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DEGREE OF CRYSTALLINE STRUCTURE OF POLYMER OBTAINED FROM MELT AT VARIOUS COOLING RATES

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An analytical dependence of the final degree of crystalline structure on the rate of temperature variation is obtained for polymer material. It is shown that the formula obtained ensures satisfactory agreement with experiment in a broad range of cooling rates.

In the real technological production of components from polymers which are crystallized from a melt, the crystallization always occurs in nonisothermal conditions, as a result of heat transfer with the surrounding medium and the low thermal conductivity in the bulk of the material. At the same time, it is well known that the structure of polymer (and other) materials and hence a whole set of their physical and mechanical properties depend on the cooling rate. In addition, even the degree of crystalline structure of the finished component depends on the cooling rate.

In nonisothermal polymer crystallization, specific kinetic phenomena arise as a result of the very nonlinear temperature dependence of the crystallization rate, on the one hand, and the relation between the heat loss to the surrounding medium and the heat input due to the existence of an internal heat source (the heat of crystallization), on the other.

The aim of the present work is to establish the relation between the cooling rate of the polymer material obtained from the melt and the final degree of crystal structure attained at the temperature at which crystallization no longer occurs. In fact, the temperature dependence of the crystallization rate takes the form in Fig. 1a. It is evident that $\dot{\alpha} = 0$ when $T < T_C$ and the final degree of crystal structure α_∞ attained at $T < T_C$ depends on the rate of crossing the region from T_m to T_C . In addition, it must be taken into account that, at any temperature in the range from T_m to T_C , the equilibrium degree of crystal structure α_e depends on the temperature, as shown schematically in Fig. 1b, but $\alpha_e < 1$ always.

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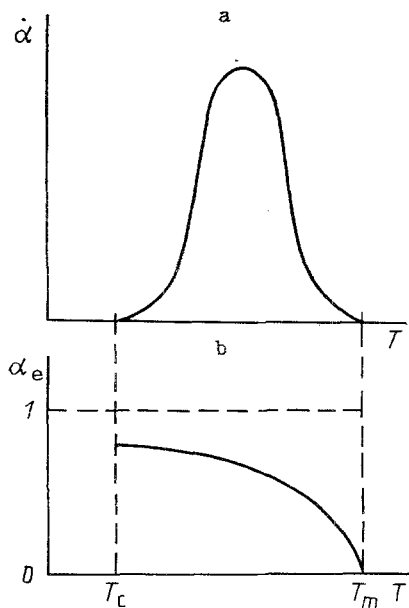


Fig. 1. Temperature dependence of the crystallization rate (a) and equilibrium degree of crystalline structure (b).

A kinetic equation of the following form is used for quantitative description of crystallization

$$\frac{d\alpha}{dt} = K(T) f[\alpha, \alpha_e(T)]. \quad (1)$$

For the sake of simplicity and clarity of the results obtained, polymer crystallization is considered in conditions of linear variation of the ambient temperature over time. Polymer crystallization in the interval $T_m - T_c$ is described using Eq. (1) in the form [1-3]

$$\frac{d\alpha}{dt} = k_0 \exp \left[-\frac{U}{T - T_c} - \frac{\psi}{T_m - T} \right] (\alpha_e - \alpha)(1 + c_0\alpha). \quad (2)$$

The temperature dependence of the equilibrium degree of crystal structure is taken in the form [4]

$$\alpha_e(T) = a \left[1 - b \sqrt{\frac{T}{T_m - T}} \right], \quad (3)$$

which approximates the known experimental data sufficiently well. The kinetic constants used below for specific calculations characterize the crystallization of polycapraamide (PA-6) samples. The values of these constants are obtained by solving the inverse problem of nonisothermal kinetics [4] on the basis of extrapolation of the experimental data of [5] over the whole temperature range from T_m to T_c : $a = 0.69$; $b = 0.11$; $k = 3.32 \text{ sec}^{-1}$; $U = 213.2 \text{ K}$; $\psi = 210.4 \text{ K}$; $c_0 = 42$; $T_c = 317 \text{ K}$; $T_m = 501 \text{ K}$.

To estimate the final degree of crystalline structure with linear temperature variation $T = T_m - vt$, the time derivative in Eq. (2) is replaced by the temperature derivative $dT = -vdt$, and integration over the whole temperature interval from T_m to T_c gives

$$\int_0^{\alpha_\infty} \frac{d\alpha}{(\alpha_e - \alpha)(1 + c_0\alpha)} = - \int_{T_m}^{T_c} \frac{k_0}{v} \exp \left[-\frac{U}{T - T_c} - \frac{\psi}{T_m - T} \right] dT. \quad (4)$$

The analytical expression for the final degree of crystalline structure takes account of the following assumptions.

First, the chosen form of $k(T)$ permits sufficiently correct approximation by Taylor series expansion of the exponent. Retaining three terms of the expansion, the result obtained is

$$K(\Theta) = k_* \exp [-(\beta_1 + \beta_2) \Theta^2], \quad (5)$$

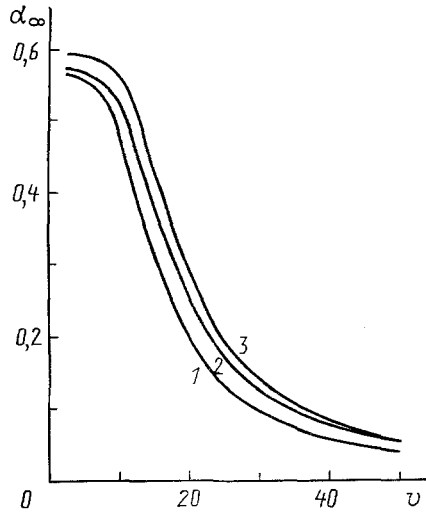


Fig. 2

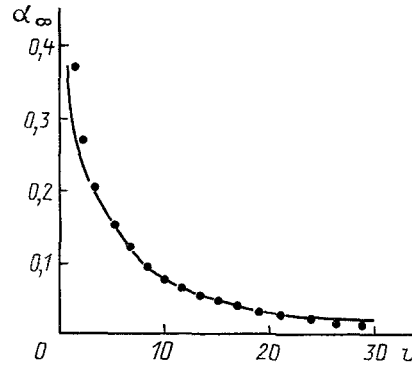


Fig. 3

Fig. 2. Dependence of final degree of crystalline structure on cooling rate according to: (1) Eqs. (2) and (3); 2) Eqs. (5) and (3); 3) Eq. (9). v , deg/sec.

Fig. 3. Comparison of theoretical (continuous curve) and experimental (points) dependence of the degree of crystalline structure on the cooling rate.

where $\theta = \kappa(T - T_*)$ is the dimensionless temperature determined by the natural scale of the temperature difference in crystallization

$$\kappa = \frac{U}{(T_* - T_c)^2} = \frac{\psi}{(T_m - T_*)^2}. \quad (6)$$

Thus, κ is determined by the distance from the temperature of maximum crystallization rate T_* ; k_* corresponds to the value of $K(T)$ at $T = T_*$

$$k_* = k_0 \exp\left(-\frac{1}{\beta_1} - \frac{1}{\beta_2}\right), \quad (7)$$

where $\beta_1 = (T_* - T_c)/U$, $\beta_2 = (T_m - T_*)/\psi$ are dimensionless parameters characterizing the kinetics of crystallization.

Second, the finite limits of integration on the right-hand side of Eq. (4) are replaced by infinite limits, permitting the use of an Euler-Poisson integral.

Finally, the left-hand side of Eq. (4) is integrated under the assumption that $\alpha_e = \alpha_e(T_c) = \alpha_{ec} = \text{const}$. Then simple manipulations lead to a formula for estimating the final degree of crystal structure

$$\alpha_\infty = \alpha_{ec} \left[1 - \frac{1 + c_0 \alpha_{ec}}{c_0 \alpha_{ec} + \exp\left(\frac{1 + c_0 \alpha_{ec}}{V}\right)} \right], \quad (8)$$

where $V = (v/k_* \sqrt{\pi}) \kappa \sqrt{\beta_1} + \beta_2$ is the dimensionless cooling rate.

As shown by numerical estimates, the third of these assumptions is the most rigorous. Nevertheless, the results in Fig. 2 show that approximate Eq. (8) gives not only qualitative but also satisfactory quantitative estimates of the final degree of crystalline structure as a function of the kinetic constants k_0 , U , ψ , c_0 and the technological parameter v over the whole temperature interval $T_m - T_c$. In addition, with a certain ratio of constants - $\alpha_e = 0.4$; $c_0 = 0.11$; $\kappa \sqrt{\beta_1} + \beta_2 / k_* \sqrt{\pi} = 7.93 \cdot 10^{-3}$ - Eq. (8) satisfactorily describes the experimental data on the final degree of crystalline structure in [6] (Fig. 3). In this case, the structural features of the measuring cell yielded controllable heat-transfer conditions for PA-6 films of thickness no greater than 0.25 mm and permitted the

use of mean cooling rates of up to 30 deg/sec [6]. The film samples were melted between glass covers, with temperature measurement by means of microthermocouples placed directly in the sample. In the present work, the mean cooling rate is interpreted as the technological parameter v in comparing the data of [6] with the present calculation scheme.

NOTATION

α , degree of crystalline structure; t , time; T , temperature; $K(t)$, temperature dependence of overall rate of crystallization; $\alpha_e(T)$, temperature dependence of equilibrium degree of crystalline structure; $f[\alpha, \alpha_e(T)]$, formal law characterizing the rate of the process as a function of the degree of crystal structure; k_0 , preexponential factor; c_0 , parameter characterizing the type (geometry) of growing structure; ψ , U , effective energetic constants characterizing nucleation and growth, respectively; T_m , equilibrium melting point; T_c , vitrification, temperature; α_∞ , final degree of crystallization structure; v , rate of temperature variation.

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NOISE SHEAR WAVES IN NONLINEAR SMECTIC LIQUID CRYSTAL

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The propagation of a narrow-band shear wave in a smectic liquid crystal is studied. It is shown that the nonlinearity makes possible a random phase modulation. The temporal correlation function, the characteristic correlation time, and the width of the spectrum are calculated. The relation between the width of the spectrum, the intensity of the wave, and the distance traversed is determined. This makes it possible to determine the coefficient of cubic nonlinearity of a smectic liquid crystal (SLC) by measuring the relative increase of the width of the spectrum at an arbitrary point.

In [1-3] it is shown that it is most important to take into account nonlinear factors in the behavior of liquid crystals when studying their smectic phase.

The propagation of regular shear waves in a nonlinear smectic was studied in [4]. Some mechanisms of the propagation of noise shear waves in SLC were analyzed in [4].

In order to describe the dynamics of SLC (smectic A) it is convenient to introduce the smectic variable $W(r, t) = (z + u)/l$. Here l characterizes at equilibrium $W_0 = z/l$ a system of layers perpendicular to the z -axis.

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