

Thermally stimulated shrinkage forces in oriented polymers: 1. Temperature dependence

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Temperature dependences of shrinkage forces appearing in oriented polymer samples when heated at constant length were recorded for polycarbonate, polyethylene terephthalate, polyethylene and polypropylene. The influence of various processing conditions on thermally stimulated shrinkage forces is demonstrated. A four-state model is proposed which qualitatively describes the temperature dependences of shrinkage forces in amorphous polymers.

(Keywords: thermal shrinkage; shrinkage forces; orientation; model; amorphous polymers)

INTRODUCTION

High orientation of polymer chains can be obtained by various mechanical treatments such as cold and hot drawing or melt spinning. Depending on the temperature of deformation, the orientation obtained is more or less stable but even in the case of high deformation temperatures it can be fixed by quenching the sample to temperatures at which considerably hindered mobility of polymer chains occurs, e.g. below the glass transition temperature. Various effects of deformation conditions on orientation in polymers are discussed in detail in the literature^{1,2}.

However, when the sample with fixed molecular orientation is subjected to increasing temperature, without being subjected to any external mechanical forces, it shrinks due to relaxation of the orientation of the extended polymer chains. Such thermally induced shrinkage of oriented polymers is a phenomenon of great practical interest as well as providing information about the state of the sample orientation. For practical uses the measurements of thermal shrinkage consist usually in placing samples of known dimensions in an oven with fixed temperature for a certain period of time and in comparing the dimensions of samples before and after thermal treatment. However, much more information can be obtained by determining shrinkage as a function of temperature under programmed temperature conditions.

Application of thermomechanical analysis (t.m.a.) for recording shrinkage or shrinkage rate has been demonstrated as a technique which provides information on the effect of stretching conditions and thermal history on thermal dimensional stability of oriented polymers³.

It has been also observed that when the oriented sample is subjected to increasing temperature with fixed ends, which makes the shrinkage impossible, a shrinkage force is generated which can be measured as a function of temperature⁴⁻⁶. These initial observations have shown that plots of shrinkage force vs. temperature are very sensitive to deformation conditions and the thermal history of the samples.

It will be demonstrated here, using several examples, that recording of thermally stimulated shrinkage force (TSSF) can also be treated as a technique for characterizing the physical state of oriented polymer samples.

The mechanism of shrinkage of oriented polymers has been discussed in various papers⁷⁻⁹. The concepts presented here are not applicable, however, to an explanation of the appearance of shrinkage forces when an oriented polymer sample is heated at constant length.

The present paper discusses the mechanism of generation of shrinkage forces and a model is proposed which can be applied for description of both shrinkage and shrinkage forces.

EXPERIMENTAL

Apparatus

The apparatus specially designed for measurements of thermally stimulated shrinkage forces is schematically shown in *Figure 1*.

The oriented polymer sample is clamped in a set of jaws and placed in the chamber with controlled or programmed temperatures. Rods R1, R2 and R3 (see *Figure 1*) are made of steel with the coefficient of thermal expansion $\alpha_1 = 1.2 \times 10^{-5}$. Rod R4 is made of brass and its length is chosen in such a way that the higher thermal expansion of brass ($\alpha_2 = 1.8 \times 10^{-5}$) compensates the expansion of rods R1 and R2 at a length equal to the distance between the jaws (sample length). It ensures an exactly constant distance between the jaws when the temperature is changed. The force of thermal shrinkage of the sample is transduced to the elastic ring with an elastic constant chosen in such a way that the deformation of the ring is smaller than 1% of the sample length under maximal observed shrinkage forces.

Under these conditions we can assume that shrinkage of the sample related to deformation of the ring is negligible. The deformation of the elastic ring is detected by an electromagnetic sensor and is considered

as a measure of the shrinkage force. The traces of TSSF vs. temperature are recorded on an X-Y recorder. All TSSF curves presented in this paper were recorded with a constant heating rate 3°C/min.

Samples

The polymers used in this study were:

- (1) amorphous polycarbonate (PC) films 0.2 mm thick;
- (2) polyethylene terephthalate (PET) in the form of bristles (diameter 1 mm), originally amorphous and unoriented;

(3) various types of polyethylene (PE) samples (Lupolene) differing in the branching density along the main chain (compare in Table 2), in the form of 0.5 mm thick films obtained by press moulding at 180°C followed by quenching in ice water;

(4) isotactic polypropylene (PP) film obtained in the same way as films of polyethylene.

The samples were oriented by cold drawing. The parameters of the drawing conditions for all samples used are specified in Table 1.

RESULTS

To demonstrate the various effects of the structural state of oriented polymers on thermally stimulated shrinkage forces various polymers were used.

An example of an amorphous polymer was commercial polycarbonate (PC). The samples were drawn at room temperature at a constant drawing rate $v = 1$ cm/min to the natural draw ratio $\lambda = 1.8$ and annealed at constant length for 3 h at temperatures 75°C and 120°C. The TSSF curves for non-annealed and annealed samples are shown in Figure 2.

For the non-annealed sample the stress of shrinkage starts to increase at a temperature a few degrees above the drawing temperature, reaches a maximum well below the glass transition and drops to zero at the glass transition temperature. The annealing of samples almost completely reduces shrinkage stresses below the annealing temperature. Stress appears in the vicinity of the annealing temperature and increases close to the values observed for the non-annealed sample and drops to zero in the same way as for the non-annealed sample. The initially negative values of stresses observed in all cases are probably caused by thermal expansion of samples.

The course of TSSF curves observed for the amorphous polymer can be roughly explained as follows: the increasing stress is an indication of the tendency towards shrinkage of the oriented polymer which in turn increases with temperature. At temperatures close to the glass transition the stress can relax so it drops and disappears at the glass transition temperature.

During long annealing times at elevated temperatures the stress of shrinkage generated below this temperature can relax also. The curves recorded for annealed samples

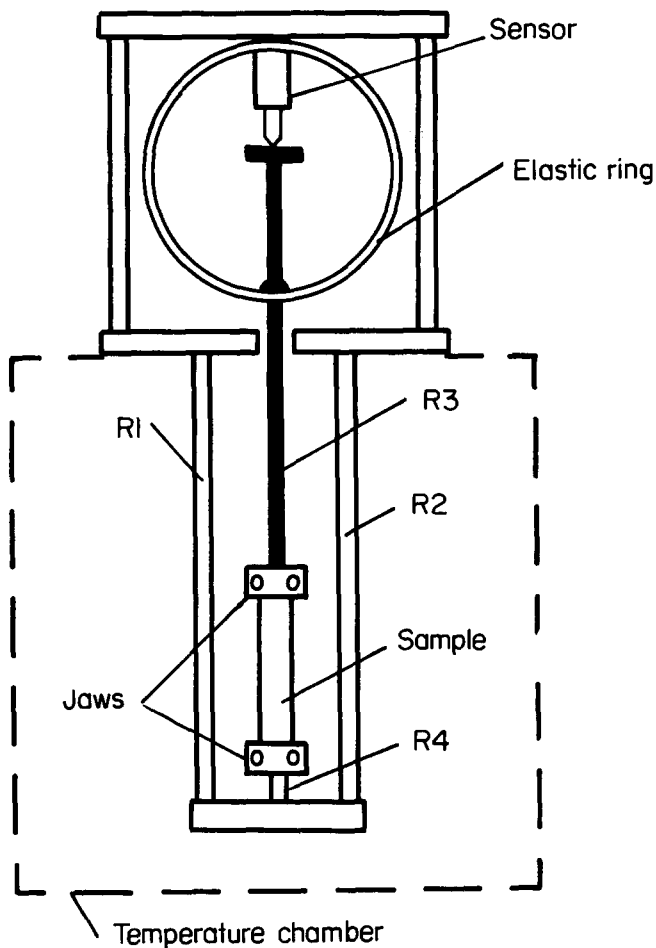


Figure 1 Apparatus used for recording thermally stimulated shrinkage forces

Table 1 Parameters of drawing conditions

Polymer	Sample no.	Temperature of drawing (°C)	Drawing rate (cm/min)	Draw ratio	Annealing temperature (°C)	Birefringence $\times 10^2$
Polycarbonate	PC1	20	1	1.8	—	3.8
	PC2	20	1	1.8	75	3.8
	PC3	20	1	1.8	120	3.6
Poly(ethylene terephthalate)	PET1	20	0.02	4.2	—	—
	PET2	20	50	6.0	—	—
	PET3	20	0.5	4.0	—	—
Polyethylene	PE1	20	5	4.3	—	—
	PE2	20	5	5.4	—	—
	PE3	20	5	8.2	—	—
	PE4	20	2	12.0	—	—
Polypropylene	PP1	20	1	4.2	—	2.69
	PP2	90	1	4.2	—	2.36
	PP3	90	1	6.3	—	2.96
	PP4	110	5	6.3	—	2.91

indicate in this way the residual shrinkage stresses which appear only above the temperature of annealing.

Polyethylene terephthalate samples were used as an example of a polymer which can be oriented both in the amorphous and crystalline state. Samples of PET1 and PET2 were drawn at room temperature from initially amorphous unoriented bristles at drawing rates of 0.2 cm/min and 50 cm/min, respectively. As is known from former studies⁶ in the first case an amorphous well oriented material is obtained while the high drawing results in a crystalline fibrillized sample. Samples of a third PET polymer PET3 were obtained from an initially crystalline material by drawing at the rate of 0.5 cm/min. Differences in the shapes of the TSSF curves for these samples can be seen in Figure 3. For the initially amorphous PET1 sample a maximum for the shrinkage stress below the glass transition is observed. In this case, however, in contrast to PC samples, the stress does not disappear at the glass transition temperature but stabilizes at a certain plateau which extends above T_g . This can

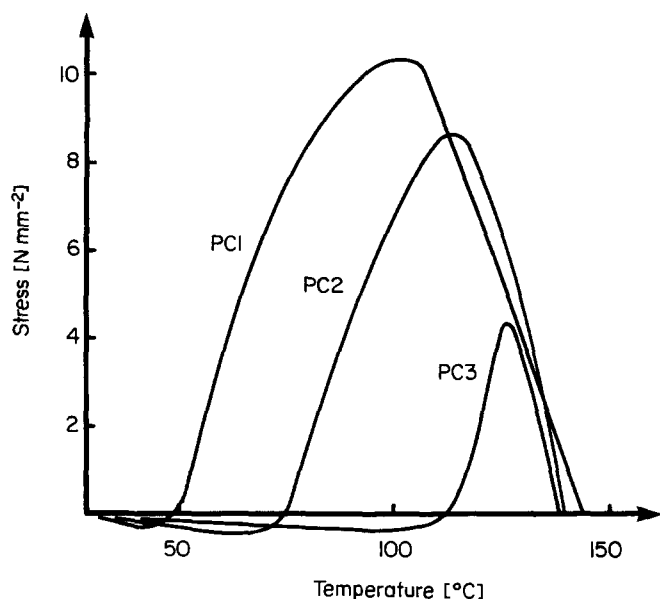


Figure 2 Temperature dependence of shrinkage stresses in amorphous polycarbonate: PC1 non-annealed sample, PC2 and PC3 samples annealed at 75°C and 120°C, respectively

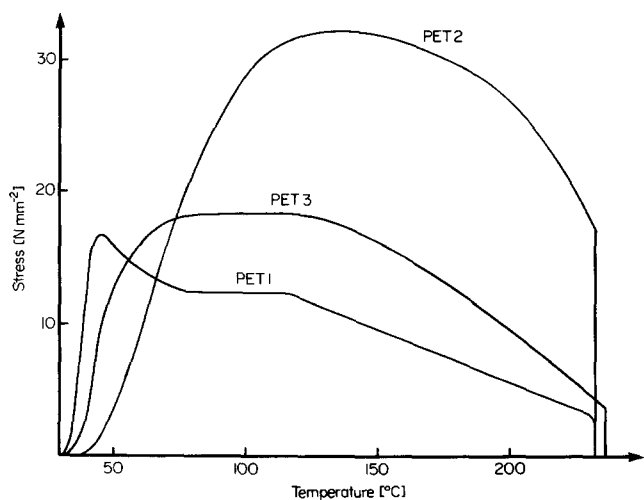


Figure 3 Temperature dependences of shrinkage stress in samples of polyethylene terephthalate oriented at various conditions

Table 2 Characteristics of polyethylene samples

Sample	Branches/ 1000 at C	T_m (°C)
PE1-Lupolen 1800S	35	112
PE2-Lupolen 2410S	20	120
PE3-Lupolen 5000K	5	128
PE4-Lupolen 6011L	2	132

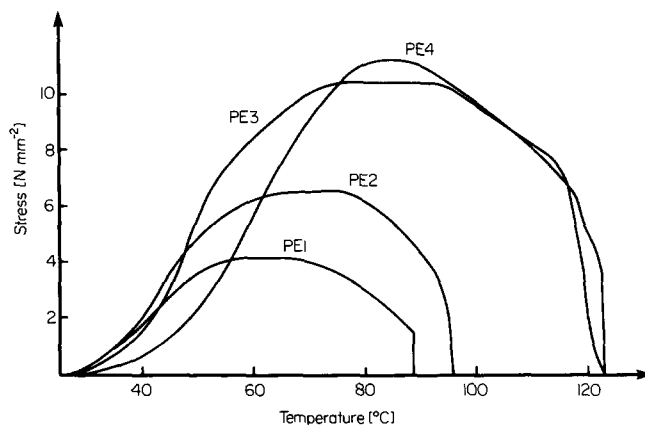


Figure 4 Temperature dependences of shrinkage stress for various polyethylene samples (compare Table 2)

be attributed to the crystallization taking place when the sample passes through the glass transition temperature. The growth of crystalline elements can stabilize the oriented state in the sample making complete relaxation of stress impossible. Following this the stress falls slowly dropping abruptly to zero when the crystalline supermolecular network is molten at the melting point of the polymer. A different kind of behaviour is observed for initially crystalline samples. For the PET2 sample which was crystallized during rapid drawing the stress of shrinkage increases to relatively high values at temperatures far higher than the glass transition temperature. For the PET3 sample which was drawn slowly from initially crystalline state the maximal stresses of shrinkage are much lower. In both these cases, however, the stress of shrinkage does not relax markedly at the glass transition which indicates that the crystalline supermolecular network resists the shrinkage forces generated in the amorphous phase.

Further examples of TSSF curves for crystalline polymers are related to polyethylene samples which differ from each other in the density of short branching along the main chain. All samples characterized in Table 2, were deformed to their natural draw ratios at room temperature. The TSSF traces shown in Figure 4 differ considerably. The details of this behaviour are better exposed by the differential curves shown in Figure 5. The maximum of the rate of stress increase shifts to higher temperatures for samples with decreasing branching density. In the same way the change of the maximum shrinkage stress is indicated on the differential plots by its passing through zero. This shows that the activation of shrinkage takes place for branched polyethylene at lower temperatures than for linear polyethylene.

In the same way the stress in branched polyethylene relaxes at lower temperatures than that for linear polyethylene. It can be noted that for all polyethylene samples the stress falls to zero below the melting point which can be considered as a result of partial melting

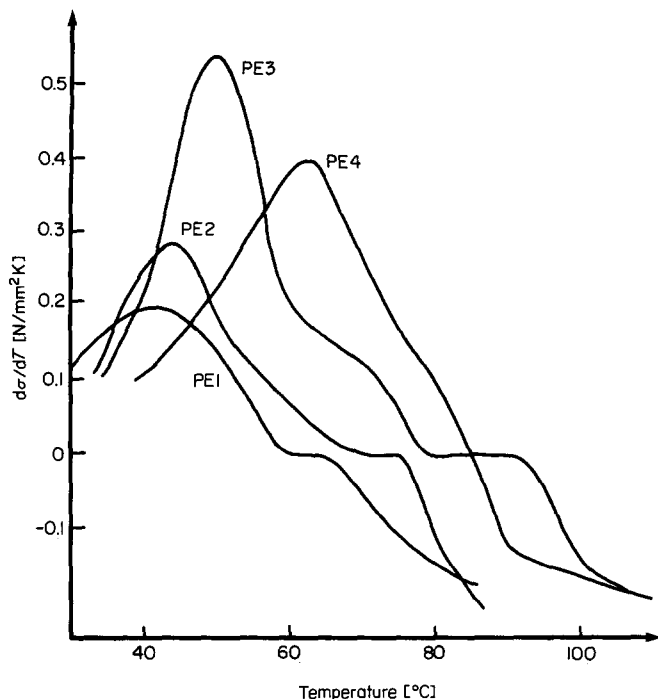


Figure 5 Differential curves related to the dependences presented in Figure 4

which takes place before the final melting point is reached, particularly in branched polyethylene.

TSSF curves for polypropylene samples drawn under various conditions (specified in Table 1) are shown in Figure 6 as examples of the influence of orientation on shrinkage forces. Samples of PP films were drawn in this case through edge-shaped dies¹⁰ under conditions specified in Table 1. Various birefringences of the samples are considered to be an indication of differences in the orientation. It can be seen that the TSSF curves depend neither on the drawing temperature nor on the rate of drawing but on the resultant birefringence which is a complex function of these processing parameters. The heights of the maxima of the TSSF curves increase with the birefringence of the samples. A similar effect was observed for amorphous PET samples drawn through dies to various extensions which resulted in various birefringences of the samples. The results discussed above show that the shapes of the TSSF curves are sensitive to the type of the polymer as well as to details of polymer morphology determined by crystallinity and orientation both being dependent on the processing conditions such as the drawing rate, annealing temperature etc. It follows that recording of shrinkage stresses as a function of temperature can be used as a method for qualitative characterization or testing of oriented polymer samples.

DISCUSSION

To discuss the mechanism responsible for the appearance of macroscopically observable shrinkage forces in oriented polymers it is necessary to take into consideration first of all the structure and interactions in the permanently oriented state. We will limit our present considerations to amorphous polymers because, as many authors believe^{4,11,12} even in semicrystalline polymers shrinkage is mainly related to changes in the amorphous phase.

Stretching of an unoriented amorphous polymer leads

to orientation of macromolecules along the stretching direction and simultaneously to an increase in the effectiveness of intermolecular interactions due to increased alignment correlation of the neighbouring molecular subunits. In this way, at appropriately low temperatures, the orientation of polymer chains can be frozen-in since the potential barriers facing the polymer subunits in their positions can be too high to be overcome by thermally activated motions which would otherwise lead to configurational changes towards lower orientation. In such an oriented frozen-in state, in which the mean end-to-end distance of chains can differ considerably from that in the unperturbed state, the structure is internally stressed by forces related to single chain elasticity¹⁶. These stresses change the heights of potential barriers by an amount proportional to the local internal stress. The change of potential barrier heights is negative for jumps in the direction of decreasing orientation and positive for jumps in the opposite direction.

For such a situation a two state model has been applied by Tanabe and Kanetsuna⁹ to describe thermal shrinkage of amorphous polymers. In that model each molecular chain constituting the oriented amorphous state is divided into submolecules which are assumed to occupy the contracted or extended state randomly. A jump from one state to the other is related to the change of length of the subunit and the total length of the assembly of units (the sample length) is calculated by a simple summation of lengths of individual elements. Although this model has been successfully applied to the description of shrinkage data in amorphous polystyrene it cannot predict shrinkage stresses because individual subunits in the model are treated as being independent and not interacting with each other. The simplest way in which interactions can be introduced into that model is by connecting two site elements by elastic springs as in the model that Joseph¹³ used for the description of plastic deformation in glassy polymers. However, such a modified model would behave as a crosslinked glassy network regardless of whether the elements are connected in series or in parallel. Although such a model would be in agreement with the concepts regarding shrinkage as a rubberlike contraction^{7,14} the shrinkage stress generated in such a model would increase instantaneously with increasing temperature because each jump from the oriented to the unoriented state of

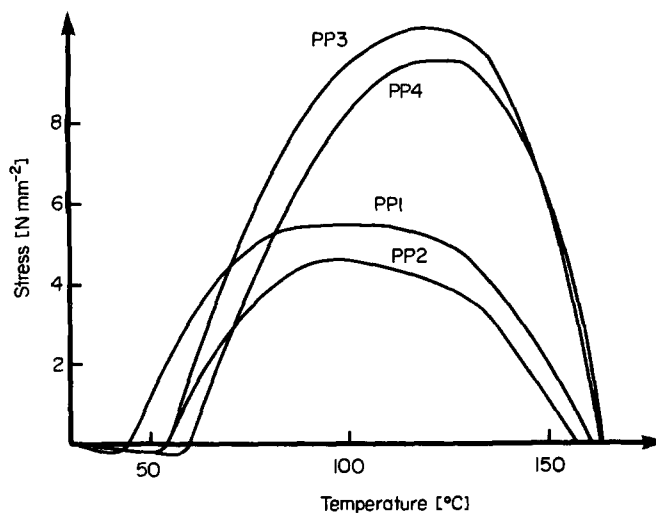


Figure 6 Temperature dependences of shrinkage stresses in polypropylene samples oriented at various drawing conditions

subunit would extend the spring connected in series with the two site elements. A more realistic model would consider a possibility of stress relaxation which in the real system is realized by an intermolecular slip which does not necessarily lead to decreased chain orientation. Notice that the simple viscoelastic model of Burgers¹⁵ (see Figure 7a) approximately satisfies the conditions required here. The model is characterized by two elastic springs with moduli E_1 and E_2 and by two viscous dashpots with viscosities η_1 and η_2 .

To adopt this model for the description of shrinkage and shrinkage stresses in amorphous glassy polymers we replace viscous dashpots by two site elements as shown in Figure 7b. We will consider such an element to be a model of the local properties of a molecular subunit and its interactions with the matrix.

In this model spring S_1 is related to the chain elasticity and can assume relaxed (1) or extended (2) states which are separated by a potential barrier. Spring S_2 represents an elastic junction of the subunit with the matrix and its eventual extension can be relaxed by overcoming the potential barrier between sites 3 and 4 as a result of intermolecular slip. In the real system both barriers are influenced by the configuration of the surrounding sub-molecular elements and local stresses which are related to extensions of springs S_1 and S_2 .

Generally, at constant length, such a model can assume four states which differ from one another in the internal stresses and external response sensitive to the change of state at constant length. These states are illustrated in Figure 8. In state A spring S_1 , being extended, occupies site 2, while spring S_2 , being relaxed occupies site 3. In this state the whole element is internally stressed but externally relaxed.

It can be transformed from this state to state B by a single jump over the barrier between sites 2 and 1 which involves relaxation of stress at spring S_1 and extension of spring S_2 on condition that the length of the model is kept constant. The stress at spring S_2 in state B can be relaxed by a reverse transition of the model to state A or by a jump from site 3 to 4 leading to state C which is both internally

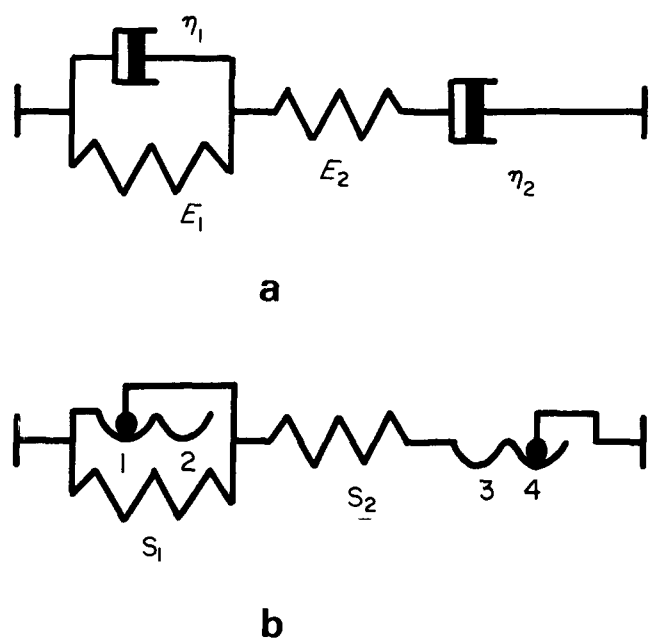


Figure 7 Symbolic representation of Burgers model (a) and the four state model (b)

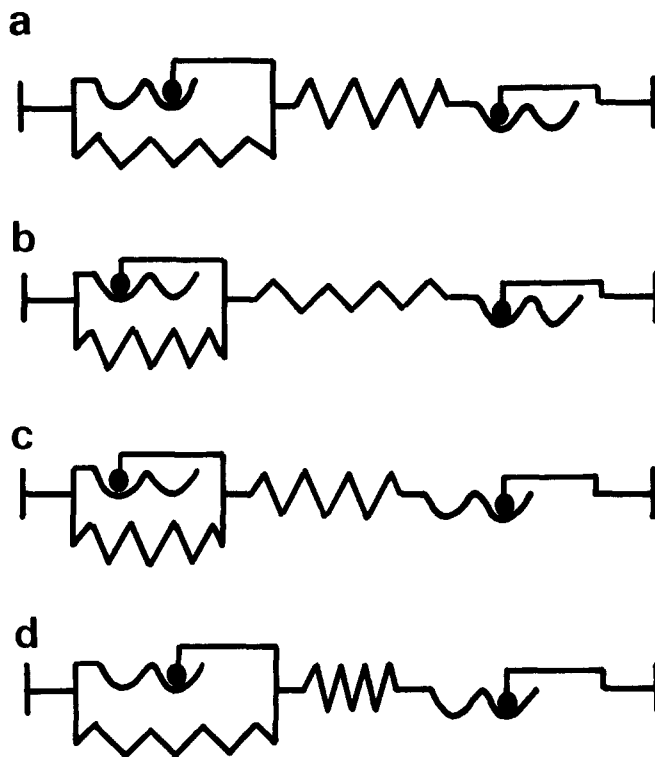
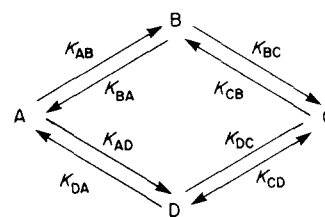


Figure 8 Illustration of various states of the four-state model

and externally relaxed. A transition from state A to C can also be realized, though with much lower probability, through intermediate state D, which is both internally and externally stressed.

To relate the behaviour of this model to the phenomena taking place in an oriented polymer sample when heated up at constant length we can consider the state A of the model as representing the local situation in the oriented glassy polymer (the initial state), states B and D as intermediate states contributing to the externally observable stresses of shrinkage and state C as final internally and externally relaxed state. The transition from state A to C can then be described as a reaction of the type



the kinetics of which is described by a set of differential equations.

$$\begin{aligned} \frac{dn_a}{dt} &= -n_a(K_{AB} + K_{AD}) + n_b K_{BA} + n_d K_{DA} \\ \frac{dn_b}{dt} &= n_a K_{AB} - n_b(K_{BA} + K_{BC}) + n_c K_{CB} \\ \frac{dn_c}{dt} &= n_b K_{BC} - n_c(K_{CB} + K_{CD}) + n_d K_{DC} \\ \frac{dn_d}{dt} &= n_a K_{AD} + n_c K_{CD} - n_d(K_{DA} + K_{DC}) \end{aligned} \quad (1)$$

where the numbers of elements in states A, B, C and D are described by n_a , n_b , n_c and n_d respectively which satisfy the condition

$$n_a + n_b + n_c + n_d = 1 \quad (2)$$

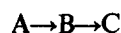
Constants K_{ij} are temperature dependent transition rates related to the height of potential barriers modified by external and internal stresses in model elements.

The elements have to be connected to each other which in the simplest cases can be realised by a parallel or series connection. In both such simple cases the external stress generated by the assembly of elements will depend on the population of states B and D

$$\sigma = (n_b - n_d)\sigma_0 \quad (3)$$

where σ_0 is the stress related to extension of spring S_1 from site 1 to 2 or to extension of spring S_2 from site 3 to 4 which are assumed to be equivalent in the considerations leading to the above equation.

Both the parallel and series models can be described by the set of equations (1) and (2) but the rate constants for the two cases are different. In the series model the stress on spring S_2 will change during the reaction which will involve dependence of the rate constants on the population of states B and D. This makes the solution of this kinetic problem very complex and analytically impossible. As an illustration of the properties of the model we will only present here a numerical solution of the most simplified case. At first we consider a parallel connection of the elements in which a one-way reaction proceeds from state A to C through the intermediate state B



Such a simplification is justified because the reaction through the intermediate state D is much less probable. In such a case the set of equations (1) reduces to

$$\begin{aligned} \frac{dn_a}{dt} &= -n_a K_{AB} \\ \frac{dn_b}{dt} &= n_a K_{AB} - n_b K_{BC} \end{aligned} \quad (4)$$

$$\frac{dn_c}{dt} = n_b K_{BC}$$

and the condition (2) reduces to $n_a + n_b + n_c = 1$. On the assumption that both of the two-site elements in the model are identical the rate constants can be defined as follows¹⁷

$$K_{AB} = K_{BC} = A \exp\left(-\frac{\Delta F - \sigma_0 V \Delta \epsilon}{kT}\right) \quad (5)$$

Where A is a constant and the exponent define the heights the potential barriers dependent on the Helmholtz free energy contour ΔF for the local rearrangement and on the mechanical energy component determined by the internal stress σ_0 , the activation volume V and the local strain change $\Delta \epsilon$ related to the rearrangement.

Assuming a constant heating rate $dT/dt = 1$, the heights of energy barriers $\Delta F = 73kT_0$, and the mechanical energy component $\sigma_0 V \Delta \epsilon = 3.7kT_0$ the set of equations (4) has

been solved numerically under the initial conditions of $n_a = 1$ and $T_0 = 273$ K. Figure 9 shows the calculated populations of states as a function of temperature. Considering the fact that externally detectable stress in the case considered is proportional to the population of state B (equation (3) with $n_d = 0$), the shape of the temperature dependence of n_b can be regarded as a qualitative illustration of the stress of shrinkage as a function of temperature under conditions of constant heating rate. A comparison of the plot of n_b vs. temperature (Figure 9) with the dependence of shrinkage stress on temperature observed for non-annealed polycarbonate sample PC1 (Figure 2) shows a good qualitative agreement.

The influence of the mechanical energy component on the course of n_b vs. temperature is illustrated in Figure 10. A comparison of the dependences of n_b vs. temperature for parallel and series connections of elements in the model is shown in Figure 11. In the case of the series model the calculations were performed assuming the rate constants being dependent on the population of state B

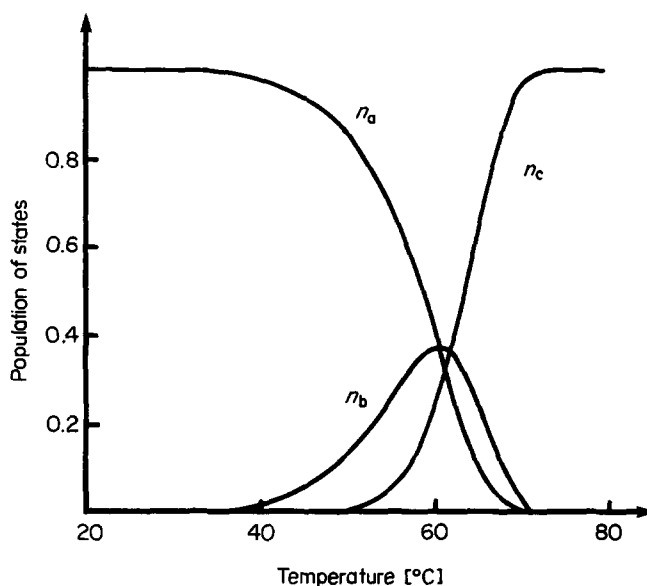


Figure 9 Calculated populations of states in the model of the $A \rightarrow B \rightarrow C$ type of reaction for parallel connection of elements

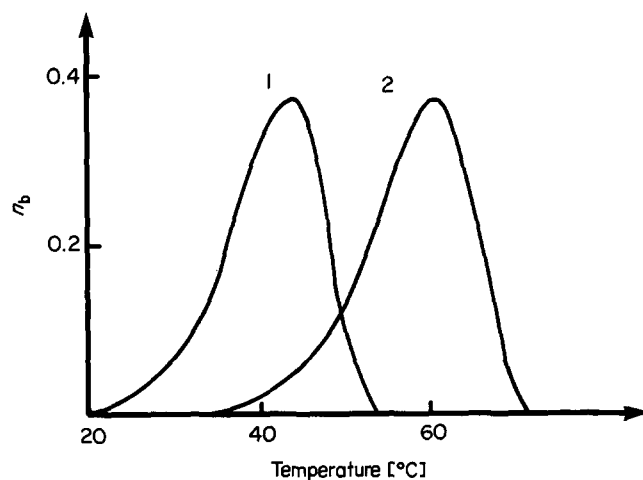


Figure 10 Illustration of the influence of mechanical energy contribution on the population of state B in the model of the $A \rightarrow B \rightarrow C$ type of reaction for parallel connection of elements: $E = \sigma_0 V \Delta \epsilon$; (1) $E = 7.3 kT_0$, (2) $E = 3.7 kT_0$

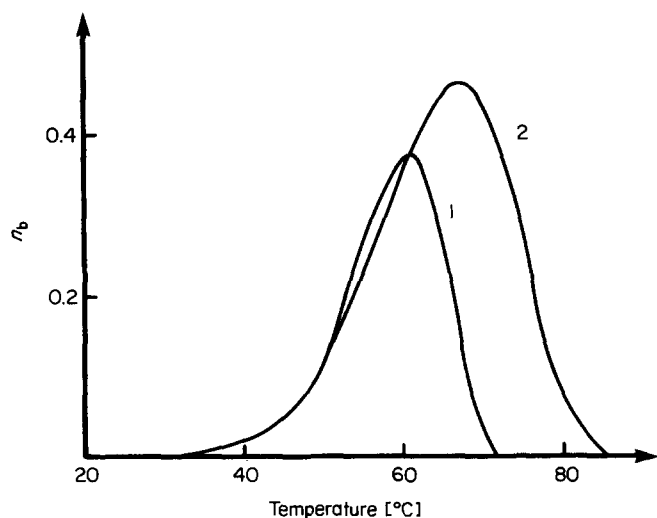


Figure 11 Comparison of n_b vs. T dependences predicted by the (1) parallel and (2) series models

$$K_{AB} = A \exp\left(-\frac{\Delta F - (1 - n_b)\sigma_0 V \Delta \varepsilon}{kT}\right) \quad (6)$$

$$K_{BC} = A \exp\left(-\frac{\Delta F - n_b \sigma_0 V \Delta \varepsilon}{kT}\right)$$

and the numerical values of the quantities appearing in the above equations are the same as for the parallel model. In all cases the constant $A = 10^{22}$ was assumed.

All these results show that the model introduced can describe the temperature dependences of shrinkage stresses influenced by the parameters characterizing the initial, oriented state.

It is clear that these simple cases of the model considered here cannot be used for the quantitative adjustment of the calculated dependences to the observed ones. At this stage, however, the model introduced explains the observed temperature dependences of shrinkage stresses for initially oriented amorphous polymers. For more complex cases the model should consider multiple transitions, distribution of local stresses and shapes of potential barriers as well as various connections of elements in an assembly. The model will be discussed in greater detail in subsequent papers.

Finally it has to be noted that the model introduced in this paper can be applied for the description of shrinkage. Under the conditions at which shrinkage is observed, i.e. under zero external stress, the series model will behave in the same way as the model proposed by Tanabe and Kanetsuna and successfully applied for the description of shrinkage in amorphous polystyrene⁹.

CONCLUSIONS

The experimental results presented in this paper show that thermally stimulated shrinkage forces are observed for all oriented polymer samples and are sensitive to the type of polymer being investigated as well as to its structural state determined by previous thermal or mechanical treatment.

A discussion of the mechanism of the appearance of shrinkage stresses in amorphous polymers leads to the conclusion that it is a highly cooperative process involv-

ing disruption of intermolecular interactions due to internal stresses of elastic chains frozen-in in their extended state. It was shown that the two-state model applied for the description of shrinkage is not directly applicable to the description of shrinkage forces. A four-state model is proposed for the description of shrinkage forces in amorphous oriented polymers. The present analysis of the model is very simplified but it shows that this model can provide a tool for more refined investigations.

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APPENDIX

Derivation of the equation (3)

Parallel connection of model elements in constant length conditions. In the parallel connection of N elastic elements each element acts independently with a force $+F_0$, in state B or $-F_0$ in state D. If N_B and N_D are the numbers of elements in states B and D respectively, the total external force exerted by the parallel connection is given by the equation

$$F = N_B F_0 - N_D F_0$$

The cross-section of such a connection

$$S = N S_0$$

where S_0 is a cross-section of each element. External stress

$$\sigma = \frac{F}{S} = \left(\frac{N_B}{N} - \frac{N_D}{N}\right) \frac{F_0}{S_0} = (n_b - n_d) \sigma_0$$

Series connection in constant length conditions. In a series connection of N elastic elements a force (or a stress) is the same on each element and is equal to the external force (or external stress). If one element shrinks by α due to passing from state A to state B (it means that α is the distance between points 1 and 2 (Figure 7)) then the

change of the length of each spring S_2 is α/N if all the springs S_2 are identical. In the same way if one element extends by α due to passing from A to D (α is also the distance between points 3 and 4) the elongation of each spring S_2 in series connection is $-\alpha/N$. The total change of the length of each spring S_2 is

$$\Delta l = N_B \frac{\alpha}{N} - N_D \frac{\alpha}{N} = (n_b - n_d)\alpha$$

for N_B elements occupying state B and N_D elements in state D. If l_0 is the initial length and E is the Young's modulus of each spring S_2 then

$$\frac{\Delta l}{l_0} = (n_b - n_d) \frac{\alpha}{l_0}$$

$$\sigma_0 = E \frac{\alpha}{l_0}$$

$$\sigma = E \frac{\Delta l}{l_0}$$

and by combination of these equations equation (3) can be easily obtained.

Derivation of the equation (6)

Energetical barriers between the states are decreased by the value proportional to the external stress on particular element for jumps $A \rightarrow B$ and $B \rightarrow C$. In the case of parallel connection each element acts independently so K_{AB} and K_{BC} do not depend on external stresses. If the initial stress on the spring S_1 before the $A \rightarrow B$ jump and the initial stress on the spring S_2 before the $B \rightarrow C$ jump are equal to σ_0 then K_{AB} and K_{BC} are given by equation (5) for parallel connection of the elements.

In the case of series connection the stress is the same on each element and equal to the external stress σ .

The initial stress on S_1 before the $A \rightarrow B$ jump is $\sigma_0 - \sigma$ and the initial stress on the spring S_2 is σ before the $B \rightarrow C$ jump. In this way the change of Gibbs free energy

$$\Delta G_{AB} = \Delta F - (\sigma_0 - \sigma)V\Delta\varepsilon \quad \Delta G_{BC} = \Delta F - \sigma V\Delta\varepsilon$$

According to the equation (3) for $n_d = 0$

$$\sigma = n_b \sigma_0$$

and

$$\Delta G_{AB} = \Delta F - (1 - n_b)\sigma_0 V\Delta\varepsilon \quad \Delta G_{BC} = \Delta F - n_b \sigma_0 V\Delta\varepsilon$$

$$K_{AB} = A \exp\left(-\frac{\Delta G_{AB}}{kT}\right) \quad K_{BC} = A \exp\left(-\frac{\Delta G_{BC}}{kT}\right)$$