Thermally stimulated shrinkage forces in oriented polymers: Induction time

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The four-state model proposed in earlier papers for the description of thermal shrinkage is developed to describe the induction time that occurs when an oriented polymer sample is kept under constant temperature conditions. It is shown that the effect of induction time can be explained on the basis of this model as the result of interactions between neighbouring regions of shrinking polymer units.

(Keywords: thermal shrinkage; shrinkage forces; orientation; induction time)

INTRODUCTION

Thermal shrinkage of highly oriented polymers is dependent on time and temperature. Time dependence can be observed through change of length of an unconstrained sample at constant temperature or appearance of stresses at the ends of a sample kept at constant length[1-4].

The measurements of temperature and time dependent shrinkage forces generated by the sample of oriented polymer kept at constant length have been described in our earlier papers[5,6].

The measurement apparatus was made from two materials (brass and steel) of different thermal expansivities in such a way that the dimension between the jaws was constant (25 mm) in the whole range of temperatures used[6]. The samples were up to 0.3 mm thick so their thermal expansions were complete after about 5 s after being placed in the oil bath which was stabilized at the elevated temperature. In that time the distance between the jaws was slightly increased to compensate for the compressive stress caused by thermal expansion of the sample.

Further details of the experiments performed and the results obtained have been previously described[5]; this paper gives a further explanation of those results.

Typical time dependences of shrinkage stresses obtained for oriented amorphous polycarbonate maintained at constant length are shown in *Figure 1*.

An induction time, t_0, at which nonzero stress appears, is observed in all cases. After the induction period the stress increases quickly, and then more slowly at longer times. Similar dependences were observed for oriented poly(ethylene terephthalate) and were recorded for both polymers well below their glass transition temperature.

The time dependences of shrinkage forces for $t > t_0$ have been discussed and explained in terms of the four-state model[5]. In the present study the same model was used to describe the induction time and the initial stages of the stress–time curves.

MODEL

The model has been described in detail[6]. Graphical representation of a single unit is shown in *Figure 2*. It consists of two springs: S_1, connected in parallel with a two-site element, and S_2, connected in series with another two-site element. Molecular interpretation assumes that S_1 represents the chain elasticity and, when extended (in site 2), it represents an oriented configuration of a molecular subunit; in site 1 it represents a relaxed chain orientation. S_2 represents an elastic junction of the subunit with the matrix and its extension can be relaxed by overcoming the potential barrier between sites 3 and 4.

At constant length the whole element can assume four states depending on whether S_1 assumes site 1 or 2 and whether S_2 assumes site 3 or 4:

2,3	state A	internally stressed state, represents the local situation in oriented polymer
1,3	state B	intermediate state, contributes to the externally observable stresses of shrinkage
1,4	state C	final, internally and externally relaxed state
2,4	state D	theoretically possible but the least probable, state (not considered in this paper).

Sites 1 and 2 are separated by Helmholtz free-energy barrier of height ΔF_1, sites 3 and 4 by a barrier of height ΔF_2. The temperature and time dependences of shrinkage stresses were explained[6] by solving the kinetic equations of transitions through the barriers in model units connected in parallel or in series. A single model unit represents a certain volume in oriented, amorphous polymer and a simple parallel or series connection assumes a lack of interactions between the neighbouring regions inside the polymer. In reality, when a macromolecule (or part of it) tends to reduce its end-to-end distance owing to thermal vibrations it influences surrounding macromolecules. Such interactions make

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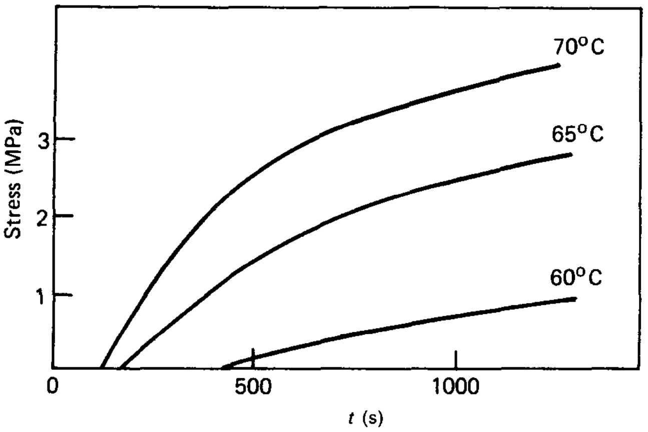

Figure 1 Shrinkage stress vs. time at various temperatures for oriented polycarbonate

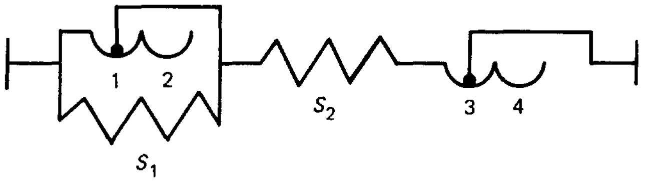

Figure 2 Representation of the four-state model

shrinkage of the macromolecule difficult and the shrinking part tends to compress its nearest surroundings. In the vicinity of the shrinking macromolecule compressive stresses appear that make shrinkage of the neighbouring regions easier. In the model description of the shrinkage phenomenon it is necessary to take into account this influence, which can be achieved in the simplest way by parallel connection of model units in groups.

THE GROUP

A single group of N elements connected in parallel is shown in *Figure 3*. As the whole assembly has to be kept under constant length conditions it is necessary to add an elastic element, S_3, to transduce the action of the group. S_3 is part of S_2 and it has the same molecular interpretation; it represents a resultant elastic junction of N model elements with the matrix so that its elastic constant is N times greater than the constant of S_2.

In the initial state all elements occupy state A. Owing to thermal activation and internal stress on S_1 the elements in state A are able to overcome the energy barrier and pass to state B. The stiff junction J (J representing the interaction between neighbouring shrinking regions in oriented polymer) enables the units to interact with each other; shrunk elements (in state B) compress the elements in state A and the local stresses on these elements make their shrinkage more probable. The number of elements in the group cannot be large because such a stiff junction assumes that interactions between shrinking regions of oriented polymer propagate immediately, which generally is not true but over sufficiently small distances this assumption is reasonable. The external effect of shrinkage of such a group is small at the beginning owing to the great resistance of compressed elements, but then, with the increase of shrunk units, the shrinkage of the group will be spontaneous, leading in a short time of all the units passing to state B.

Such a group represents a certain volume of oriented polymer around the shrinking polymer unit where interactions between this unit and its surroundings propagate, while the whole sample, as a set of such volume elements, can be represented by an assembly of connected groups. There are many possible connections but, no matter which one is being considered, it is necessary to describe the shrinkage stress exerted by one single group at first, then knowing the shrinkage behaviour of the group it is much easier to calculate the stress exerted by the assembly of groups which represents the sample.

Let us consider the group of N elements, where N_A, N_B, N_C occupy states A, B, C respectively: state D, being the least probable, is not considered. As an illustration of the properties of the model, a numerical solution of the most simplified case—one way transition of the $A \to B \to C$ type—is presented here. The kinetics of this reaction are described by a set of differential equations[6]:

$$\frac{dn_A}{dt} = -n_A K_{AB}$$

$$\frac{dn_B}{dt} = n_A K_{AB} - n_B K_{BC} \qquad (1)$$

$$\frac{dn_C}{dt} = n_B K_{BC}$$

where n_I denotes the population of state I ($n_I = N_I/N$) and

$$n_A + n_B + n_C = 1 \qquad (2)$$

The constants K_{AB} and K_{BC} are temperature-dependent transition rates related to the heights of potential barriers modified by local stresses on the model elements and can be defined as follows[7]:

$$K_{AB} = A \exp\left(-\frac{\Delta F_1 - \sigma_{01} V_1 + \sigma_A V_1}{kT}\right)$$
$$K_{BC} = A \exp\left(-\frac{\Delta F_2 - \sigma_B V_2}{kT}\right) \qquad (3)$$

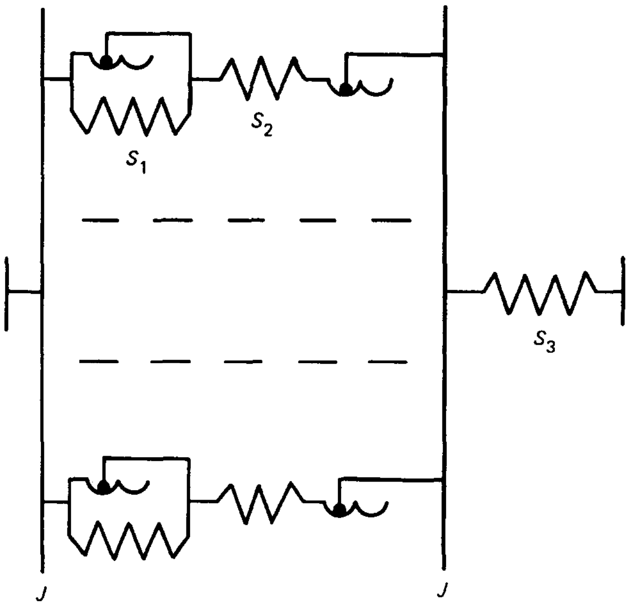

Figure 3 Representation of a single group of model elements

where A is a constant and the exponents define the heights of the potential barriers dependent on the Helmholtz free energy ΔF_1 and ΔF_2 modified by mechanical energy components determined by the local stresses σ_A and σ_B, on elements in state A and B respectively, and the internal stress, σ_{01}, related to the extension of spring S_1 from site 1 to 2.

V_1 and V_2 are the activation volumes of elastic elements, S_1 and S_2. These simplified relations are valid on the assumption that the Helmholtz free energy contour is described by the nonzero strain resistance in such a way that elements S_1 and S_2 can assume only sites 1 or 2 and 3 or 4 located precisely at the bottom of the ΔF contour. It should be noted that the energy

$$\Delta G = \Delta F_1 - \sigma_{01} V_1 \qquad (4)$$

denotes the height of the Gibbs free energy barrier for element S_1 in site 2.

The local stresses, σ_A and σ_B, and the external stress, σ_g, exerted by a group depend on the population of states and are given by the equations (see Appendix):

$$\sigma_A = -0.5\,\sigma_0 n_B \qquad (5a)$$

$$\sigma_B = \sigma_0 - 0.5\,\sigma_0 n_B \qquad (5b)$$

$$\sigma_g = 0.5\,\sigma_0 n_B \qquad (5c)$$

where σ_0 is the internal stress related to the extension of spring S_2 from site 3 to 4.

Equations (1), (3) and (5) permit calculation of the population of state B and the characteristic $\sigma_g(t)$ of one single group. As an illustration of the properties of the group these equations have been solved numerically assuming the following values of parameters:

$$\begin{aligned} \Delta G/k &= 12\,000\ \text{K} \\ V_1 &= 3000\ \text{Å}^3 \\ V_2 &= 500\ \text{Å}^3 \\ \sigma_0 &= 50\ \text{MPa} \\ A &= 10^{14} \\ T &= 300\ \text{K} \\ n_A(t=0) &= 1 \end{aligned} \qquad (6)$$

The time dependence of the population of state B is shown in *Figure 4* for transitions of type $A \to B \to C$ and $A \to B$ (without relaxation). According to equation (5c) the stress σ_g exerted by a group is proportional to n_B so that curve $\sigma_g(t)$ is similar to curve $n_B(t)$—the effect is small at the beginning (curves 2, 3 and 4) and then the stress increases abruptly to its maximum value, slowly falling for greater times as a result of relaxation.

If the relaxation is greater, i.e. when the energy barrier between sites 3 and 4 is relatively small, the group exerts no significant stress (curve 1). As can be seen in *Figure 4*, curves 2, 3 and 4 are very close to each other for the initial stages so that, if the relaxation is small enough to make the external stress possible, it becomes significant for greater times. For the description of the initial stages of shrinkage stress the relaxation transitions of type $B \to C$ can be neglected.

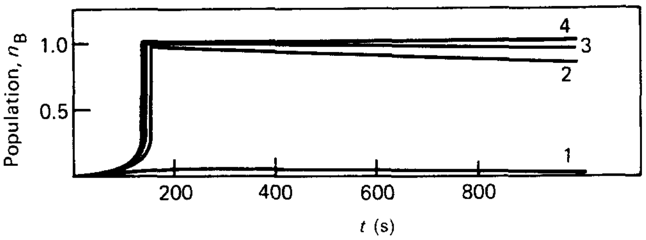

Figure 4 Time dependence of population n_B of state B in one group. 1, $\Delta F_2/k = 12\,600$ K; 2, $\Delta F_2/k = 13\,200$ K; 3, $\Delta F_2/k = 13\,500$ K; 4, $\Delta F_2/k = \infty$ ($A \to B$ transition)

For a model description of the generation of shrinkage stresses the groups have to be connected to each other, which in the simplest case can be realized by a parallel or series connection. The problem of solving a series connection of groups is very complex and analytically impossible because groups do not act independently. Parallel connection kept under constant length as an assembly of independently acting groups is easier to solve and provides a good explanation of the initial stages of shrinkage. For this reason only this connection is described below.

PARALLEL CONNECTION OF GROUPS

It is further assumed that in the initial state such an assembly consists of elements in state A and the length of the system is kept constant. The group is considered as active if at least one element of this group has been activated (has left state A). Since all the groups act independently of one another the change of the number of active groups is given by the equation:

$$dL/dt = (M - L)\nu P \qquad (7)$$

where M is the total number of groups, L is the number of active groups, ν is the frequency of vibrations and P is the probability of one group's activation. If P_0 denotes the probability of activation of the first element in the group and $P_0 \ll 1$, then for the group consisting of N elements

$$P \approx NP_0 \qquad (8)$$

According to equations (7) and (8) the number of active groups in time is described by the following equation:

$$L = M[1 - \exp(-NK_0 t)] \qquad (9)$$

where $K_0 = \nu P_0$ is the rate of activation of the first element in the group. Each group acts independently with its own characteristic $\sigma_g(t)$ from the moment when at least one of its elements has been activated. All the groups are identical and the function $\sigma_g(t)$ is the same for each group—the external stress, σ, exerted by a system of M groups is given by a mean value of stresses exerted by all groups in a given time, t:

$$\sigma(t) = \frac{1}{M}\int_0^M \sigma_g(t - \tau)\,dL \qquad (10)$$

where τ is the time when the number of active groups is increased by dL. By differentiating equation (9) and substituting in equation (10) we obtain:

$$\sigma(t)=NK_0\int_0^{\infty}\sigma_g(t-\tau)\exp(-NK_0\tau)\mathrm{d}\tau \qquad (11)$$

Assuming that $\sigma_g(t)$ is constant for $t\leqslant 0$:

$$\sigma_g(t)=\begin{cases}\sigma_g^0 \text{ for } t\leqslant 0\\ \sigma_g(t) \text{ for } t>0\end{cases}$$

and

$$\sigma(t)=NK_0\int_0^{t}\sigma_g(t-\tau)\exp(-NK_0\tau)\mathrm{d}\tau+\sigma_g^0\exp(-NK_0t)$$

Finally converting the convolution

$$\sigma(t)=\left[\sigma_g^0+NK_0\int_0^{t}\sigma_g(\tau)\exp(-NK_0\tau)\mathrm{d}\tau\right]\exp(-NK_0t) \qquad (12)$$

Equation (12) enables the calculation of the external stress exerted by a parallel connection of groups if the characteristic $\sigma_g(t)$ of a single group is known.

For the group of elements acting according to transitions $A\rightarrow B\rightarrow C$ or $A\rightarrow B$ without any initial stresses, $\sigma_g^0=0$ and

$$K_0=K_{AB}(n_B=0)=A\exp(-\Delta G/kT) \qquad (13)$$

Functions $\sigma(t)$ calculated according to equations (12) and (13) (for $N=10$) on the basis of characteristics given in *Figure 4* are shown in *Figure 5*. The growth of the stress is initially small then increases rapidly and slows down for greater times. The induction period is clearly seen and by comparison of *Figures 4* and *5* it can be treated as the time needed for one group to reach its maximum activity.

Previously[5] the initial stages of shrinkage were described by solving the parallel connection of single elements. The solution had the form of a simple exponential function that was in good agreement with experiment but did not predict the effect of induction time. The same exponential function can be derived from equation (12) for $\sigma_g(t)$ given by the step function so that the curve of shrinkage stress for $t\geqslant t_0$ predicted on the basis of parallel connection of groups is nearly identical to that predicted on the basis of parallel connection of the elements because the curves $n_B(t)$ shown in *Figure 4* are similar to the step function.

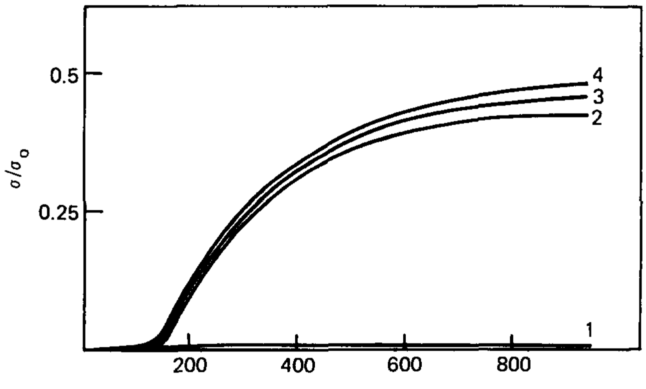

Figure 5 Time dependence of stress exerted by a parallel connection of group acting according to the characteristics shown in *Figure 4*

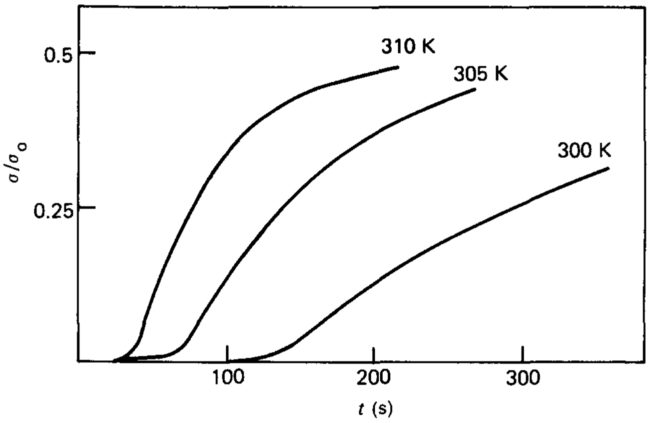

Figure 6 Time dependence of shrinkage stress at various temperatures predicted on the basis of parallel connection of groups

TEMPERATURE DEPENDENCE OF INDUCTION TIME

From comparison of the curves in *Figure 5* it is seen that the relaxation transitions $B\rightarrow C$ are significant for times much greater than t_0 so that for a good description of the initial stages of shrinkage only transitions of type $A\rightarrow B$ need be considered. The time dependences of the shrinkage stresses predicted on the basis of parallel connection of groups of the models with single transition $A\rightarrow B$ for various temperatures are shown in *Figure 6.*

The values of the quantities appearing in the solved equations are the same as previously. It is seen that the induction time is very sensitive to temperature and the calculated curves are in good qualitative agreement with the experimental curves shown in *Figure 1.* For $A\rightarrow B$ transition the kinetic equations (1) for one group reduce to one equation:

$$\mathrm{d}n_B/\mathrm{d}t=(1-n_B)A\ \exp[-(\Delta G-0.5\sigma_0 n_B\ V_1)/kT] \qquad (14)$$

It was previously noted that t_0 is a time when a single group reaches its maximum activity, but the increment of n_B is very rapid in this region so that for mathematical calculations it is possible to assume that the value of n_B for $t=t_0$ is between 0.6 and 1. Assuming that $n_B(t=t_0)=0.95$ equation (14) leads to the value of t_0 given in the form:

$$t_0=\frac{I}{A}\exp\left(\frac{\Delta G}{kT}\right) \qquad (15)$$

where

$$I=\int_0^{0.95}\frac{\exp(-\sigma_0 V_1 n_B/kT)}{1-n_B}\mathrm{d}n_B \qquad (16)$$

For physically reasonable values of A, σ_0 and V_1 the quantity $\ln(I/A)$ is a weak function of temperature and changes by less than 0.4% of its value in the temperature interval 290–350 K, while t_0 changes by several orders of magnitude in the same temperature interval so that according to equation (15) a plot of $\ln t_0$ vs. $1/T$ should be a straight line with a slope $\Delta G/k$. As an example, such a plot of numerically calculated values t_0 for data given by equation (6) is shown in *Figure 7*. The slope of a fitted line is equal to 11940 K while the strict value of $\Delta G/k$ is 12000 K.

RESULTS AND DISCUSSION

The induction times were measured for the polycarbonate (PC) Macrolon 2408 and commercial films of polyethylene terephthalate (PET). Samples were oriented by cold drawing (at room temperature) with a drawing rate of 1 cm min^{-1} for PC and 0.5 cm min^{-1} for PET to the natural draw ratios of about 2 for PC and 4 for PET.

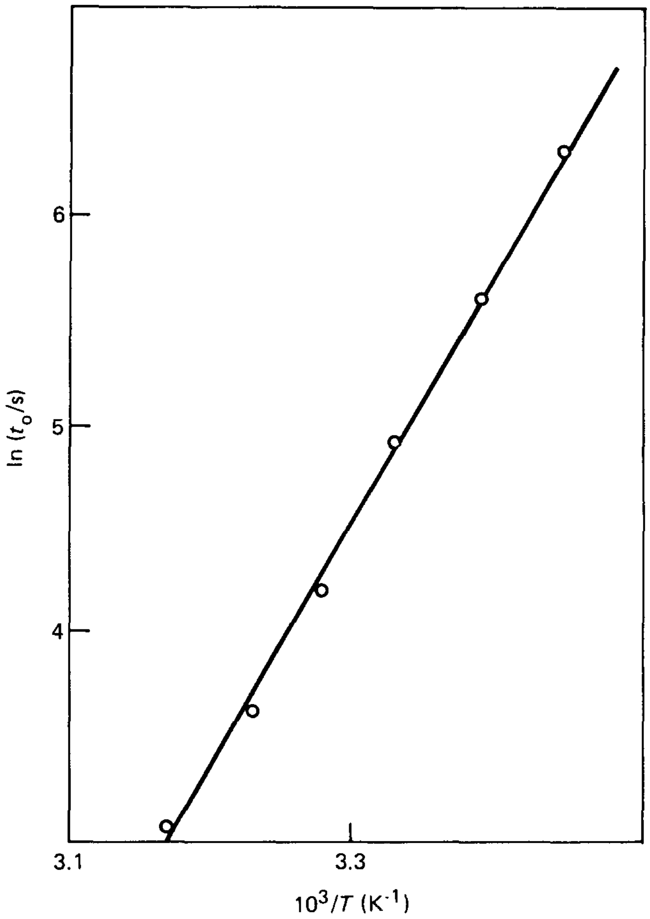

Figure 7 Plot of $\ln t_0$ vs. $1/T$ for values calculated with parallel connection of groups

Table 1 Induction time of appearance of shrinkage forces at constant temperature for polycarbonate (PC) and polyethylene terephthalate (PET)

Temperature (°C)	Induction time (s) PC	PET
45	5600	144
50	2700	90
55	1300	22
60	405	
65	165	

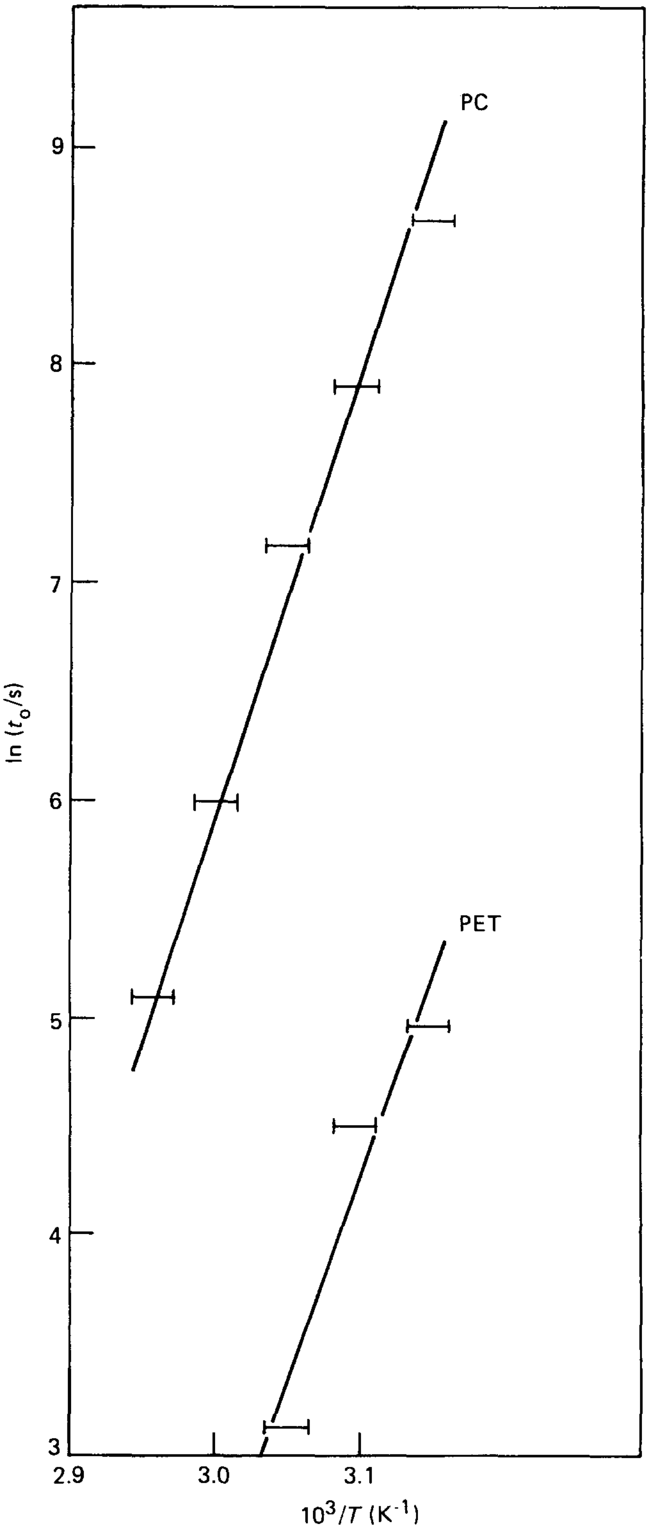

Figure 8 Plots of $\ln t_0$ vs. $1/T$ for polycarbonate (PC) and poly(ethylene terephthalate) (PET) samples

The induction times measured for both polymers are shown in *Table 1*. The values of induction times obtained at higher temperatures are measured with considerable error as a result of delayed heat transfer from the immersion oil to the sample at the beginning of the experiment[5]. The plot of $\ln t_0$ vs. $1/T$ for the values taken from *Table 1* is shown in *Figure 8* and the activation energies obtained from the slopes of the lines are:

$$\Delta G = 42 \text{ kcal mol}^{-1} \text{ for PC}$$

$$\Delta G = 37 \text{ kcal mol}^{-1} \text{ for PET}$$

The activation energy values obtained are in good

Table 2 Activation energy for thermal shrinkage of polycarbonate (PC) and poly(ethylene terephthalate) (PET) calculated by various methods

		Activation energy (kcal mol^{-1})	
Method	Ref.	PC	PET
Initial stages of shrinkage force	5	46	30
Induction time	this paper	42	37

agreement with those calculated from the curves shrinkage stress vs. time for times $t \geqslant t_0$ (ref. 5). The two sets of values are compared in *Table 2*.

CONCLUSIONS

The good agreement between the observed temperature dependences of induction times and those predicted on the basis of a connection of groups of four-state models, as well as the similarity of values of activation energies obtained from this dependence to those obtained from the initial stages of shrinkage stress curves, seems to lend further support for the model.

The effect of induction time is explained on the basis of this model as a result of interactions between neighbouring shrinking regions in oriented amorphous polymers. The time dependences of shrinkage stress predicted by the parallel connection of groups of the model elements for times greater than the induction period are very close to those predicted on the basis of parallel connection of the model elements.

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APPENDIX

Derivation of equation (5)

Let us consider a group of N elements of which N_A, N_B, N_C occupy states A, B, C respectively. As a result of internal stresses the group changes its length by Δl_1 so the spring S_3 changes its length by Δl_3 (see *Figure 3*).

$$\Delta l_1 + \Delta l_3 = 0$$

The local forces exerted by elements occupying various states are equal to

$$F_A = N_A f \Delta l_1$$
$$F_B = N_B f(\Delta l_1 + a)$$
$$F_C = N_C f \Delta l_1$$

where f is an elastic constant of spring S_2, and a is the distance between sites 3 and 4 or 1 and 2.

The local stresses on those elements are given by equations:

$$\sigma_A = F_A/N_A S_0 = f\Delta l_1/S_0$$
$$\sigma_B = F_B/N_B S_0 = f(\Delta l_1 + a)/S_0 \qquad \text{(A1)}$$
$$\sigma_C = \sigma_A$$

where S_0 is the cross-section of one element.

The external force F exerted by a group is given by the sum of local forces

$$F = F_A + F_B + F_C = Nf\Delta l_1 + N_B fa \qquad \text{(A2)}$$

For spring S_3 of elastic constant f_3

$$F = f_3 \Delta l_3 = -f_3 \Delta l_1 \qquad \text{(A3)}$$

From equations (A2) and (A3)

$$\Delta l_1 = -\frac{N_B fa}{Nf + f_3} \qquad \text{(A4)}$$

Internal stress σ_0 related to the extension of spring S_2 from site 3 to 4 is equal to

$$\sigma_0 = fa/S_0$$

From equations (A1) and (A4) it is easy to obtain σ_A and σ_B in the following form:

$$\sigma_A = -\frac{fN_B}{Nf + f_3}\sigma_0$$
$$\sigma_B = \sigma_0 - \frac{fN_B}{Nf + f_3}\sigma_0 \qquad \text{(A5)}$$

The external stress σ exerted by the group is equal to

$$\sigma = \frac{F}{NS_0} = \frac{f_3 N_B}{Nf + f_3}\sigma_0 \qquad \text{(A6)}$$

The elastic action of spring S_3 is a resultant action of N springs S_2

$$f_3 = Nf$$

and equations (A5) and (A6) are identical to equation (5).

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