

Recovery of compressive strain in atactic polystyrene

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Atactic polystyrene rods were compressed in an Instron universal testing machine to about 35% strain and then annealed near the glass transition temperature, T_g , (100°C) in a thermal mechanical analyser. The change of length during annealing was recorded and the compressive strain was found to recover obeying second-order kinetics at least during the later part of recovery. The activation enthalpy obtained from the temperature dependence of the second-order rate constant varied from 126 to 260 kcal mol⁻¹ as the annealing temperature decreased from 112 to 94°C. These activation enthalpies are attributed to the diffusion of positive or negative defects or configurations which annihilate during recovery. While these activation enthalpies agree with the findings of Andrews on retraction of hot-stretched filaments, they differ considerably from the spectrum obtained by Kimmel and Uhlmann using the data from Andrews' work. The reason for such differences is discussed.

1. Introduction

In 1955, Andrews [1] carried out retraction measurements on two polystyrene filaments with different degrees of orientation. The time needed to reach the same percentage of length recovery were plotted logarithmically against reciprocal absolute temperature. Values of the activation energies, calculated from the slopes of the curves, were a function of both the length (or time) and temperature. The activation energy increased with time (or per cent recovery) but tended to approach a final constant value. Such final activation energy increased from 130 to 220 kcal mol⁻¹ (or 116 to 217 kcal mol⁻¹ for another filament) as the temperature decreased from 95 to 80°C.

In 1971, Kimmel and Uhlmann [2] analysed the data obtained by Andrews, using a modified analysis similar to that used by Primak [3, 4]. The recovery process was considered to consist of many processes with a distribution of activation energies. An approximation was introduced so that the activation energy spectrum could be obtained from experimental information. By using the retraction data of Andrews, they obtained a

spectrum of activation energies covering the range of 15 to 35 kcal mol⁻¹, which were much smaller than Andrews' results.

Recently, Li [5] reported second-order kinetics in the later part of recovery of shear strain of the coarse shear band in polystyrene. An activation enthalpy of 160 kcal mol⁻¹ in the temperature range from 102 to 112°C was obtained. Second-order kinetics were also found to be valid for the indentation recovery of polystyrene [6]. The activation enthalpy in a temperature range from 98 to 108°C was 163 kcal mol⁻¹.

It is the purpose of this research to study compressive strain recovery in atactic polystyrene over a wide temperature range, and to compare the activation enthalpy values with those obtained by Andrews and Kimmel and Uhlmann and also with those obtained from shear band and indentation recovering studies.

2. Experimental details

2.1. Sample preparation

Atactic polystyrene was obtained from the Westlake Company in the form of sheets of thick-

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ness 0.25 inch. The glass transition temperature of the polystyrene was 100°C . Samples of size $70\text{ mm} \times 8\text{ mm} \times 6\text{ mm}$ were cut from the sheet and annealed at 115°C in air for 20 h and oven-cooled to room temperature. They were ground on a sand wheel into roughly cylindrical shapes and then machined into rods of about 6 mm diameter which were annealed again at 115°C for 10 h and oven-cooled to room temperature. These rods were machined in a lathe to 3.8 mm diameter and cut and machined again into cylinders of length about 5.5 mm. Great caution was exercised to keep the end surfaces parallel. Shorter disc-shaped samples of thickness 1.1 mm and diameter 3.8 mm were also prepared by sectioning in a diamond saw, grinding on 600 grit emery paper and polishing with $1\text{ }\mu\text{m}$ and $0.05\text{ }\mu\text{m}$ alumina slurries. All these samples were put into a furnace, maintained at 115°C for 15 min and then quenched in air. The purpose of quenching was to promote formation of fine shear bands in subsequent compression [7] so that large strains could be sustained without failure.

These samples were compressed in an Instron universal testing machine with a cross-head speed of 0.001 mm sec^{-1} . The compression strains were about 35%.

2.2. Apparatus

A Perkin-Elmer TMS-1 thermal mechanical analyser was used to anneal the samples and to monitor their dimensional changes during annealing. The operation of the TMS-1 is described schematically in Fig. 1. The sample is placed on the bottom of a quartz sample tube. A quartz probe for sensing the sample length (or thickness) is attached to the core of a linearly variable differential transformer (LVDT). Any change in the sample length or in the position of the core results in a measurable change in the electrical output from the transformer. The top of the probe assembly has a weight tray which is supported by a plastic float rigidly fixed to the probe and immersed in a fluocarbon fluid. In this experiment, a small load of 1.7 g on the weight tray is required to balance the buoyant force on the float. The advantage of this float arrangement is that, since there is almost no load on the sample, creep during the recovery experiment is avoided. The probe and the sample tube are both made of fused quartz so that thermal expansion is minimized. The temperature is measured by a K-type thermo-

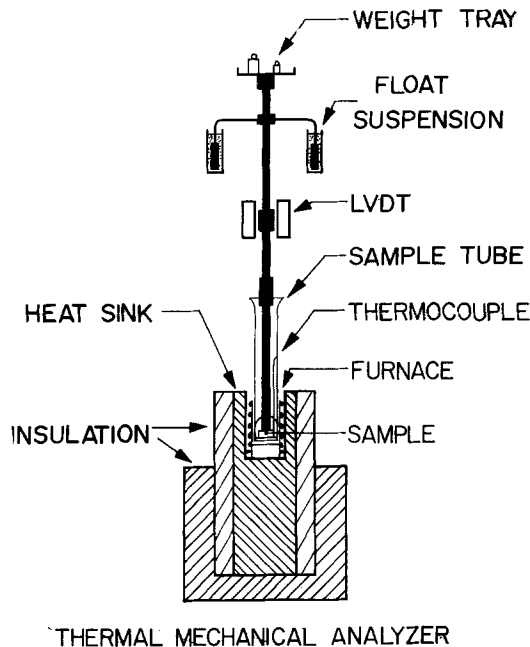


Figure 1 Schematic diagram of the thermal mechanical analyser.

couple with stainless steel sheath (of outside diameter 0.5 mm). The thermocouple is placed next to the sample in the sample tube. Since the furnace is open at the top, there is a temperature gradient of about $0.33^{\circ}\text{C mm}^{-1}$ in the tube.

2.3. Experimental procedure

At the start of a recovery experiment, the temperature of the furnace was first set at a predetermined value. The furnace assembly was lowered to expose the sample tube. The sample was positioned in the tube and the quartz probe was placed on the sample. A dual-channel recorder was used to record both the sample displacement and the temperature simultaneously. Initially, the recorder was set in the 10 mV range.

The furnace was then raised to its operating position. The time required for the sample to reach the equilibrium temperature was about 10 to 15 min. The recovery data obtained during this period of time was discarded. During annealing, the deformed sample gradually recovered its length. The recorder voltage-range sensitivity was increased as the sample recovery slowed, and hence the rate of change in voltage decreased. In the 2 mV range, the smallest division (0.02 mV) on the chart paper corresponds to a displacement of 0.0005 mm in the LVDT.

The temperature range used was from 94 to

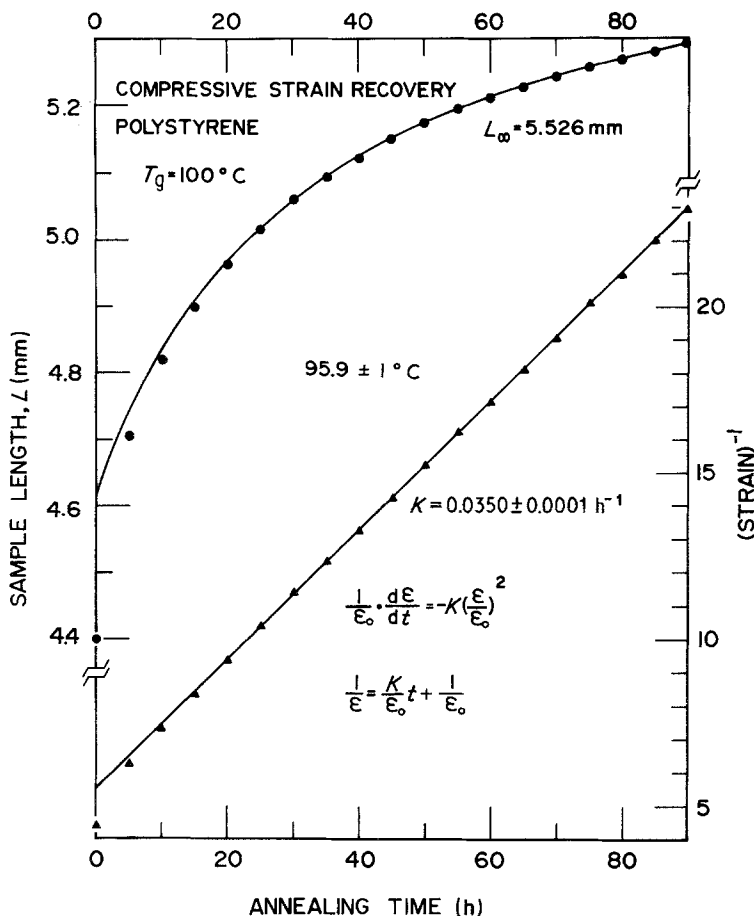


Figure 2 Variation of sample length with annealing time and the demonstration of second-order kinetics.

112°C. Above 112°C, most of the strain would be recovered before the sample reached its equilibrium temperature. Below 94°C, the recovery rate was too slow to study its kinetics.

After annealing, the furnace was lowered again to expose the sample and an extra weight of 0.5 g was put onto the weight tray to ensure that the probe-sample contact was maintained as the sample was shrinking upon cooling. After the sample had reached room temperature, it was removed from the sample tube and its thickness measured again by a micrometer with 1 μm accuracy. The change in sample thickness corresponded to the change in millivolts of LVDT. This calibration was employed to calculate the sample length at any time, t , at the annealing temperature.

3. Experimental results

As reported before [7], compression of atactic polystyrene produces coarse or fine shear bands or both. In this experiment, the strain rate was low (0.0002 sec^{-1}) and the sample was quenched

from 115°C. Both factors made fine bands the major contributor to the compressive strain [7]. After deformation, a certain amount of cold work [8] was stored inside the material which provided the driving force for dimensional recovery.

The sample length, L , was plotted against the annealing time, t , as shown in Fig. 2. It is seen that the recovery rate of the sample length was extremely high in the beginning and gradually decreased with time. The compressive strain, ϵ , is given by $\ln(L_\infty/L)$, where L_∞ is the final sample length. Since it was impractical to measure L_∞ , the quantity L_∞ was left as an adjustable parameter. By a trial-and-error method, an appropriate value of L_∞ could be selected such that the reciprocal of strain, ϵ^{-1} , varied linearly with annealing time at least for the later part of recovery. Such a behaviour suggested the applicability of second-order kinetics consistent with a mechanism involving the motion and annihilation of defects or configurations of opposite signs.

TABLE I Effect of initial strain on the second-order rate constant, k

Initial Strain, ϵ_0	Rate constant, $k(\text{h}^{-1})$	Temperature, $T(^{\circ}\text{C})$
0.102	0.376 ± 0.014	99.4
0.155	0.415 ± 0.017	99.4
0.186	0.478 ± 0.023	99.5
0.213	0.536 ± 0.028	99.3
0.254	0.383 ± 0.015	99.4
0.266	0.433 ± 0.019	99.4
0.270	0.430 ± 0.015	99.3
0.297	0.539 ± 0.029	99.5
0.300	0.523 ± 0.027	99.4

The defect concentration was assumed to be proportional to ϵ/ϵ_0 , where ϵ_0 was the strain at time $t = 0$. With this assumption, the second-order rate equation is

$$\frac{1}{\epsilon_0} \frac{d\epsilon}{dt} = -k \left(\frac{\epsilon}{\epsilon_0} \right)^2 \quad (1)$$

or

$$\frac{1}{\epsilon} = \frac{k}{\epsilon_0} t + \frac{1}{\epsilon_0}, \quad (2)$$

where k is proportional to the second-order rate constant and is independent of ϵ_0 . The applicability of these equations was confirmed by the following experiment. Samples with different initial strains, ϵ_0 , were annealed at the same temperature. The values of k did not show any consistent change with respect to ϵ_0 , as shown in Table I. The average value of rate constant, k , at a temperature of 99.4°C , was found to be, from Table I, equal to $0.457 \pm 0.064 \text{ h}^{-1}$.

In the beginning of recovery, the data did not follow second-order kinetics. This could be explained by the possible inhomogeneous distribution of defects inside the sample during deformation.

As mentioned earlier, a sample reached its equilibrium temperature in 10 to 15 min. As a result, there was no way of exactly determining the starting time, t_0 . Hence, it was difficult to obtain the intercept $1/\epsilon_0$ at $t = t_0$ in a plot of $1/\epsilon$ against t . However, the following lower and upper bounds could be established:

(a) $1/\epsilon_0$ should not be smaller than $1/\epsilon_1$, where $\epsilon_1 = \ln(L_{\infty}/L_1)$, with L_1 being the initial sample length before recovery, corrected for thermal expansion;

(b) For lower annealing temperatures (94 to 102°C), second-order kinetics started from

about 40% of ϵ_1 . Hence $1/\epsilon_0$ should not be larger than $1/(0.4\epsilon_1)$.

With the help of these two limits, it was possible to reduce the uncertainty for k to about $\pm 40\%$ at annealing temperatures higher than 103°C . At lower temperatures, such as 94°C , the uncertainty was only about 0.1%. At 99°C , the uncertainty was about 5%, as shown in Table I.

Fig. 3 shows the relation between L and t for various annealing temperatures. Their respective $1/\epsilon$ against t plots are shown in Figs 4 and 5. The temperature dependence of these rate constants is shown in Fig. 6. The error bars were larger than had been expected and several short samples (1.1 mm thick) were prepared and subjected to the same treatment; their rate constants were also included in Fig. 6. The agreement between the two sets of data seems satisfactory. The activation enthalpy as shown in Fig. 7 was a function of temperature, being higher at lower temperatures.

Also included in Fig. 7 are the apparent activation enthalpies obtained by Andrews [1] who plotted the logarithm of time needed to retract orientated polystyrene filaments to the same length at different temperatures. The activation enthalpies were found to change with length but reach plateau values at short lengths. The plateau values varied with temperature as shown in Fig. 7 in a similar way to the results found in this work. Also included in Fig. 7 are the activation enthalpies found in shear band recovery [5] and indentation recovery [6] in the respective temperature ranges covered. The activation enthalpies obtained by Karam *et al.* [17] on creep are also shown for comparison.

4. Discussion

The second-order kinetics observed in this work implies that defects of opposite signs, created by deformation, annihilate each other during recovery. Such kinetics and defect mechanisms have been also observed in crystalline materials such as LiF and metals [15]. The activation enthalpy obtained from the temperature dependence of the second-order rate constants agrees well with the results of Andrews [1] both in magnitude and its variation with temperature, as shown in Fig. 7. Furthermore, the activation enthalpy values agree with those obtained in indentation recovery and in the recovery of shear bands, also by using second-order kinetics in both recovery measurements.

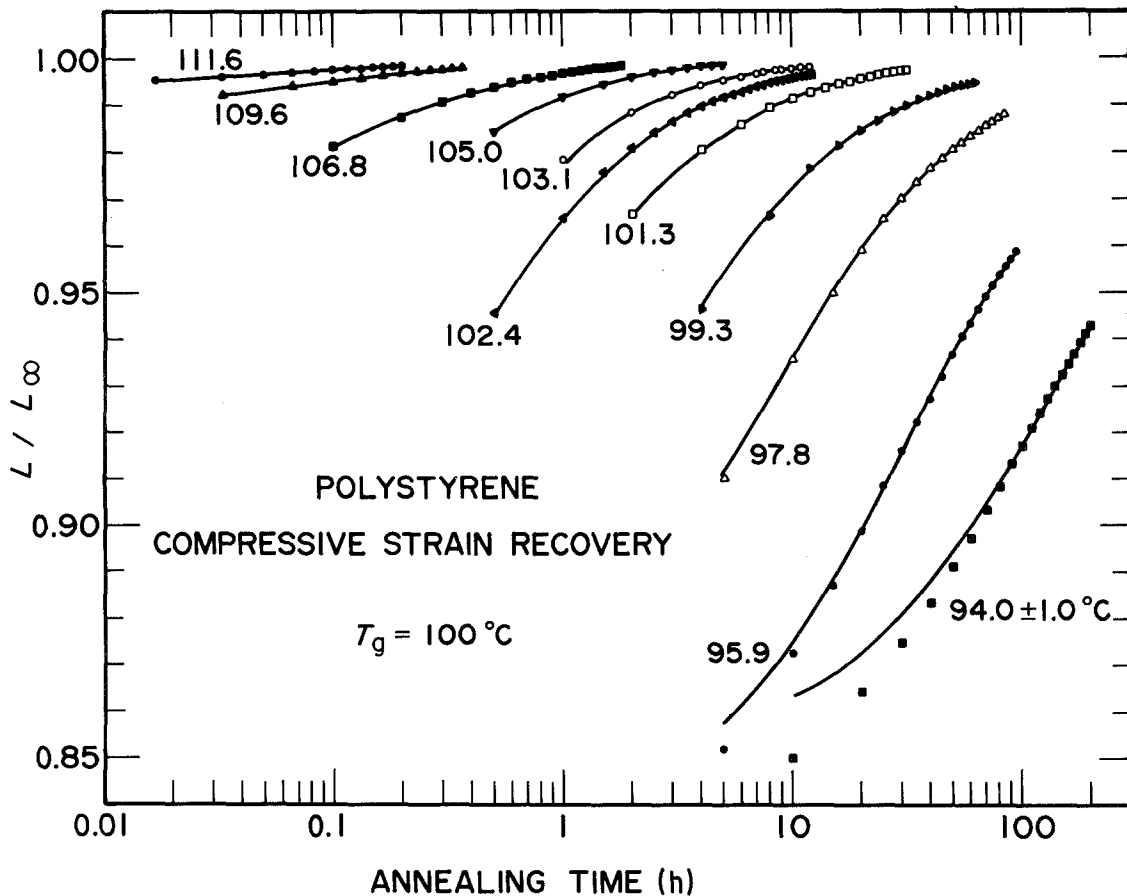


Figure 3 Variations of sample length at various temperatures.

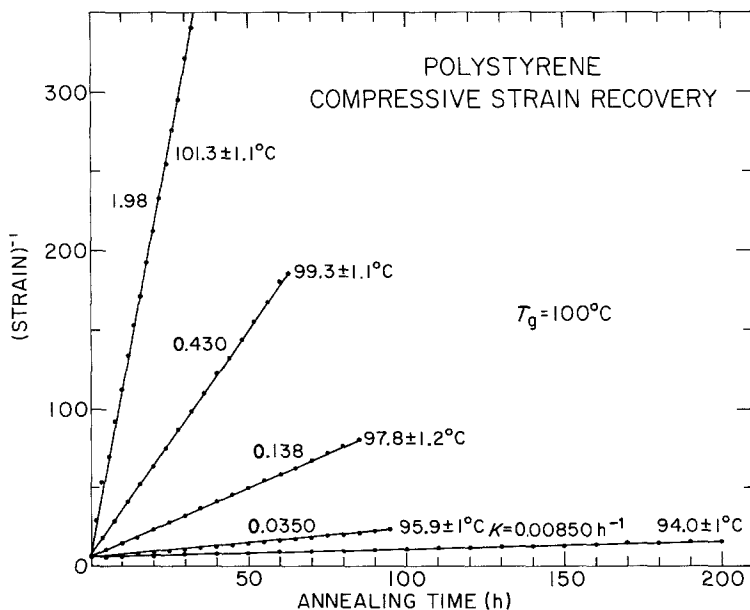


Figure 4 Second-order kinetics from 95.9 to 101.3 °C.

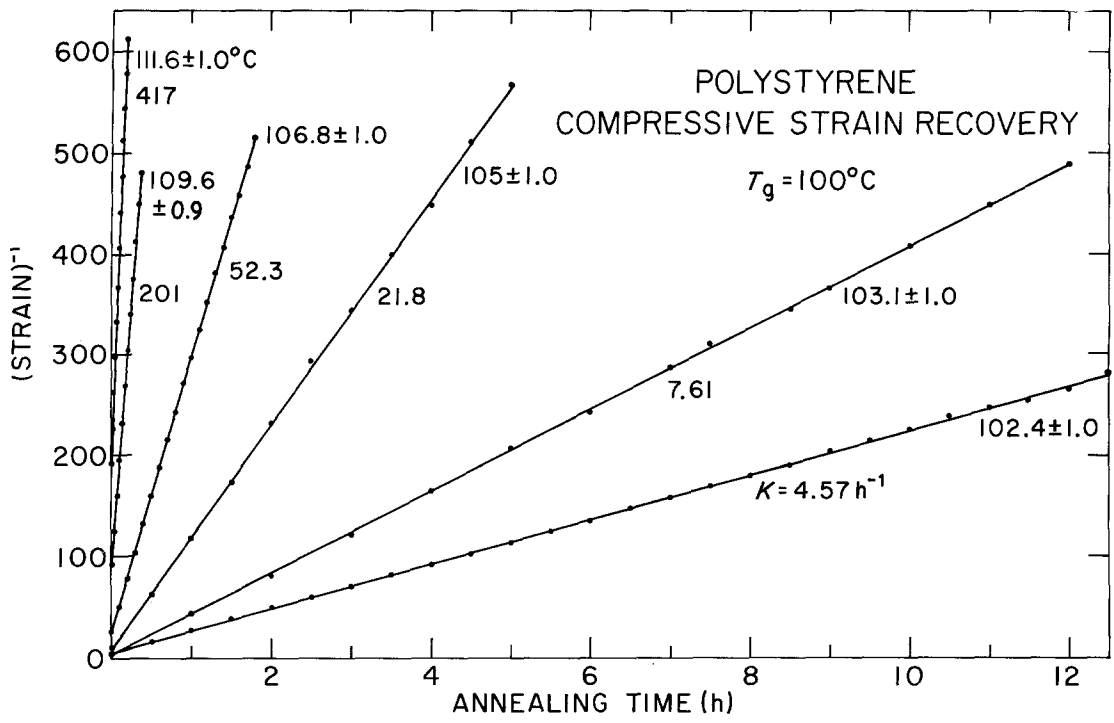


Figure 5 Second-order kinetics from 102.4 to 111.6° C.

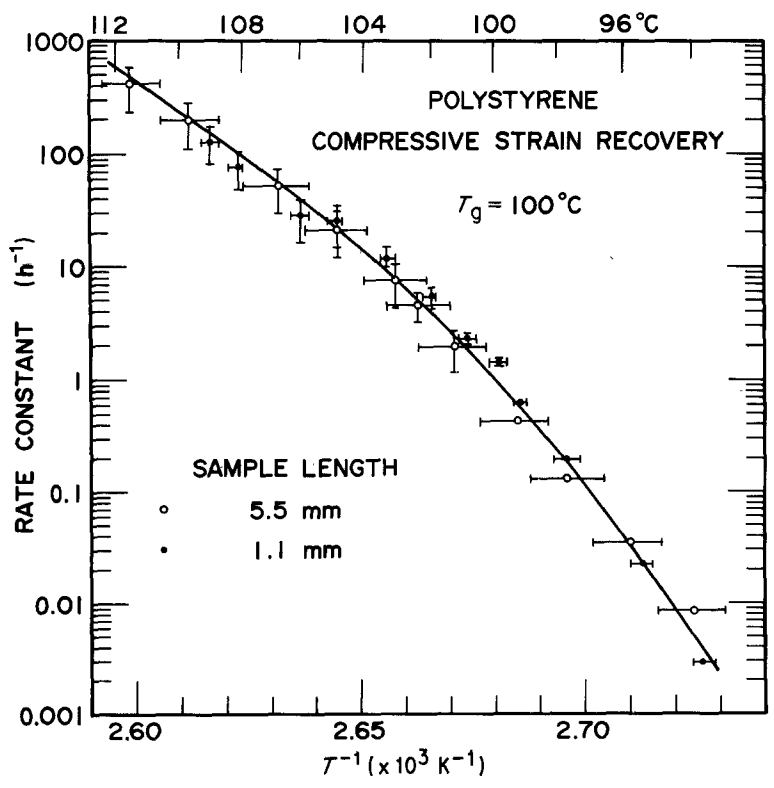


Figure 6 Second-order rate constants plotted against reciprocal absolute temperature.

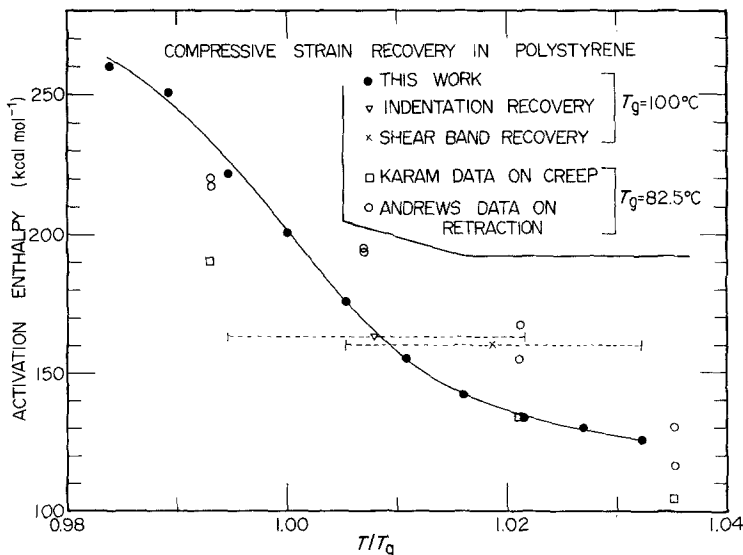


Figure 7 Temperature dependence of activation enthalpy for compressive strain recovery in polystyrene.

However, these activation enthalpies differ considerably from those values obtained by Kimmel and Uhlmann [2], of 15 to 35 kcal mol⁻¹, using the data of Andrews. It is attempted to seek the reason for such differences and to discuss the probable validity of the conflicting values obtained by different workers.

4.1. Primak analysis

Kimmel and Uhlmann [2] used a modified analysis similar to that used by Primak [3, 4] for multiple recovery processes distributed in activation enthalpy. A brief account of such an analysis is given in the following. Let the reduction in concentration of some species, q , take place by a first-order process with an activation energy, E , such that

$$-\frac{d(\ln q)}{dt} = A \exp\left(-\frac{E}{RT}\right), \quad (3)$$

where t is the time, A is a frequency factor, R is the gas constant and T is the temperature. Many such processes with different E values are taking place simultaneously. Whilst the value of q may not be directly measurable, it is assumed that a property, p , which is proportional to q , such as the strain, can be measured. For each species, the variation of concentration with time can be obtained by integrating Equation 3. Let $p(E, t)$ be the distribution function at any time t so that the measurable macroscopic property P is

$$P(t) = \int_0^\infty p(E, t) dE, \quad (4)$$

where

$$p(E, t) = p_0(E)\theta(E, t) \quad (5)$$

and

$$\theta(E, t) = \exp[-At \exp(-E/RT)], \quad (6)$$

where $p_0(E)$ is the distribution at $t=0$ and the frequency factor A is assumed to remain constant and have the same value for all the processes.

The function θ varies from $\exp(-At)$ at $E=0$ to unity at $E=\infty$. Its partial derivative with E , or θ' , is $-(\theta \ln \theta)/RT$ which has a maximum value of $1/eRT$ at $\theta = 1/e$ or $E = E_0 = RT \ln(At)$. As time increases, its variation with E remains the same since θ' is independent of t at the same θ . At constant E the time derivative of θ , $\dot{\theta}$, is $(\theta \ln \theta)/t$ so that $\dot{\theta} = -RT\theta'/t$. The time variation of P as given by Equation 4 is therefore

$$\dot{P}(t) = -\frac{RT}{t} \int_0^\infty p_0(E)\theta'(E, t) dE. \quad (7)$$

Since the integral of $\theta' dE$ is $1 - e^{-At}$, or almost unity for large t , and since θ' is appreciable only when $E \approx E_0$, the integral in Equation 7 can be approximated by the value of p_0 at E_0 . Hence for a "zeroth"-order approximation the activation energy distribution $p_{00}(E_0)$, is

$$p_{00}(E_0) = -\frac{1}{RT} \frac{dp}{d(\ln t)}, \quad (8)$$

where $E_0 = RT \ln(At)$. The rate average of activation energy at time t is $E_0 + \gamma RT$ where $\gamma = 0.577 \dots$ is Euler's constant. But, in view of the approximation of Equation 8, γRT can be ignored for the present discussion.

To obtain the activation energy distribution using Equation 8 the value of A has to be found. By assuming that the distribution remains the same between two temperatures, T_1 and T_2 , the two times t_1 and t_2 for the same p_{00} must be such that E_0 is the same; A can then be obtained from

$$T_1 \ln(At_1) = T_2 \ln(At_2). \quad (9)$$

With this value of A , Equation 8 gives the distribution which Kimmel and Uhlmann [2] applied to the data obtained by Andrews [1].

For processes of higher order the function θ is more complicated. Primak [3] suggested that a similar approximation can be made so that Equation 8 is still applicable if, within the θ expression, the variation of $p_0(E)$ with E is ignored.

4.2. Kimmel-Uhlmann spectra

In analysing the data obtained by Andrews [1], Kimmel and Uhlmann [2] did not explain how they obtained their value of A of $10^{7.44} \text{ sec}^{-1}$. It turns out that they used the same value of A as the one they obtained [11] from the volume relaxation data of Kovacs [12]. For such data the value of A was chosen so that the spectra obtained in the temperature range from -9 to 70°C superposed. However, the same A value did not cause the high temperature data to superpose. Since, in the work of Kovacs, polystyrene was quenched to different temperatures and relaxed at those temperatures, the total volume change was different at different temperatures. Thus, the activation energy spectra may not be the same. On the other hand, the filaments tested by Andrews [1] (Sample numbers 3 and 7) were all stretched at 104°C for 118% and quenched to 49°C before retraction at different temperatures. It is more likely in each of these cases that the activation energy spectra are the same in the starting condition. Yet they were found to be not superposable and an accurate A value could not be obtained.

In view of the difficulty of obtaining the A values, the spectra obtained by Kimmel and Uhlmann [2] are not very meaningful. Furthermore these spectra are not broad enough to justify the approximation of Equation 8. The spectra half-widths are about 3 to 5 kcal (or about $(4$ to $6)RT$) so that the activation energies are 28.5 ± 5 and $26.5 \pm 4 \text{ kcal mol}^{-1}$ for the No. 3 and No. 7 filaments, respectively, almost describable by a single activation energy for each.

4.3. Single process approach

The second-order kinetics observed in this work indicates the possibility of only one important recovery process with a single activation enthalpy. As pointed out by Kimmel and Uhlmann [9] a spectrum of activation energies can still, even in this case, be obtained using Primak's analysis. Let P be a measured property such as the strain ratio ϵ/ϵ_0 of Equation 1 and let $k = k_0 \exp(-\Delta H/RT)$, where ΔH is the activation enthalpy. Then

$$P^{-1} - P_0^{-1} = k_0 t \exp(-\Delta H/RT). \quad (10)$$

The distribution function p_{00} as represented by Equation 8 has a maximum value at

$$\ln(k_0 P_0 t) = \Delta H/RT. \quad (11)$$

RT), with ΔH being the activation enthalpy. Then the distribution of activation energy E_0 is given by

$$p_{00}(E_0) = \frac{P_0}{RT} \frac{\exp[(E_0 - \Delta H)/RT]}{[1 + \exp(E_0 - \Delta H)/RT]^2}, \quad (12)$$

which is a function that is symmetric about ΔH , as found also by Kimmel and Uhlmann [9]. It is seen that the maximum of p_{00} is a value $P_0/4RT$, and the half-width of the distribution is $3.5RT$; both are dependent on the temperature. Hence, the spectra at different temperatures are not superposable, and so k_0 cannot be obtained by superposition.

Of course, if k is determined by kinetics as has been performed here, ΔH can be obtained from its variation with temperature. Or, in view of Equation 10, t for the same P value must be proportional to $\exp(\Delta H/RT)$; hence the ΔH value can be obtained from the temperature dependence of t , as has been performed by Andrews [1]. In the temperature range in which Equation 12 shows a clear peak, the curve must obey Equation 11 so that both ΔH and k_0 can be obtained from the temperature dependence of peak time. There may be other ways of obtaining ΔH , but it is seen from Equation 12 that an arbitrarily chosen k_0 value can result in an incorrect spectrum with an incorrect peak even for a single second-order process.

Andrews' data [1] were found to obey second-order kinetics, as shown in Figs 8 and 9 for filaments No. 3 and No. 7, respectively. Unfortunately only five rate constants were obtainable since data measured over a long time span were needed for the analysis. Nevertheless, the activation enthalpies, as shown in Fig. 10, appear to

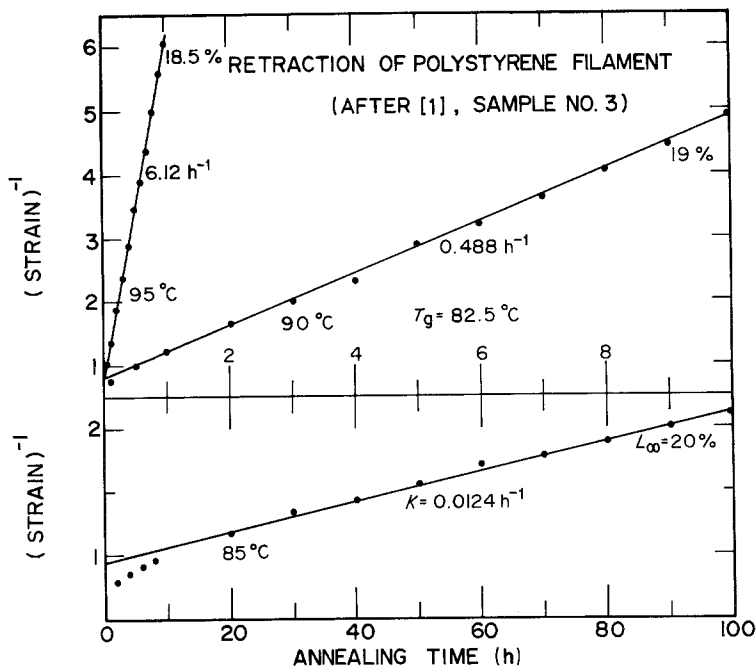


Figure 8 Second-order kinetics for the data of Andrews on the retraction of polystyrene filaments, Sample No. 3.

be reasonable. They are comparable to all the previous results, as shown in Fig. 7.

4.4. Possible microstructural mechanisms

The observed second-order kinetics do not imply a single process even though such a process is possible. There may be several processes which combine together to appear as obeying second-order kinetics. Then the average activation enthalpy (from a

$\ln k$ against $1/T$ plot) may vary with temperature. On the other hand, it is possible that the activation enthalpy for a single second-order process varies with temperature because of rapid structural changes near the glass transition.

It is also possible that other kinetics may fit the data in the early part of recovery which do not seem to follow second-order kinetics. As indicated in Andrews' data the activation enthalpy

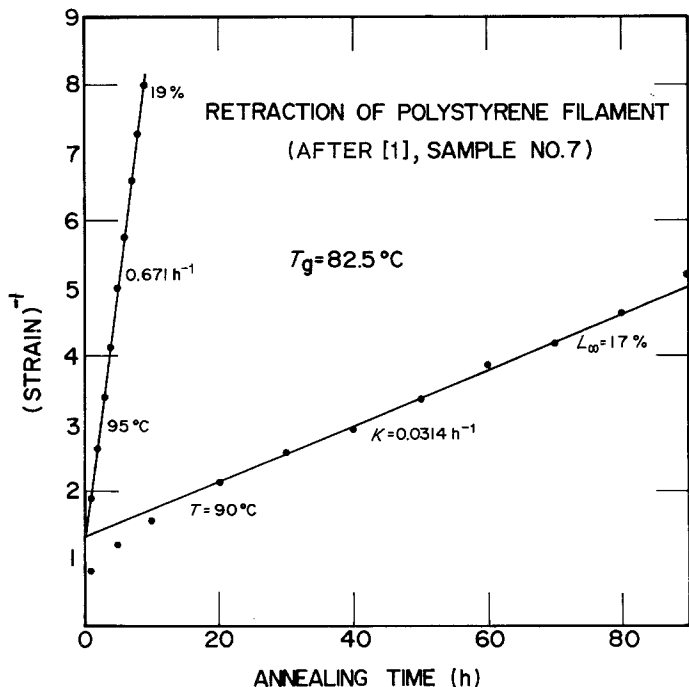


Figure 9 Second-order kinetics for the data of Andrews on the retraction of polystyrene filaments, Sample No. 7.

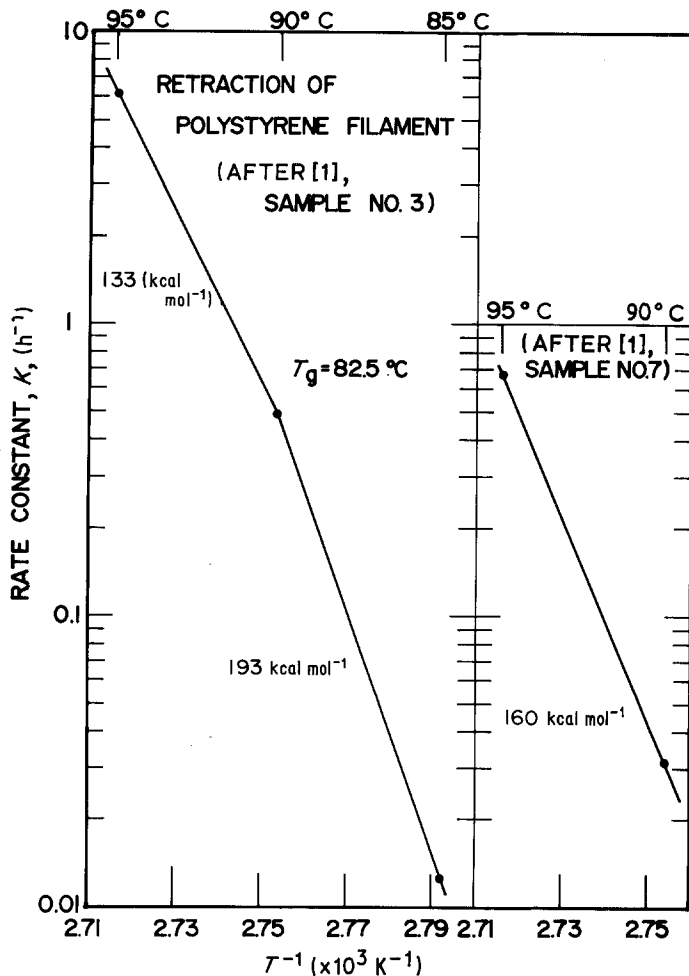


Figure 10 Activation enthalpies for the data of Andrews on the retraction of polystyrene filaments.

may be smaller in the early part of recovery than that in the later part of recovery. However the analysis may not be realistic if the defect as well as temperature distributions are inhomogeneous in the beginning of recovery. These inhomogeneities gradually disappear with increasing time.

Nevertheless, second-order processes do imply that microstructural defects of opposite signs annihilate each other during annealing, in a way similar to crystalline materials [15]. These defects could be dislocation-like displacement inhomogeneities or conformational distortions [16] along molecular chains which are created during deformation and become mobile at the annealing temperature. The motion of these defects may not be easy; it may involve the motion of many atomic groups and their neighbours. Certainly it is conceivable that it should be more difficult than single atomic motion in crystalline solids. Therefore the high activation energy, as shown in Fig. 7, may

be more reasonable than the Kimmel-Uhlmann spectrum in the range 15 to 35 kcal mol⁻¹.

Acknowledgement

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