

## **STUDY OF STRUCTURAL RELAXATIONS IN POLYCAPROAMIDE BY THE LINEAR DILATOMETRY METHOD**

N.B. VALIOTTI and G.E. ZAIKOV

*Institute of Chemical Physics, Academy of Sciences of the U.S.S.R., Kosygin str. 4,  
117334 Moscow (U.S.S.R.)*

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### **ABSTRACT**

Structural relaxations in polycaproamide are studied by linear dilatometry during heating in the temperature range 20–130°C. The method of determining the kinetic parameters (relaxation times, pre-exponential factor, activation energy) of the relaxations in polymers is suggested according to the data of linear dilatometry.

### **INTRODUCTION**

The technique of linear dilatometry is widely used for investigating relaxations in polymers. As a rule, it is used for determining the temperature at which relaxation is observed from the change in the slope of the curve showing the temperature dependence of the thermal expansion of the polymer sample [1], or from the abrupt changes in the polymer's linear thermal expansion coefficient during its heating [2]. However, we believe that the potential of linear dilatometry in studying relaxation processes in polymers is far from being exhausted. Whereas the determination of kinetic parameters of relaxations in polymers (relaxation times, pre-exponential factor and activation energy) by mechanical means has been well documented [3], there are no similar reports on the use of linear dilatometry. In addition, it is of independent interest to compare the results obtained during mechanical and structural relaxation of a polymer when the polymer under study is subjected only to the temperature effect, as is the case in the linear dilatometry method.

### **EXPERIMENTAL**

During the study, use was made of polycaproamide (PCA) films 0.125 mm thick with a fusion temperature of 215°C and a degree of crystallinity

of ca. 50%. The temperature relationships of the change in the linear size of the sample under study were obtained on a UIP-70M instrument at a heating rate of  $2.5^{\circ}\text{C min}^{-1}$ . The accuracy of measurement was  $\pm 5 \times 10^{-7}$  m.

## RESULTS AND DISCUSSION

Figure 1 illustrates the relationship of the thermal expansion of the PCA sample. A linear relationship between the thermal deformation  $\epsilon$  and the temperature is observed approximately to  $70^{\circ}\text{C}$ , which shows the constancy of the thermal linear expansion coefficient or (which is the same) the absence of phase and relaxation transitions in this temperature range.

In fact, with the absence of transitions and relaxations, the increase in the linear size of a polymeric sample during heating is described by the well-known equation [4]

$$l = l_0(1 + \beta T) \quad (1)$$

where  $l_0$  and  $l$  are the linear sizes of the sample at temperatures of 293 K and  $T$  K and  $\beta$  is the linear thermal expansion coefficient.

Equation (1) can be represented in the form

$$\epsilon = \beta T \quad (2)$$

Let us differentiate eqn. (2) with respect to time, taking into account that the heating occurs at a constant rate

$$T = T_0 + vt$$

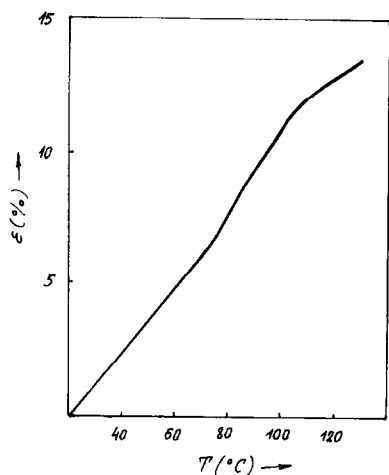


Fig. 1. Temperature relationship of the thermal deformation of PCA.

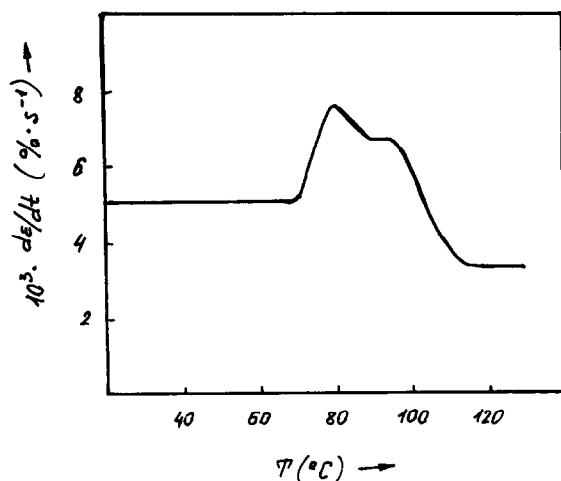


Fig. 2. Temperature relationship of the thermal deformation rate of PCA.

where  $T_0$  is the initial temperature (293 K) from which heating begins;  $v$  is the heating rate and is the heating time. Differentiation gives

$$(d\epsilon/dt) = \beta v$$

Hence, in the absence of temperature transitions in a polymer when heating takes place at a constant rate, the value  $d\epsilon/dt$ , which represents the rate of thermal deformation, will be constant. Conversely, a change in the value  $d\epsilon/dt$  shows that relaxation processes take place in a polymer during the heating process.

Figure 2 represents  $d\epsilon/dt$  as a function of temperature for a PCA sample. The value  $d\epsilon/dt$  was determined by drawing tangential lines to the  $\epsilon(T)$  curve. As is evident from Fig. 2, on the given relationship one can identify three temperature regions in which the value  $d\epsilon/dt$  is constant. These are the intervals 20–70°C, 90–95°C and 115–125°C, for which  $\beta$  assumes constant values of  $12 \times 10^{-4} \text{ K}^{-1}$ ,  $16 \times 10^{-4} \text{ K}^{-1}$  and  $8 \times 10^{-4} \text{ K}^{-1}$ , respectively.

In the temperature ranges 70–90°C and 95–115°C the value  $d\epsilon/dt$  alters, which points to temperature transitions in the polymer. It is worth noting that, on the temperature relationship of the heat capacity, irregular rises and drops were observed for polyamides at temperatures higher than room temperature [5]. Since the value  $d\epsilon/dt$  is linearly connected with  $\beta$ , and  $\beta$  in its turn is directly proportional to heat capacity in accordance with the Gruneisen equation [6], one can expect good correspondence of results for thermal expansion to the heat capacity measurements. In fact, relaxations in PCA determined from the heat capacity measurements were recorded in the same temperature intervals [7]. According to the cited paper, the first transition is due to the mobility of  $\text{CH}_2$  groups in the crystalline regions of a polymer and the next transition is due to the mobility of

large-scale kinetic units. The following expression is valid for the relaxation process [8].

$$\Delta x = \Delta x_0 \exp(-t/\tau) \quad (3)$$

where  $\Delta x_0$  and  $\Delta x$  are the deviations of the measured values from the equilibrium value, initially and at a given time instant  $t$ , and  $\tau$  is the relaxation time.

In our case  $\epsilon$  is a measured parameter. Hence, we can write eqn. (3) in the form

$$\epsilon_\infty - \epsilon = (\epsilon_\infty - \epsilon_0) \exp(-t/\tau) \quad (4)$$

where  $\epsilon_\infty$ ,  $\epsilon_0$  and  $\epsilon$  are the equilibrium, initial and current values of thermal deformation.

Let us differentiate eqn. (4) with respect to time, bearing in mind that the values  $\epsilon_\infty$  and  $\epsilon_0$  are constant for the given relaxation process

$$(d\epsilon/dt) = (\epsilon_\infty - \epsilon_0) \exp(-t/\tau)(1/\tau) \quad (5)$$

From eqn. (5) the expression for the relaxation time can be written

$$\tau = (\epsilon_\infty - \epsilon_0) \exp(-t/\tau)/(d\epsilon/dt) \quad (6)$$

Replacing the numerator in the right part of expression (6), one obtains, in keeping with eqn. (4)

$$\tau = (\epsilon_\infty - \epsilon)/(d\epsilon/dt) \quad (7)$$

In its turn,  $\tau$  as a function of temperature is described by the well-known equation

$$\tau = \tau_0 \exp(E/RT) \quad (8)$$

where  $\tau_0$  is the pre-exponential factor,  $E$  is the activation energy of the relaxation process, and  $R$  is the universal gas constant.

Substituting expression (7) into eqn. (8) gives

$$(\epsilon_\infty - \epsilon)/(d\epsilon/dt) = \tau_0 \exp(E/RT) \quad (9)$$

By taking the logarithm of eqn. (9), one finally obtains

$$\log[(\epsilon_\infty - \epsilon)/(d\epsilon/dt)] = \log \tau_0 + (E/2RT) \quad (10)$$

It is evident from eqn. (10) that the expression on the left hand side, which is equal to  $\log \tau$ , linearly depends on the reciprocal temperature, and this relationship will appear on a graph as a straight line; the tangent of the inclination angle of this line characterizes the value  $E$  and the intercept on the  $Y$  axis gives the value  $\tau_0$ .

The dependence of  $\log \tau$  on reciprocal temperature for the observable relaxation transitions is shown in Fig. 3. The data fall on a straight line with  $E_1 = 100 \text{ kJ mol}^{-1}$ ,  $\tau_0 = 3 \times 10^{-13} \text{ s}$  and  $E_2 = 66 \text{ kJ mol}^{-1}$ ,  $\tau_0 = 10^{-7} \text{ s}$ .

Relaxation constants for these transitions determined at 1 Hz frequency [7] are as follows:  $E_1 = 98 \text{ kJ mol}^{-1}$ ,  $\tau_0 = 1.6 \times 10^{-13} \text{ s}$ ,  $E_2 = 64 \text{ kJ mol}^{-1}$ ,  $\tau_0 = 6.3 \times 10^{-6} \text{ s}$ .

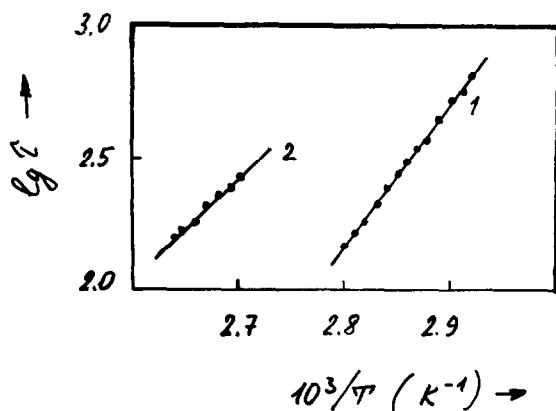


Fig. 3. Temperature relationship of relaxation times for relaxations due to small-scale (1) and large-scale (2) motions in PCA.

As is evident from comparison of data obtained by mechanical and structural relaxation, the values of activation energies for both cases practically coincide. In addition, it is known that the absorption band in the IR spectrum of PCA ( $140\text{--}160\text{ cm}^{-1}$ ) results from torsional oscillations of the methylene segments of chains [9], and corresponds to an oscillation period of  $2.1 \times 10^{-13}$  s, relatively close to the value of  $3 \times 10^{-12}$  s determined in the case of structural relaxation by the linear dilatometry method.

To sum up, linear dilatometry makes it possible to determine the temperature intervals of structural relaxation and their succession upon heating, and to calculate the kinetic parameters of the observed relaxations in polymers.

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