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# Size distribution of nanocrystalline elements of the polyethylene structure

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A method for calculating the size distribution of nanocrystalline elements of the polymer structure is proposed. The longitudinal size distribution (thickness) of ultrahigh molecular weight polyethylene lamellae was calculated from calorimetric data. The results of calculating the maximum values of the distribution are consistent with the known data obtained by other methods.

**Keywords:** heat capacity, size effect, lamella, polyethylene.

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The traditional physics of three-dimensional solid bodies is facing problems when considering objects of nanometer scale. It is known [1] that in this case thermodynamic parameters, such as entropy, enthalpy, free energy, specific heat capacity and melting temperature are changed depending on size of morphology of these objects. This phenomenon is named „size effect". This effect is observed when the size of structural elements is decreased below certain threshold, which is about 100 nm for many materials, and the most clearly manifested at sizes of 10−20 nm. A number of approaches are suggested for connecting the above-listed thermodynamic parameters with the crystal geometry of low-molecular and high-molecular polymer substances. A common feature of these approaches in considering the processes of melting is the dependence of melting temperature ($T_m$) on surface energy ($\sigma$) and linear dimension of the structural element ($L$) that has the following form:

$$T_m = T_0(1 - k\sigma/L),$$

where $T_0$ — melting temperature of the three-dimensional material, $k$ — coefficient taking into account geometry of the element.

Size effects in organic compounds (synthetic polymers and biological objects) have a somewhat different character. Biological molecules, polymers and intracellular structures are nano-sized, however their properties (functions) are defined to a significant extent not only by size, but so called supermolecular structure (SMS). SMS is a multilevel system and includes structural elements with a wide variation range of linear sizes of these elements. In this context, to understand physical processes in polymer organic compounds and to create, in particular, state-of-the-art polymer composite materials and ultrastrong materials based on them [2,3], it is necessary to analyze the SMS taking into account the distribution of SMS elements by size. In this work, based on the analysis of shape of the heat capacity peaks corresponding to melting, a method is suggested that makes it possible to obtain information on the distribution of nanocrystalline formations by thickness in polycrystalline polymer materials.

For the role of specimens in the experimental studying of the SMS polymer, films were selected, being produced by dissolving in decalin with further drying in the air of an ultra-high-molecular-weight polyethylene (UHMWPE) with a molecular mass of $M_\eta \geqslant 1 \cdot 10^6\,\mathrm{g \cdot mol^{-1}}$. Fig. 1 shows a photoshot of the produced film of UHMWPE xerogel made in SUPRA 55 VP electron microscope (Carl Zeiss, Germany). Disordered laminar formations can be seen that are multilayer stacks of nanometer-thick lamellae, as it follows from the x-ray diffraction analysis [4].

Thermophysical characteristics of the specimen were studied using a DSC-2 Perkin−Elmer calorimeter with heating speed $V$ varied from 0.3 to $5\,\mathrm{K \cdot min^{-1}}$. The temperature scale was calibrated by points of ice melting (273.1 K) and indium melting (429.7 K), the heat flux scale was calibrated by heat capacity of sapphire, and the heat

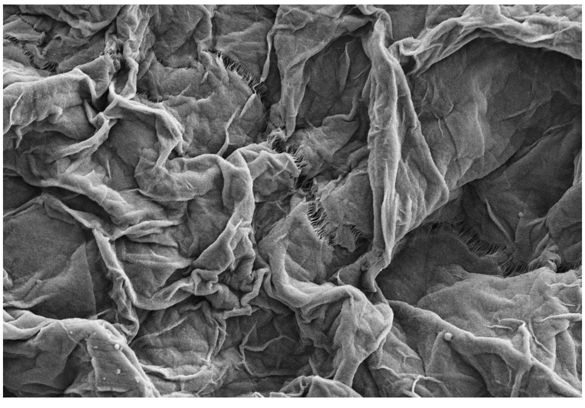

**Figure 1.** Microphoto of a film produced from 1.5% solution of UHMWPE powder in decalin.

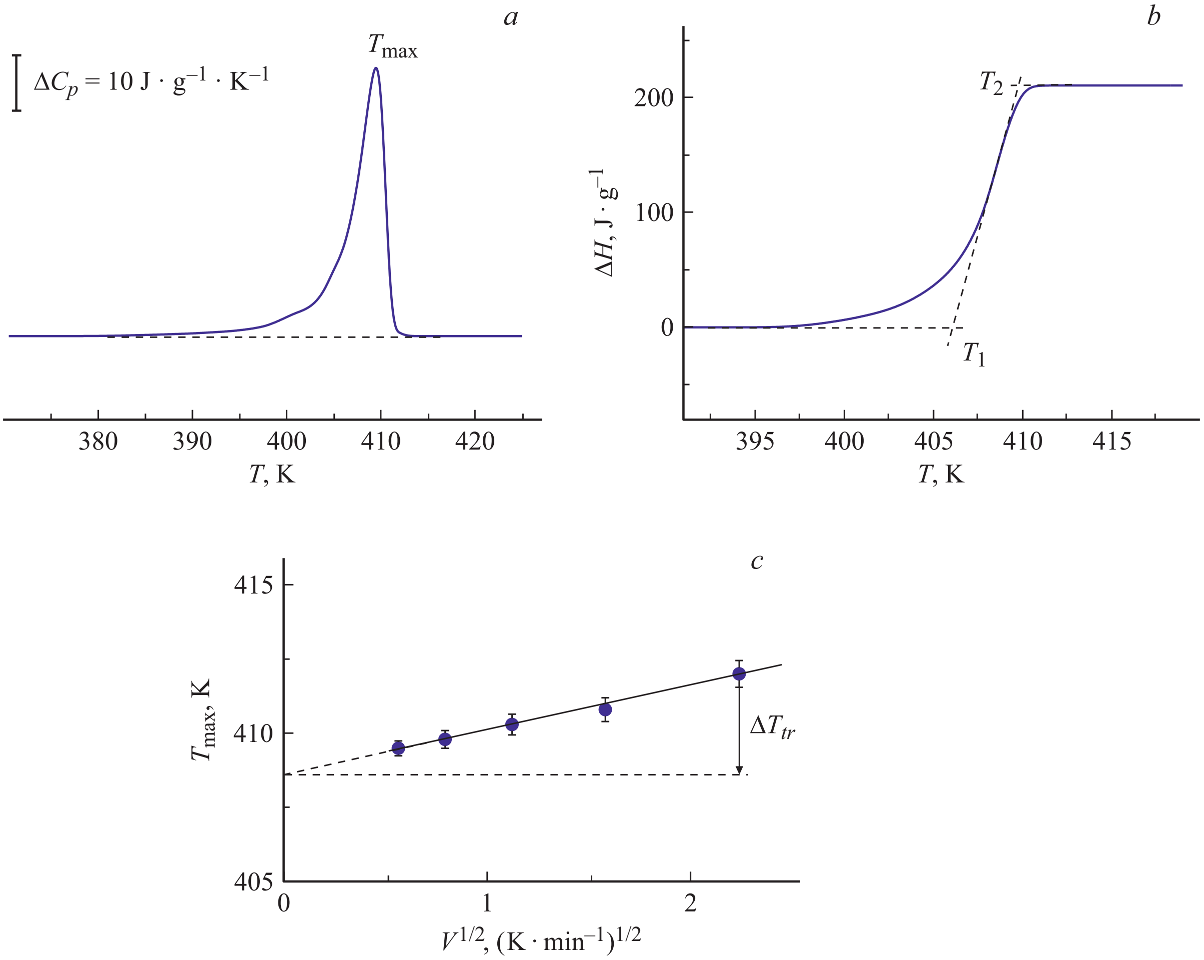

**Figure 2.** Temperature dependencies of heat capacity $\Delta C_p$ $(a)$ and melting enthalpy $\Delta H$ $(b)$ of the UHMWPE film. $c$ — determination of procedural error $\Delta T_{tr}$.

effect determined by the area on the differential scanning calorimetry (DSC) curve was calibrated by indium melting enthalpy ($\Delta H_f = 6.80\,\mathrm{cal \cdot g^{-1}}$).

Fig. 2 shows temperature dependencies of heat capacity $\Delta C_p$ $(a)$ and melting enthalpy $\Delta H$ $(b)$ of the UHMWPE film specimen with a weight of 5 mg produced with heating at a rate of $V = 5\,\mathrm{K \cdot min^{-1}}$. It was shown [5] that this data can be used to evaluate the parameter of intrachain cooperativity of melting ($\nu$), which physical meaning is that it defines the minimum sequence of $\nu$ repeating units in a chain that transform as a whole from crystallite to contracted random coil in the molten mass. The $\nu$ value was evaluated by the following formula:

$$\nu = 2RT_{\max}^2/\Delta T \Delta H, \qquad (1)$$

where $R$ — gas constant, $T_{\max}$ — temperature of maximum melting peak on the DSC curve, $\Delta T = T_2 - T_1$ (Fug. 2, $b$). The dimensionless parameter $\nu$ is expressed by the number of $CH_2$-groups in the trans-section of polyethylene chain that simultaneously participate as a whole in the melting action. If $\nu$ is multiplied by the length of single bond C$-$C (the size of projection of the C$-$C bond of the main chain onto the axis of macro molecule $h = 0.124\,\mathrm{nm}$), this parameter can be collated with the parameter of supermolecular structure, i.e. the thickness of lamellar crystals $L$. It was found that the parameter of cooperativity for the specimens investigated by us is $\nu = 180 \pm 20$, which corresponds to the size of crystal cores in UHMWPE lamellae $L = 22 \pm 2\,\mathrm{nm}$. The obtained values are well matched with the data generally cited in literature, which is just averaged data and does not uncover the possible wide distribution of lamellae by their sizes.

As noted before, based on the analysis of DSC curves shape, a method can be suggested making it possible to obtain a distribution of crystalline formations in a polymer by thickness. This method is based on the fact that at a certain temperature the heat flux on the DSC melting curves is proportional to the mass fraction of the crystallites that are melted at this temperature. According to this approach, the dependence of heat flux on temperature is transformed to the distribution curve of the heat flux depending on the number of atomic groups (for example, for polyethylene it is the number of –$CH_2$– groups, or any other dimensional factor related to these groups). Indeed, if the melting heat in a time interval between $t$ and $t + dt$ is equal to $(dH/dt)dt$, the same melting heat corresponds to the transition from the crystalline state to the melted mass state of a certain number $(dn)$ of $-\mathrm{CH_2}-$ groups in an interval corresponding to $dt$. The the melting heat can be written as $(dH/dn)dn$, whence it follows that $(dH/dn)dn = (dH/dt)dt$. This equation can be expressed as follows:

$$dH/dn = [(dT/dt)^{-1}(dT/dn)]dH/dt = (dT/dn)(dH/dT), \tag{2}$$

where $dT/dt$ — heating rate, which is usually a constant in DSC-experiments; $dH/dT$ — experimental dependence of heat capacity on temperature determined on the basis of the DSC-curve taking into account certain scanning rate over temperature; $dT/dn$ can be calculated from the general Gibbs-Thomson [6] based on the balance of surface and volume energies:

$$T_m(L) = T_0\left[1 - 2/\Delta H_0(\sigma/a + \sigma/b + \sigma_e/L)\right], \tag{3}$$

where $a$ and $b$ — dimensions of the crystallite in the plane of cross-section normal to the longitudinal axis that coincides with the macromolecule direction; $L$ — longitudinal dimension of the crystallite equal to $L = hn$; $\sigma$ — surface energy of side surfaces of the crystallite; $\sigma_e$ — surface energy of the end surface; $\Delta H_0$ — melting heat. Taking into account the equation of $L = hn$, expression (2) can be written as follows:

$$dH/dL = [(dT/dt)^{-1}(dT/dn)]dH/dt = (dT/dL)(dH/dT). \tag{4}$$

In the supermolecular lamellar structure of the polymer parameters $a$ and $b \gg L$, therefore in expression (3) the $\sigma/a$ and $\sigma/b$ terms can be neglected and the expression can be simplified as follows:

$$T_m(L) = T_0[1 - 2\sigma_e/\Delta H_0 L] \tag{5}$$

or

$$L = 2\sigma_e T_0/\Delta H_0(T_0 - T_m). \tag{6}$$

Thus, the data obtained from the DSC-curves of melting can be transformed using relationships (2) and (6) to the dependence of heat flux on crystal thickness relating the heat flux with the number of crystals melting at an instant temperature of $T_m$. In calculations of lamellae thicknesses distribution in UHMWPE the following data can be used: $T_0 = 415.5\,\mathrm{K}$, $\sigma_e = 87.4\,\mathrm{erg \cdot cm^{-2}}$, $\Delta H_0 = 2.79 \cdot 10^9\,\mathrm{erg \cdot cm^{-3}}$ [7].

Prior to use the above data for calculation, it is necessary to take into account the error $\Delta T_{tr}$ in the determination of $T_m$, because with a small difference of $T_0 - T_m$ the error in determination of $L$ can be significant. It is commonly known that method error of the DSC-method (offset of temperature peak by $\Delta T_{tr}$) arises due thermoresistance $R_0$ of the specimen under test in a calorimetric cell. The error is determined as follows: since $\Delta T_{tr}$ depends on weight of the specimen $m$ and scanning speed $V$ as follows: $\Delta T_{tr} = R_0(mV)^{1/2}$ [5], it is necessary to use the experimental data obtained at variation of heating rates $V$ to plot the dependence $T_{\max} = f(V^{1/2})$, which should be a linear function in the entire interval of variations $V$, if there are no any structural transformations. The extrapolation of the linear dependence to $V \to 0$ makes it possible to determine the method error $\Delta T_{tr}$. In this work such a dependence $T_{\max} = f(V^{1/2})$ was obtained for specimens with equal weights (Fig. 2, *c*) and used to determine the error $\Delta T_{tr} = 3.8\,\mathrm{K}$.

Fig. 3 (curve *1*) shows the distribution of lamellae thicknesses for a UHMWPE film as calculated on the basis of relationships (4) and (6) taking into account the method error $\Delta T_{tr}$. It can be seen that maximum heat flux for the melting is accounted for by lamellae this thicknesses of 24–26 nm. However, this distribution is not a distribution of lamellae number by $L$ because lamellae with higher $L$ absorb larger quantity of heat when melting. In this case to determine the distribution $N(L)$ of lamellae number by $L$ a normalization is needed, i.e. a calculation should be made on the basis of the following relationship: $N(L) = L^{-1}dH/dL$. This calculation is presented in Fig. 3 (diagram *2*) in percentage.

In can be seen from the diagram that there is a significant difference between distributions *1* and *2*. Thus, an offset of the distribution *2* towards lower values of $L$ is observed, and maximum number of lamellae is now accounted for by the range of 22–24 nm. Also, a more considerable fraction of lamellae with low thickness can be noted. At the same time the major part of lamellae ($\sim 80\%$) is accounted for by lamellae in a wider range of variation of $L$: from 14 to 28 nm.

In relation to the distributions obtained by the calorimetric method an issue arises regarding the comparison of this data with the data obtained by other methods. we think that to compare the distributions obtained by different methods, it is reasonable to consider a weighted value of lamella thickness $L_m$ obtained by the calorimetric method. The later can be calculated by the following relationship:

$$L_m = \Sigma L_i(dH/dL)_i/\Sigma(dH/dL)_i, \tag{7}$$

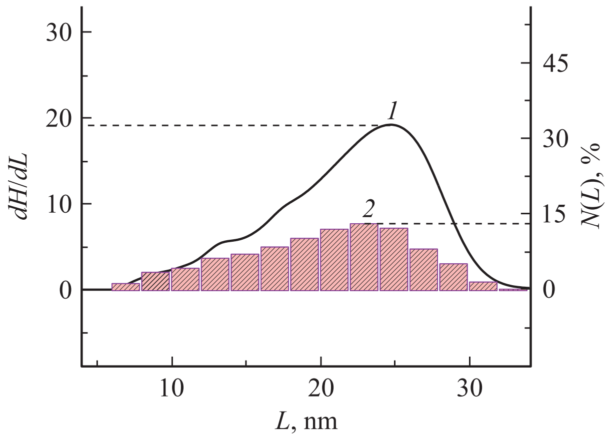

**Figure 3.** Dependencies of heat flux(*1*) and number of lamellae (*2*) on thickness of lamellae in the UHMWPE film.

where $L_i$ — current value of $L$ in the distribution, $(dH/dL)_i$ — current value of $dH/dL$ at $L = L_i$. The calculation by relationship (7) and the distribution represented in Fig. 3 yields $L_m = 20\,\text{nm}$. This value is significantly lower than maximum values in the distribution by heat flux $dH/dL$ (curve *1* in Fig. 3) and somewhat lower than in the „quantitative“ distribution $N(L)$ (diagram *2* in Fig. 3).

Thus, in this work a method is suggested to calculate distribution by size of nanocrystalline elements of UHMWPE structure. This method is based on the analysis of shape of the heat capacity peak, which allows obtaining the data that considerably refines features of the lamellar structure of polymer. If a comparison is needed with the data obtained by other methods, it is necessary to refer to average weighted dimensions of the structural elements. In general, the calculation results of calorimetric method reported in this work are matched with the known data obtained by other methods.

### Conflict of interest

The authors declare that they have no conflict of interest.

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