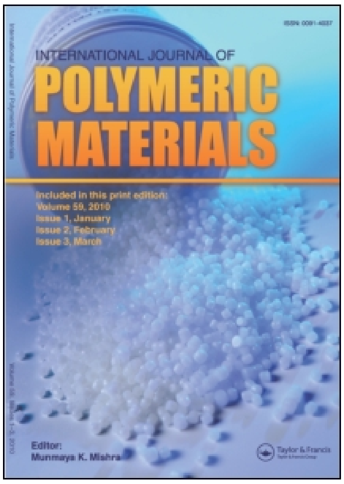

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Study of Relaxation Transitions in Polycaproamide by the Linear Dilatometry Method

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

KEY WORDS transitions, polycaproamide, dilatometry

INTRODUCTION

The linear dilatometry method is widely used for investigating relaxation transitions in polymers. As a rule, it is used for determining the temperature of the relaxation transition from the change in the inclination angle of the curve showing the temperature dependence of the thermal expansion of the polymeric sample[1–3] or from the abrupt changes in the polymer's linear thermal expansion coefficient during its heating.[4] However, we believe that the potential of the linear dilatometry method in studying relaxation processes in polymers is far from exhausted. Whereas the determination of kinetic parameters of relaxation transitions in polymers (relaxation times, the pre-exponential factor, activation energy) by mechanical relaxation methods is well elaborated,[5,6] there are no similar techniques of using the linear dilatometry method. In addition, of independent interest is the comparison of results obtained during mechanical and structural relaxation of a polymer, when the polymer under study is subjected only to the temperature effect, as in the case of using the linear dilatometry method.

EXPERIMENTAL SECTION

During the study use is made of 0.125-mm thick PCA films with a melting temperature of 215°C and with degree of crystallinity of about 50%. The temperature relationships of the change in the linear size of the sample under study are obtained on the UIP-70M instrument at a heating rate of 2.5 deg/min. The accuracy of measurements is ±3 mcm.

RESULTS AND DISCUSSION

Figure 1 illustrates the relationship of the thermal expansion of the PCA sample. A linear relationship between the thermal deformation and the temperature is observed to approximately 70°C, which shows the constancy of the thermal linear expansion coefficient or the absence of phase and relaxation transitions in this temperature range, which is the same.

In fact, with the absence of phase and relaxation transitions the increase in the linear size of a polymeric sample during the heating is described by a well-known equation:

$$l = l_0(1 + \beta T) \tag{1}$$

where l_0 and l are the linear size of the sample at temperature 293 K and T, K and β is the linear thermal expansion coefficient.

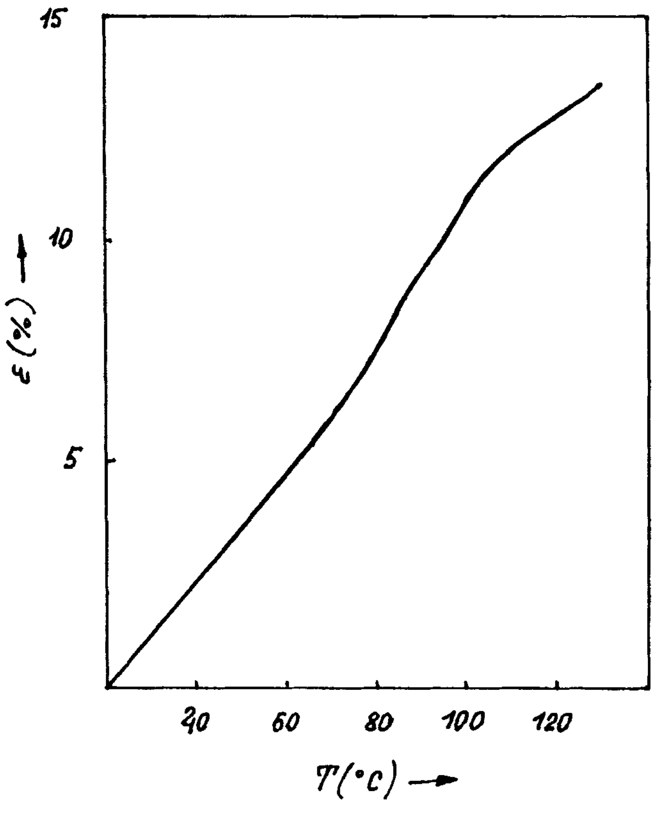

FIGURE 1 Temperature relationship of the thermal deformation of PCA.

Equation (1) can be represented in the form

$$\varepsilon = \beta T. \tag{2}$$

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

$$T = T_0 + \nu t$$

where T_0 is the initial temperature (293 K) from which the heating begins, ν is the heating rate and t is the heating time.

Upon differentiating Equation (2), we obtain

$$\frac{d\varepsilon}{dt} = \beta\nu.$$

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

Figure 2 represents $d\varepsilon/dt$ as a function of temperature for a PCA sample. The value $d\varepsilon/dt$ is determined by drawing tangent lines to the $\varepsilon(T)$ curve. As is evident from Figure 2, on the given relationship one can single out three temperature regions in which the value $d\varepsilon/dt$ is constant. Temperature intervals of from 20 to 70°C, 90 to 95°C and 115 to 125°C correspond to those for which β assumes constant values of $12\cdot10^{-4}$, $16\cdot10^{-4}$ and $8\cdot10^{-4}\ K^{-1}$, respectively.

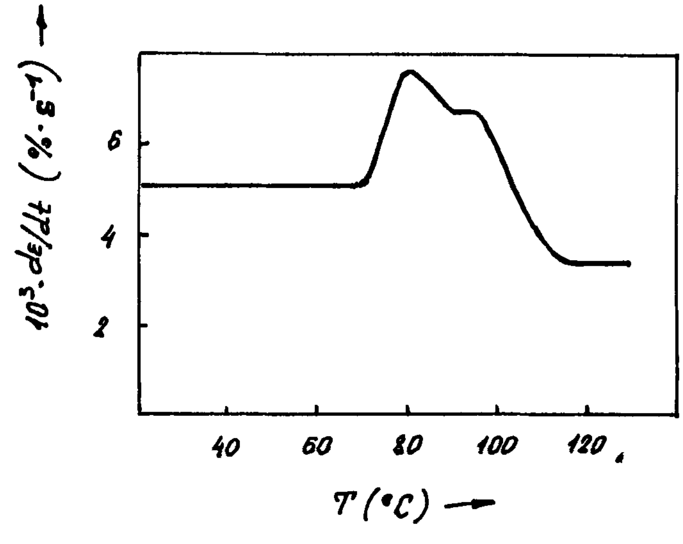

FIGURE 2 Temperature relationship of the thermal deformation rate of PCA.

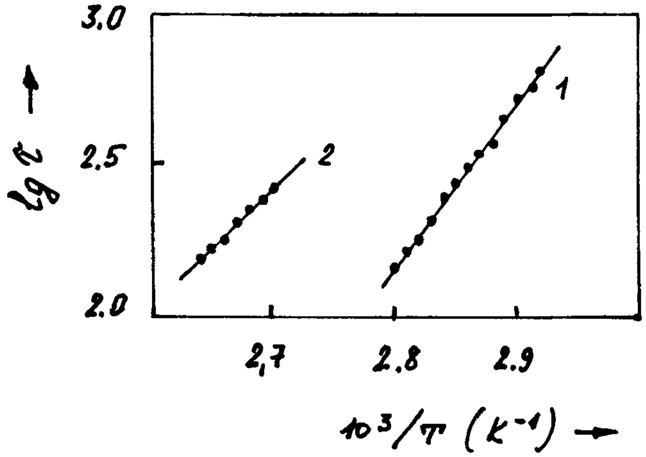

FIGURE 3 Temperature relationship of relaxation times for relaxation transitions due to (1) small-scale and (2) large-scale motions in PCA.

In the temperature range of from 70 to 90°C and 95 to 115°C the value $d\varepsilon/dt$ alters, which points to temperature transitions in a polymer. It is worth noting that in the temperature relationship of the heat capacity irregular rises and drops are observed for polyamides at temperatures higher than room temperature.[7] Since the value $d\varepsilon/dt$ is linearly connected with β, and β in turn is directly proportional to the heat capacity in accordance with the Gruneisen equation,[8] one can expect good correspondence of results of studying thermal expansion to the heat capacity measurements. In fact, relaxation transitions in PCA determined from heat capacity measurements are recorded in the same temperature intervals.[9] According to the above-mentioned paper the first transition is due to the mobility of 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 (see Reference 10) is valid for the relaxation process:

$$\Delta X = \Delta X_0 \exp(-t/\tau) \tag{3}$$

where ΔX_0 and ΔX are the deviation of the values of the magnitude under measurements from the equilibrium value for the initial and given time instant t, and τ is the relaxation time.

In our case ε is a magnitude under measurements. Hence, we can write Equation (3) in the form

$$\varepsilon_\infty - \varepsilon = (\varepsilon_\infty - \varepsilon_0)\exp(-t/\tau) \tag{4}$$

where ε_∞, ε_0 and ε are the equilibrium, initial and current values of thermal deformation, respectively.

Let us differentiate Equation (4) with respect to time, bearing in mind that values ε_∞ and ε_0 are constant for the given transition:

$$\frac{d\varepsilon}{dt} = (\varepsilon_\infty - \varepsilon_0)\exp(-t/\tau)\cdot\frac{1}{\tau}. \tag{5}$$

From Equation (5) let us write the expression for relaxation time:

$$\tau = \frac{(\varepsilon_\infty - \varepsilon_0)\exp(-t/\tau)}{d\varepsilon/dt}. \tag{6}$$

Replacing the numerator in the right part of expression (6) we obtain, in keeping with Equation (4),

$$\tau = \frac{\varepsilon_\infty - \varepsilon}{d\varepsilon/dt}. \tag{7}$$

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

$$\tau = \tau_0 exp\left(\frac{E}{RT}\right) \tag{8}$$

where τ_0 is the pre-exponential factor, E is the activation energy of the relaxation transition and R is the universal gas constant.

Substituting expression (7) into Equation (8), we obtain

$$\frac{\varepsilon_\infty - \varepsilon}{d\varepsilon/dt} = \tau_0\exp\left(\frac{E}{RT}\right). \tag{9}$$

Taking a logarithm of Equation (9), we finally obtain

$$lg\,\frac{(\varepsilon_\infty - \varepsilon)}{d\varepsilon/dt} = lg\,\tau_0 + \frac{E}{2.3\,RT}. \tag{10}$$

It is evident from Equation (10) that the expression on the left-hand side which is equal to $lg\,\tau$ linearly depends on the inverse temperature. This relationship is depicted on the graph by a straight line the tangent of whose inclination angle characterizes the value E and the intercepted segment on the Y-axis the value $lg\,\tau_0$.

Relaxation constants for these transitions determined by the relaxation spectrometry method on the 1 Hz frequency[9] are as follows: $E_1 = 98$ kJ/mole, $\tau_0 = 1.6\cdot10^{-13}$ s, $E_2 = 64$ kJ/mole, $\tau_0 = 6.3\cdot10^{-6}$ s.

As is evident from comparison of data obtained by mechanical and structural relaxation, the values of activation energies for both transitions practically coincide. Besides, it is known that the absorption band in the infrared spectrum of PCA (140–160 cm^{-1}) belongs to the torsional oscillations of methylene segments of chains,[11] which corresponds to the oscillation period $2.1-2.4 \cdot 10^{-13}$ s and is relatively close to the value $3 \cdot 10^{-12}$ 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 relaxation transitions, the succession of their heating process and to calculate the kinetic parameters of observed relaxation transitions in polymers.

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