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Indentation recovery of atactic polystyrene

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Indentations made on the surface of atactic polystryene were annelaed for different lengths of time at various temperatures. The depths of these indentations were measured by using a modified Sloan surface profilometer. The variation of depth with time was found to follow second order kinetics at least for the later part of recovery. The activation energy associated with the second order rate constant was 163 kcal mol^{-1} which is comparable to the value of 160 kcal mol^{-1}, measured in the same material for the recovery of coarse shear bands.

1. Introduction

The application of chemical kinetics to the recovery of crystalline materials is well known. Examples are the annealing of quenched-in vacancies in gold [1] by the use of first order kinetics and the annihilation of dislocation dipoles [2] in LiF by the use of second order kinetics. The latter kinetics were also applied [2] to the recovery of stored energy after deformation [3] and to the rate of recrystallization with simultaneous recovery [4–8].

Dimensional changes during recovery are usually absent for crystalline materials. One exception is the indentation made on a cleaved surface of a zinc single crystal [9] by impacting with a steel ball. The indentation disappeared completely on heating to 400° C. Dimensional changes during the recovery of polymers are common. Examples are nylon [10, 11], poly (ethylene terephthalate) [12–14], polypropylene [15] and polystyrene [16].

However, the kinetics of the recovery of polymers were difficult to deal with. Benbow [17] twisted polyethylene rods and watched the recovery of twist angle as a function of time. If the initial shear strain was less than 0.001, the recovery conformed to Boltzmann's Superposition Principle, but increasing deviation from such principle was observed at large strains. Turner [18, 19] defined a "fractional recovery" (FR) as the strain recovered divided by the creep strain and a "reduced time" (t_R) as the time of recovery divided by the creep time. He found a single relation between FR and t_R for several polymers provided that the maximum creep strain was sufficiently small (0.017, in PVC). Park and Uhlmann [20–22] modified Primak's analysis [23, 24] and assumed the existence of many processes with different activation energies. With several simplifying assumptions they were able to obtain a spectrum of these energies.

Recently, Li [25] reported some annealing experiments of C. C. Chau on the recovery of shear strain in the coarse shear band in polystyrene. Second order kinetics were found to be applicable in the later part of recovery. The rate constant was found to follow the Arrhenius relation with temperature and an activation enthalpy of 160 kcal mol^{-1} was obtained. Similar kinetics were found to be obeyed in the compressive strain recovery of polycarbonate and PMMA [26]. Our preliminary experiments [27] showed that an indentation made by a Knoop hardness tester on the surface of polystyrene could be recovered completely. It is the purpose of this communication to study the kinetics of such recovery and to compare the activation enthalpy with that of shear band recovery in the same material.

2. Experimental details

2.1. Sample preparation

The atactic polystyrene used in this study was obtained from the Westlake Co. in the form of

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0.25 in. thick sheets. Its glass transition temperature was 100° C. A block of material about $11 \times 16\,\text{cm}^2$ was cut from the sheet and annealed at 115° C in air for about 20 h and oven-cooled to room temperature. Samples of $1.2 \times 1.2\,\text{cm}^2$ were then cut from the block and annealed again as previously. The samples were then mechanically ground and polished, first with 1 μm and then with 0.05 μm alumina slurries. These samples were annealed again at 95° C for 15 h and oven-cooled.

The sample was then put in a brass basket and dipped into a silicone oil bath maintained at the same temperature as for later recovery experiments. After 5 min it was removed from the bath, quenched in silicone oil at room temperature, and rinsed with ethanol. This procedure was an attempt to maintain the same quenched state before and after annealing.

2.2. Hardness indentation

To make the indentations, the sample was placed in a Kentron microhardness tester at room temperature. A conical diamond indentor was used with 1200 g weight applied for 30 sec. Three widely separated indentations were made on one sample surface, each of about 20 μm deep and 270 μm diameter. The indentor had a cone angle of 120°, with a 190 μm radius tip.

2.3. Annealing

Annealing was achieved in a glass dewar containing about $1\frac{1}{2}$ qt* silicone oil furnished with a heating coil and a stirrer with adjustible speed. The temperature variation was within ± 0.1° C. Since the sample needed some time (about 5 min) to heat up and cool down, it was necessary to keep the annealing time sufficiently long to reduce uncertainty. The sample had no weight change over a period of 1 day after soaking in the silicone oil bath at 99° C, indicating that the sample did not absorb or dissolve in silicone oil.

2.4. Indentation-depth measurements

The indentation-depth was measured with a Sloan surface profilometer-Dektak as shown in Fig. 1. The Dektak has a diamond stylus of 55° cone angle and 12.5 μm radius tip. The stylus contacted the sample surface with a small load of 50 ± 10 mg. Since the alternation of depth-measurements and sample annealings was practiced, the Dektak was modified to possess the capability of making consistent measurements along the same trace on the sample surface. A thin and light $X-Y$ mechanical stage was designed and equipped with a micrometer head for movements as fine as one micron. Also, an MJ model Olympus microscope situated on a heavy $X-Y$ mechancial stage was utilized to aim at the tip of the conical indentation. A layer of Dykem layout ink was put on the surface of a dummy sample at the fixed position on the light $X-Y$ stage. A scratch was made by the tracing of the stylus and served to align the microscope by matching with the cross-hairs in its eyepiece. Through such a procedure we were able to measure the surface profile along the same trace after every annealing.

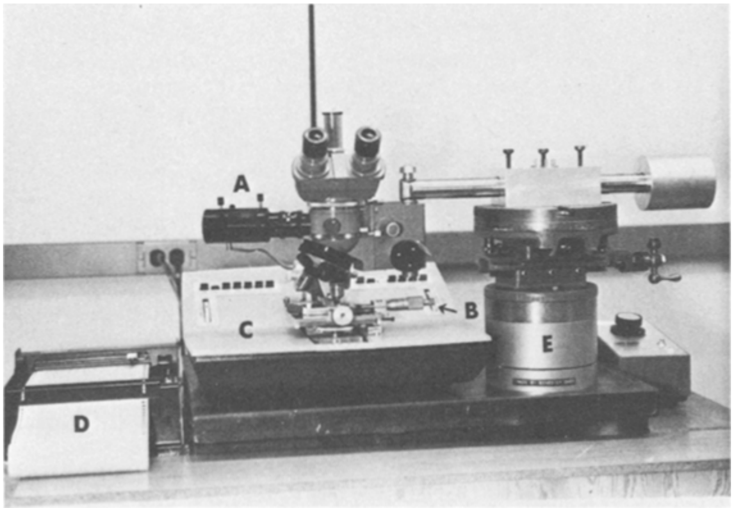

Figure 1 Indentation depth measurement assembly. A, MJ model Olympus microscope; B, light weight $X-Y$ sample stage with micrometer head; C, Dektak; D, recorder; E, heavy duty $X-Y$ mechanical stage to move the microscope.

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*1 qt ≡ 0.9464 litre.

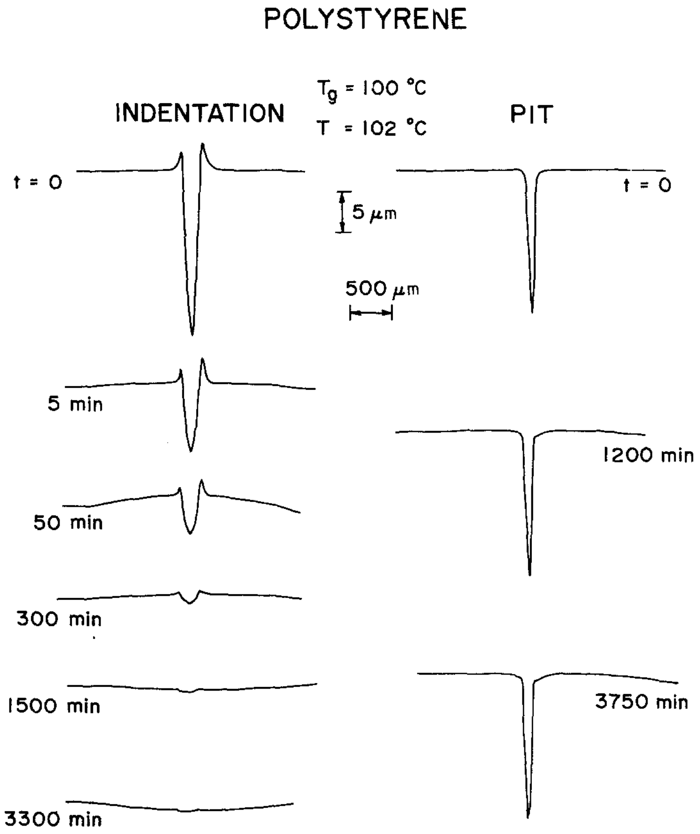

Figure 2 Dektak traces of an indentation and a pit during annealing of polystyrene.

3. Experimental results

As the indentation was created by deformation, a certain amount of cold work was stored around and beneath the indentation. The internal stresses could be revealed in a polarized light. During annealing, such internal stresses gradually disappeared and the shape was also recovered, as shown in Fig. 2. In contrast, a pit of 17.3 µm deep made by drilling and polishing did not change its shape at all after 100 h annealing at 102° C. This comparison ruled out the possibility that surface diffusion was a mechanism for indentation recovery. As mentioned earlier [27], the driving force for the recovery process is the stored energy. A possible mechanism is the motion and annihilation of defects such as the excess volumes [28] of opposite signs introduced during the indentation deformation. Both the indentation depth (h) and its reciprocal were plotted versus the time of annealing as shown in Fig. 3. It is seen that the rate of recovery ($-\,\mathrm{d}h/\mathrm{d}t$) is extremely high in the beginning and gradually decreased with the passage of time. After about 1 h when more than half of the original depth had recovered, the reciprocal of depth (h^{-1}) varied linearly with time for the next 50 h or longer. Such regular behaviour for the later part of recovery strongly suggests the applicability of second order kinetics consistent with a mechanism involving the motion and annihilation of defects of opposite signs.

However, to obtain the second order rate constant, it is necessary to know more about the defect concentration. From our studies of impression creep [29], it is likely that the defect concentration (in crystalline materials these are dislocations) is a constant [30] during steady state creep, independent of the depth of the impression. On the other hand, after recovery, when the indentation disappears, the defect concentration is necessarily zero. Hence it can be assumed that the defect concentration is proportional to h/h_0 where h is the depth at any time t during recovery and h_0 is the depth at $t = 0$ before recovery. Now the proportionality constant should be independent of h_0. With this assumption, the second order rate equation is

$$-\frac{1}{h_0}\frac{\mathrm{d}h}{\mathrm{d}t} = \kappa\left(\frac{h}{h_0}\right)^2 \qquad (1)$$

or

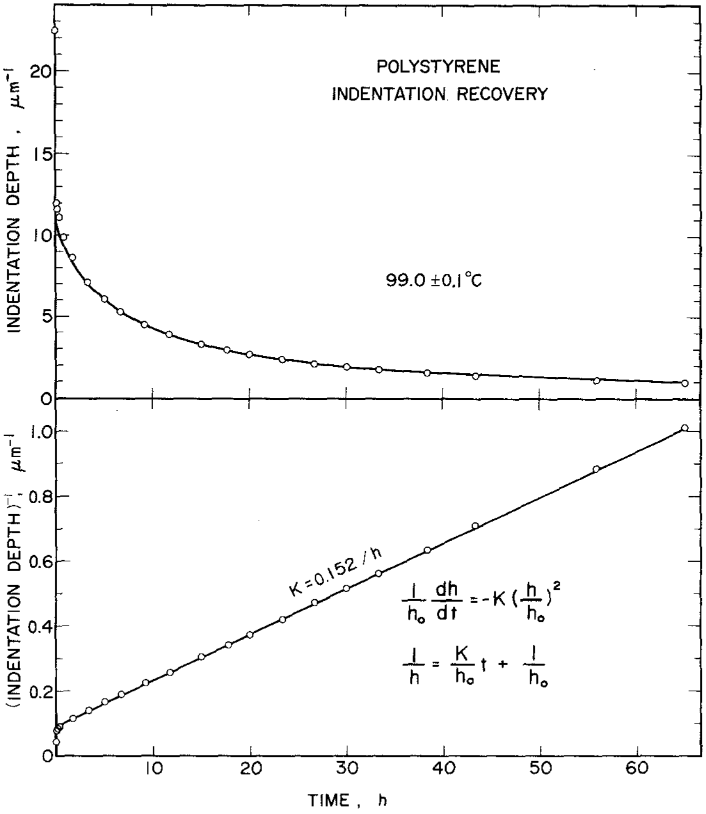

Figure 3 The variation of indentation depth during annealing and the demonstration of second order kinetics for indentation recovery in polystyrene at 99° C.

$$\frac{1}{h} = \frac{\kappa}{h_0}t + \frac{1}{h_0}, \tag{2}$$

where κ is proportional to the second order rate constant and here again the proportionality constant should be independent of h_0. Equation 2 shows that the experimental slopes of $1/h$ versus t plots should be proportional to $1/h_0$.

To verify quantitatively this possibility, the experimental slope κ/h_0 obtained from the linear plots between $1/h$ and t is plotted versus $1/h_0$ as shown in Fig. 4. It is seen that the aforementioned possibility is confirmed for large h_0. When the indentation was too shallow, the plastic zone was probably not fully developed so that the concentration of defects was smaller than the fully developed situation. As a result, the second order rate constant appeared smaller for shallow indentations as indicated in Fig. 4. For deep indentations, the straight portion of the curve does go through the origin, indicating a fully developed plastic zone which contains a constant average concentration of defects independent of the depth of the indentation. The h_0 used in Fig. 4 is the extrapolated value rather than the real value of the depth before recovery. The reason for using the extrapolated value is that there may be other factors such as inhomogeneous distribution of defects which cause deviation from second order phenomena in the initial stages of recovery. As a result, the initial depth may not represent the homogeneous concentration which enters into Equations 1 and 2. By assuming that the initial homogeneous concentration (if it is possible to homogenize before recovery starts) also obeys second order kinetics, it should be represented by the extrapolated value of $1/h_0$.

Fig. 5 shows the relation between h and t for various annealing temperatures. The respective relations between $1/h$ and t are shown in Figs. 6 and 7. The temperature dependences of these second order rate constants gave a good Arrhenius plot as shown in Fig. 8. The activation enthalpy for the indentation recovery was 163 kcal mol^{-1}

4. Discussion

As pointed out before [28], since plastic deformation such as indentation takes place by slip, and since slip is usually not homogeneous on a microscopic scale, defects of opposite signs may be produced in the plastic zone. Upon annealing, these defects may annihilate each other so as to

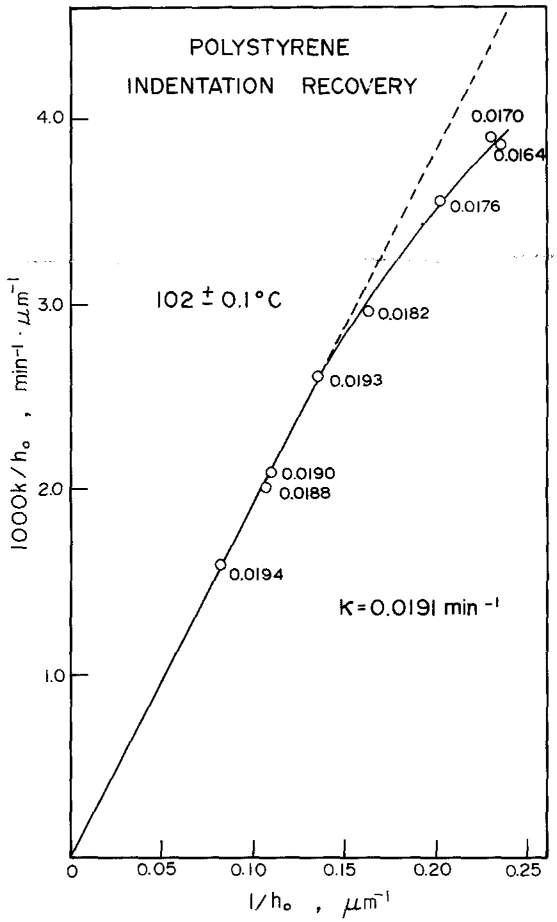

Figure 4 The effect of the depth of indentation on the recovery kinetics.

allow the material to return to its original state. However, the recovery of plastic strain is not a necessary consequence of the annealing out of defects. In crystalline materials, dislocations can be annealed out with or without simultaneous recovery of plastic strain [2,9]. Nevertheless, when shape change is accompanied by defect annealing, a relation between the shape change and the concentration of defects is expected to exist.

In this work, a direct proportion between the depth of the indentation and the concentration of defects is assumed. Based on this assumption, second order kinetics are found applicable in the later part of recovery, consistent with the annihilation of defects of opposite signs. The fact that dislocations also annealed out following second order kinetics [2] suggests that defects created during the deformation of polymers may behave likewise. Obviously these defects are mobile at the annealing temperatures.

In a related work, the shear strain in a thick shear band was found recoverable completely [25] upon annealing. Based on some measurements made in crystalline metals, the dislocation density was found proportional to plastic strain [31]. By assuming that the concentration of defects was proportional to strain during the recovery of shear band, second order kinetics were found to be obeyed also during the latter part of annealing. The activation energy, 160 kcal mol^{-1}, agrees

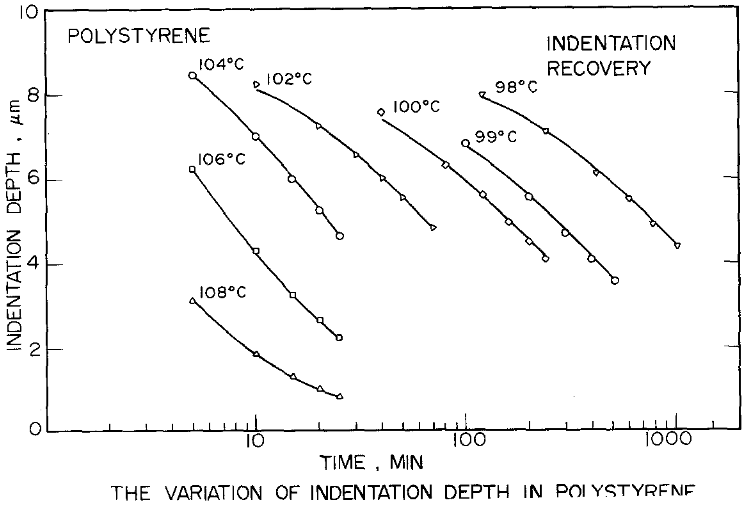

Figure 5 The variation of indentation depth in polystyrene during annealing.

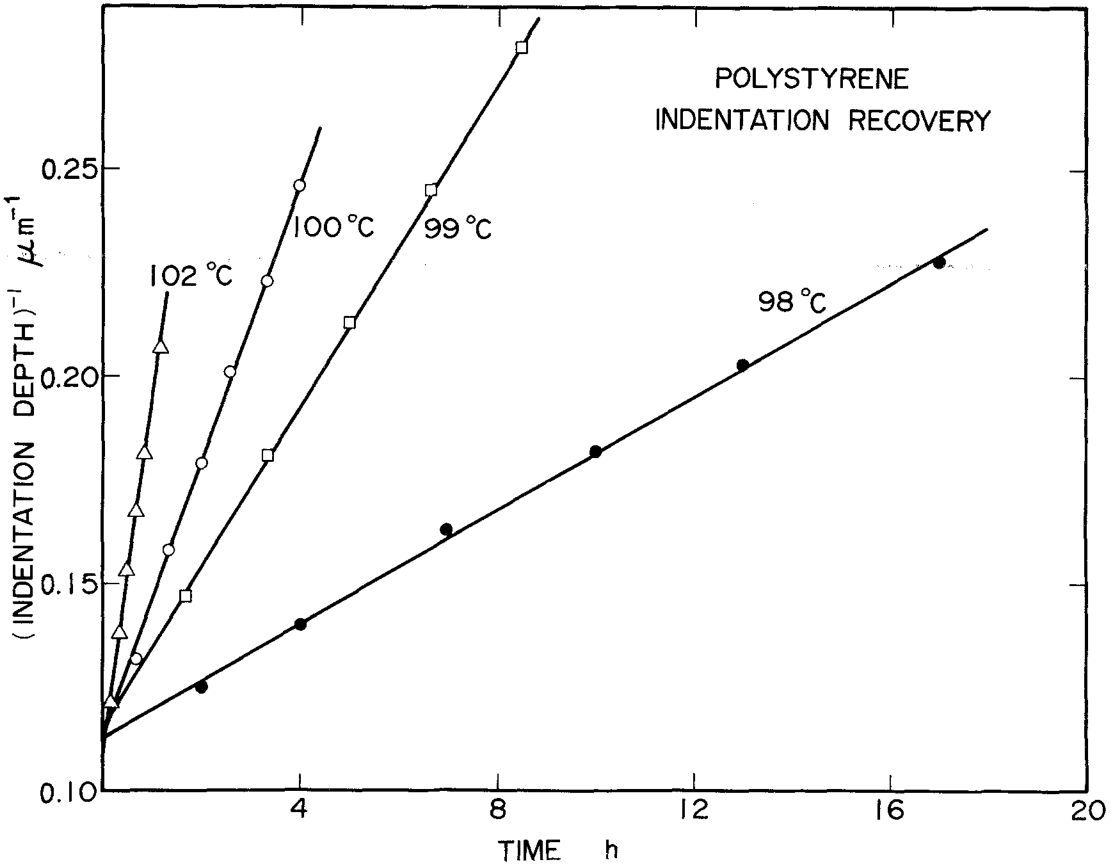

Figure 6 Second order kinetics for indentation recovery in polystyrene at 98, 99, 100, 102° C.

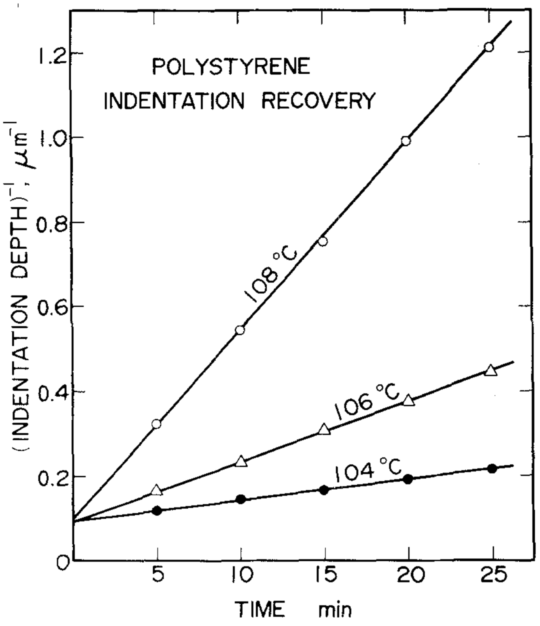

Figure 7 Second order kinetics for indentation recovery in polystyrene at 104, 106, 108° C.

very well with that of 163 kcal mol^{-1} found in this work. Such agreement seems to support the analysis and assumptions involved in both studies. It also indicates that the indentation is a reliable method of studying the recovery of amorphous materials, particularly, in the case of very brittle ones, such as oxide glasses, which cannot take a substantial amount of plastic deformation without failure in tension or compression.

In the literature, other ways of analysing the recovery data exist. However, none of them is very mechanism-revealing except, perhaps, that of Primak [23, 24] as modified by Park and Uhlmann [20–22]. A spectrum of activation energies could be obtained in that method. Unfortunately, our data here on indentation recovery are not suitable to be analysed by such a method. This method was, however, applied to our data in the compressive strain recovery of polystyrene and compared to our analysis using a single second order process. These results will be presented in our next communication.

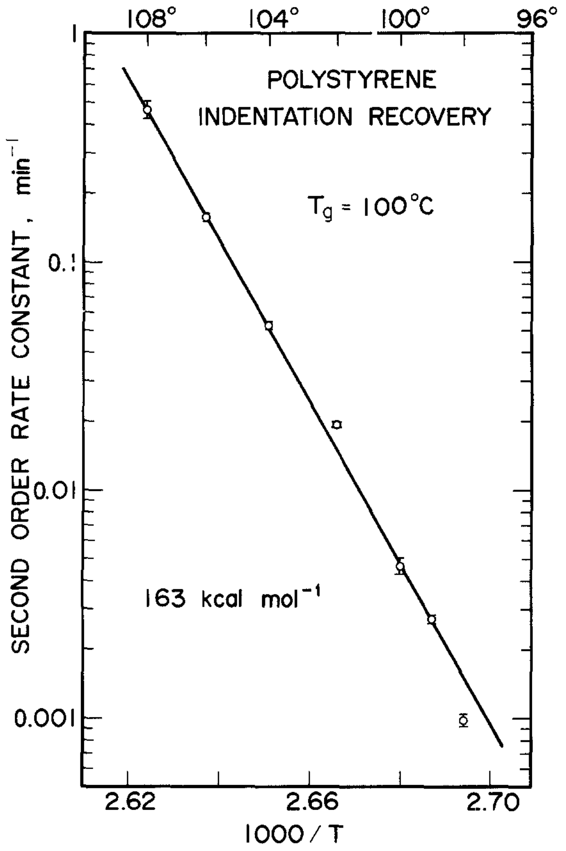

Figure 8 Activation energy for indentation recovery in polystyrene.

Acknowledgement

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