delta J$ , on the magnitude of temperature pulse,  $\Delta T$ , for three values of reduced time ( $t/a_T$ ), obtained from Figure 4

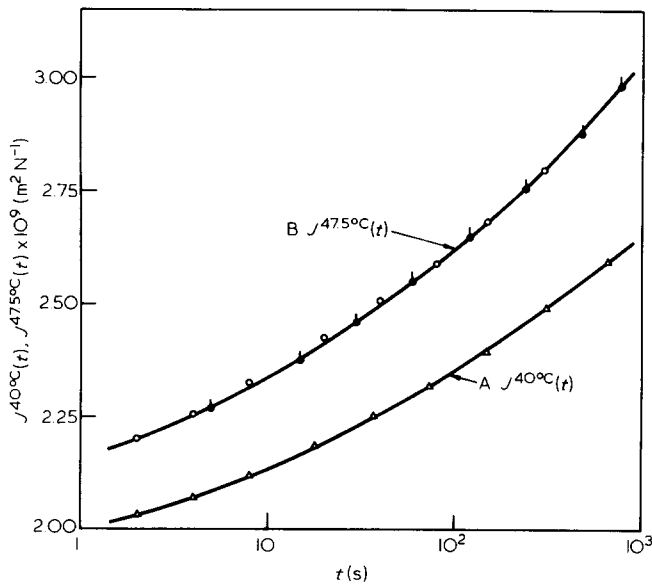


Figure 6 Isothermal dependence of the stress triggered creep compliance on time  $t$ : (A)  $\Delta$ ,  $J^{40^\circ\text{C}}(t)$  at  $T_0=40^\circ\text{C}$ ; (B)  $\circ$ ,  $\bullet$ ,  $J^{47.5^\circ\text{C}}(t)$  at  $T=47.5^\circ\text{C}$ :  $\bullet$  are repeated set of data

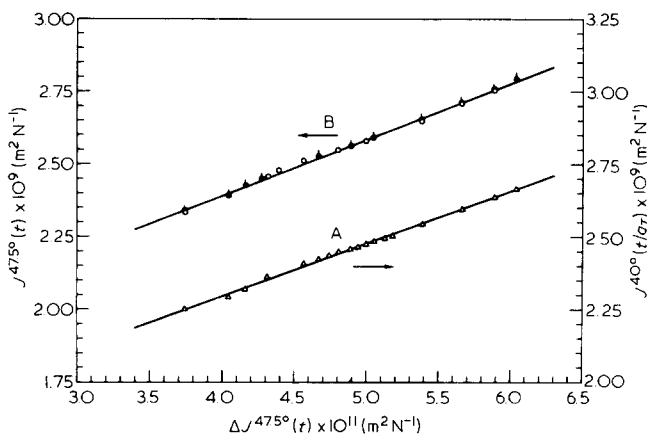


Figure 7 Cross plot of  $\Delta J^{47.5^\circ\text{C}}(t)$  for  $\Delta T = +7.5^\circ\text{C}$   $T$ -jump triggered secondary creep process (Figure 4) against: (A) the stress triggered creep compliance  $J^{40^\circ\text{C}}(t)$  determined at  $40^\circ\text{C}$  (Figure 6, curve (A)) plotted as a function of reduced time,  $J^{40^\circ\text{C}}(t/0.272)$ , in accordance to equation (16). Derived values of  $\alpha$  and  $\beta$  are given in Table 1. (B) the stress triggered creep compliance  $J^{47.5^\circ\text{C}}(t)$  determined in the experiment in which the stress is switched on at the instant of the  $T$ -jump  $40^\circ\text{C} \uparrow 47.5^\circ\text{C}$  (Figure 6 curve B). This latter plot is in accordance with equation (19). Derived values of  $\alpha$  and  $\beta$  are given in Table 1. The closed circles represent the repeat determination of  $J^{47.5^\circ\text{C}}(t)$

the compliance at  $40.0^\circ\text{C}$  at time  $(t/a_T)$ . According to equation (16) plot (A) should yield a line of slope  $(\alpha\Delta T)^{-1}$  and intercept  $J^{T_0}[1 - \beta/\alpha]$ . According to equation (19) plot (B) should yield a line of slope  $[1 + (\alpha\Delta T)^{-1}]$  and intercept  $J^{T_0}[1 - \beta/\alpha]$ . It will be seen in Figure 7 that the data in both plots is well represented by a straight line, as predicted.

A value of  $J_U^{T_0}$  (for  $T_0=40^\circ\text{C}$ ) was obtained of  $1.93 \times 10^{-9} \text{ m}^2 \text{ N}^{-1}$  by extrapolating curve (A) of Figure 6 to short times. This value was then used with the slopes and intercepts from Figure 7 to yield the values of  $\alpha$  and  $\beta$  recorded in Table 1.

Table 1 Values of  $\alpha$  and  $\beta$  (the temperature coefficients of  $(J_R - J_U)$  and of  $J_U$ ) obtained from the slopes and intercepts of the lines shown in Figure 7 according to equations (16) and (19) and the value of  $J_U T_0 = 1.93 \times 10^{-9} \text{ m}^2 \text{ N}^{-1}$  ( $T_0 = 40^\circ\text{C}$ )

Equation	$\alpha (\times 10^4 \text{ }^\circ\text{C}^{-1})$	$\beta (\times 10^4 \text{ }^\circ\text{C}^{-1})$
16	75.0	13.1
19	72.6	11.6
Mean	74	12

## DISCUSSION

It will be seen from Table 1 that at  $40^\circ\text{C}$  the temperature coefficient of  $J_U$  is positive and equal to  $0.1 \times 10^{-2} \text{ }^\circ\text{C}^{-1}$ ; the temperature coefficient of  $J_R$  is positive and equal to  $(0.7 + 0.1) \times 10^{-2} = 0.8 \times 10^{-2} \text{ }^\circ\text{C}^{-1}$ . It follows that the limiting compliances have the form indicated schematically in Figure 1b. We take up first the implications of the sign and magnitude of the coefficients as an explanation of physical ageing.

### Magnitude of coefficients

In the Introduction it is stated that for the Chai-McCrum hypothesis to have any validity, the observed value of  $\alpha$  must be at least an order of magnitude greater than the coefficient of volume expansion, which is  $\sim 6 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ . It will be seen from Table 1 that the observed value of  $\alpha$ ,  $70 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ , is sufficiently large to support the hypothesis.

From earlier work<sup>11</sup> it is known that a short ageing time, say 1 ks, does not shift long relaxation times—say those greater than 1 Ms—to longer times. It cannot, however, be ruled out that a 1 ks ageing time shifts the 1 ks relaxation times to longer times. The thermal sampling experiment of Chai and McCrum<sup>11</sup> offered no evidence on this vital point. We conclude from this that it is possible that the ageing mechanisms in crystalline polymers comprise two separate mechanisms:

- relaxation times of the order of the ageing time may shift to longer times (it being certain that relaxation times much longer than the ageing time do not shift at all).
- the strength of relaxation elements diminish during ageing.

The latter effect is somewhat complicated since the thermal sampling experiment of Chai and McCrum<sup>11</sup> offered evidence that the strength of the long relaxation time elements did not change with short ageing times: specifically it was observed that the magnitude (as well as the position) of the peak in the thermal scan (Figure 6 of ref. 11) did not change with short ageing times.

In summary, physical ageing is seen as involving, according to (i) and (ii) above, changes in magnitude and position of the short time elements: that is, elements with  $\tau$  of the order of, or less than, the ageing time. Note that Guerdoux and Marchal<sup>17</sup> report dielectric studies at temperatures well removed from  $T_g$  in an amorphous polymers that show ageing occurs by changes in  $\epsilon_U$  and  $\epsilon_R$ , the limiting dielectric constants: it will be of interest to determine whether in these experiments small shifts of the spectrum, following Struik, are excluded.

### Sign of coefficients

By definition,  $J_U$  for the  $\alpha$ -relaxation at  $40^\circ\text{C}$  is equal to the relaxed compliance of the  $\beta$ -relaxation at that temperature. That is to say, since the low temperature  $\beta$ -

relaxation at 40°C is complete, its relaxed compliance is the unrelaxed compliance of the  $\alpha$ -relaxation. The  $\beta$ -relaxation in polypropylene is the main chain, glass to liquid relaxation of the amorphous fraction ( $T_g \sim -15^\circ\text{C}$ )<sup>1</sup>. Why then should the temperature coefficient of  $J_U$  for the  $\alpha$ -relaxation be positive?

First, this is not a new paradox. Crosslinked elastomers exhibit a relaxed compliance given to within the usual ideal approximation<sup>1,18</sup>:

$$J_R = (NkT)^{-1}$$

$N$  is the number of sub-molecules per cubic metre and  $k$  is Boltzmann's constant. Yet, this type of behaviour has never been observed in the vast number of experiments in the literature on crystalline polymers. In temperature regions above the glass-liquid transition of the amorphous fraction the moduli are always found to decrease with  $T$ : the compliances increase with  $T$ . Usually further viscoelastic relaxation masks to some extent the temperature dependence. But in the experiments in this paper this effect is eliminated entirely. It is clear therefore, both from the earlier direct observations—often obscured though they may be by additional viscoelastic effects—and the results of this paper, that in semi-crystalline polymers the relaxed compliance of the crystalline-amorphous solid above  $T_g$  increases with  $T$ . That is to say, the relaxation exhibits characteristics typical of an energy driven relaxation, rather than those of an entropy driven relaxation.

The temperature coefficient of  $J_R$  for the  $\alpha$ -relaxation is also positive. There are no previous experiments to compare this with since direct observation is impossible, the specimen melting before the relaxation is complete. As for the  $\beta$ -relaxation, the  $\alpha$ -relaxation exhibits characteristics typical of energy-driven relaxations.

We accept the conclusions of Struik<sup>12</sup> that the  $\alpha$ -relaxation is an extension of the  $\beta$ -relaxation in polypropylene. This is rationalized in the following way. The low temperature  $\gamma$  and  $\beta$ -relaxations in polypropylene are the minor and major amorphous relaxations respectively<sup>1</sup>. In the partially crystalline polymer a sequence of propylene units in the amorphous fraction are pinned at the points where they enter the crystal. The  $\beta$ -relaxation—the onset of large scale motion of the sequence—is overlapped by the  $\alpha$ -relaxation which is taken to be the relaxation of the pinning points at the crystal surface due to hindered rotation of the molecule within the crystal. This hindered rotation is accompanied by movements of the molecular stems in and out of the crystal<sup>12,20</sup>. This assignment implies that there is one partial glassy relaxation ( $\beta$ ) followed immediately by a further relaxation ( $\alpha$ ) of the amorphous fraction triggered by rotation within the crystal.

#### Possibility of ageing perturbation

As explained in the Experimental section we determined  $\beta$  in two ways to examine if in our temperature triggered experiment ageing perturbed the results. We did not find any evidence of this: the two values of  $\beta$  were very close, Table 1. If ageing had an effect if perturbed both determinations of  $\beta$  equally. Such a perturbation, if it exists, would cause  $\beta$  determined in our experiments to be too low. The  $T$ -jumps made in the experiments were

purposefully kept small so that the specimen would never be (volumetrically) too far from equilibrium, and we hoped thereby to minimize perturbations to our theory due to ageing. Because of the possibility of an ageing perturbation the results in Table 1 will yield a lower bound to the equilibrium values of  $\alpha$  and  $\beta$ .

It should also be noted that the values of  $\alpha$  and  $\beta$  are sufficiently large to have a significant effect on values of  $\Delta H$  obtained by the time-temperature superposition of creep curves<sup>2</sup>. Consideration of the results in Table 1 indicates that for polypropylene at 40°C, when the temperature is changed by  $\Delta T = 7.5^\circ\text{C}$ , the retardation time  $\tau$  changes by 73% (as  $a_T = 0.2735$ ) but the limiting compliances,  $J_U^T$  and  $(J_R^T - J_U^T)$ , only increase by  $\sim 1\%$  and  $\sim 6\%$  respectively. Though the latter are small increases, they have a significant perturbation on the accurate determination of  $\Delta H$  by time-temperature superposition because the creep rates are low. It is only in the centre of extremely large relaxations—such as the  $\alpha$ -relaxation of an amorphous polymer—that coefficients of this magnitude can be neglected. There is, of course, an additional perturbation in time-temperature superposition due to physical ageing<sup>11</sup>.

#### CONCLUSION

The temperature coefficients of  $(J_R - J_U)$  and  $J_U$  are positive and of sufficient magnitude to favour the hypothesis that the freezing-in of large non-equilibrium values of  $(J_R - J_U)$  and  $J_U$  is a significant factor in the physical ageing of crystalline polymers.

#### ACKNOWLEDGEMENT

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