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Nucleation in the Crystallization of Oriented Polymer Melts

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Summary

On the basis of thermodynamic analysis of formation of folded-chain and bundle-like nuclei and taking into account the defects in their edge surfaces it was established that the edge surface free energy is the parameter determining to a great extent all the other thermodynamic values and depending not only on the temperature and size of the nucleus but also on the extent of defects in it and on parameter of molecular deformation λ .

Introduction

Various physical effects related to some technological problems are accompanied by crystallization or at least by nucleation. Caused by orientation during which a melt containing random-coil macromolecules is transformed into a melt of partially or completely extended chains /1/.

It has already been shown /2/ that the structure of the amorphous state of the polymer that plays the main part in the processes of nucleation and growth of polymer crystals may be determined by the structure of heterophase fluctuations /3/ (Fig.1 in ref./2/). Their properties profoundly affects the thermodynamic and kinetic characteristics of processes accompaning crystallization.

Theory

The surface of a nucleus based on these heterophase fluctuations showed exhibit defects /4,5/: loops, tie chains and chain ends. The change in the free energy, ΔF, caused by its formation can be expressed by /2/

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$$\Delta F = 2\sigma_e \nu a + C\sqrt{(\nu a)}\ell\sigma_s - \nu a\ell\Delta f + 2T\sum_{i=0}^{n}\sum_{j=0}^{m_i}\Delta S_{ij}(\ell,\lambda) =$$

$$= \Delta F_0 + 2T\sum_{i=0}^{n}\sum_{j=0}^{m_i}\Delta S_{ij}(\ell,\lambda) \qquad (1)$$

where the first term takes into account the change in ΔF when the interface is formed on the plate edge; (σ_e - is the specific value of the edge surface free energy, ν is the number of chains emerging on the edge surface and a is the cross-sectional area of one chain), the second term takes at into account when the interface is formed on the side surface (σ_s is the specific value of the side surface free energy, ℓ is the plate height and C is a constant depending on the geometry of the platelike nucleus), the third term is the change in the free energy when the crystalline phase of volume $\nu a\ell$ is formed (Δf is the specific value of the volume free energy) and the fourth term reflecting the polymer nature of the nucleus is the total change in conformational entropies of all the regions that did not form a part of the nucleus. In this term the summations over i and j take account various types of defective regions and the number of these regions, respectively. Eq.(1) differs from that presented in ref./2/ because it takes into account the "defective regions" on both edges of the nucleus and the summation over various types of defects is introduced.

If it is assumed that

1)all the macromolecules that form a part of the heterophase fluctation in the amorphous state obey a Gaussian distribution,

2)the condition of affinity deformation is fulfilled, and

3)the concept of effective length of defective regions is introduced, i.e.,

$$L_{1i}=L_{2i}=\ldots=L_{mi}=L_i$$

eq.(1) can be obtained in the following form /6,7/

$$\Delta F = \Delta F_0 + 2T\nu a\sum_{i=0}^{n}\eta_i\,\Delta S_i(\ell,\lambda) \qquad (2)$$

where η_i is the measure of different types of nucleus defects, $\eta_i = m_i/\nu a$, m_i is the number of regions of each type of defects and $\Delta S_i(\ell,\lambda)$ are the corresponding averaged changes in the conformational entropies of these defective regions vs parameter of molecular deformation λ.

Bearing in mind that the first and the fourth terms in eq.(2) represent changes occurring on the surface of the nucleus, eq.(2) becomes

$$\Delta F = 2\,\nu a \sigma'_e(\ell,\lambda,T) + C\sqrt{(\nu a)}\,\ell\,\sigma_s - \nu a \ell \Delta f \qquad (3)$$

where
$$\sigma'_e(\ell,\lambda,T) = \sigma_e + T\sum_{i=0}^{n} \eta_i\,\Delta S_i(\ell,\lambda) \qquad (3a)$$

Eq.(3) just as the classical equation represented in eq.(1) by ΔF_0 /8/ describes a surface that has a saddle point with the coordinates ℓ^* and $(\sqrt{\nu a})^*$ determined from the following system /2/

$$\left.\frac{\partial \Delta F}{\partial \ell}\right|_{\nu a} = 0 \ ; \qquad \left.\frac{\partial \Delta F}{\partial(\nu a)}\right|_{\ell} = 0 \qquad (4)$$

One finds from system (4) that the critical values of $(\sqrt{\nu a})^*$ can be given by

$$(\sqrt{\nu a})^*_\lambda = \frac{C\ell^*(\lambda)\,\sigma_s}{2\ /\ell^*(\lambda)\,\Delta f - 2\sigma'_e(\ell,\lambda,\ T)/} \qquad (5)$$

The range of fold lengths is found from eq.(4) by using the condition that the free energy, ΔF, will monotonically increase at high values of ν untill

$$\ell(\lambda)\,\Delta f \geqslant 2\,\sigma'_e(\ell,\lambda,T) \qquad (6)$$

i.e., untill the crystallization nucleus becomes capable of growing. Eq.(6) determines the range of fold lengths ℓ for which the potential barriers to the free energy is given by

$$\Delta F^*(\lambda) = \frac{/C\ell^*(\lambda)\ \sigma_s/^2}{4\ /\ell^*(\lambda)\ \Delta f - 2\ \sigma'_e(\ell,\lambda,T)/} \qquad (7)$$

Knowing the free-energy barrier it is possible to calculate the nucleation rate /9/

$$N(\lambda)/N(\lambda = 1) = \exp\left(-(\Delta F^*(\lambda) - \Delta F^*)/kT\right) \qquad (8)$$

where $\Delta F^* = \Delta F^*(\lambda = 1)$.

Proceeding from the condition of the stability of the metastable nucleus it is possible to determine its melting temperature /2/

$$T_m(\nu a \ell, \lambda) = \frac{T_m^o\left(1 - \frac{2\sigma_e}{\ell \Delta H} - \frac{C\sigma_s}{\Delta H \sqrt{\nu a}}\right)}{1 + \frac{1}{\Delta H \ell}\left[\sigma_e'(\ell, \lambda, T_m^o) - \sigma_e\right]} \qquad (9)$$

Discussion

Comparison with the classical theory /8/ shows that eqs(5),(6) and (7) are identical with the equations of the corresponding parameters in ref./8/ with the exception that the value $\sigma_e'(\ell, \lambda, T)$ taking into account the polymeric nature of the monocrystals is introduced instead of σ_e.

The above considerations suggest that knowing the changes in conformational entropies of loops and tie chains related to the decreas in their length (as in ref./5/, it is assumed that chain ends do not contribute to the conformational entropy) one can investigate various morphological forms of nucleation both with and without molecular deformation taking into account the defects of the edge surfaces of polymer monocrystals.

Assuming that the distance between loop ends for nucleation without deformation remains constant and that the distance between the ends of the tie chain changes /5/ we have calculated the corresponding changes in conformational entropies /6,7/ and considered two cases of nucleation under the conditions of molecular deformation /6,7/.

1.Folded-chain nuclei, $m = \nu/2$, where m is the number of loop-shaped portions /6/ and

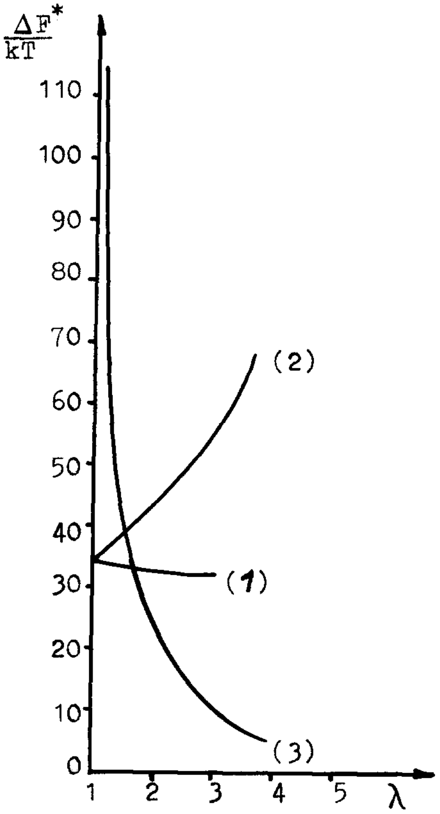
2.Bundle-like nuclei, $m = \nu$ where m is the number of tie chains /7/.

It has been established /7/ that at $\lambda \approx 2$ the transition from nucleation with chain folding to that with extended chains occurs. The changes in potential barriers to the free energy are shown in Fig. 1.

Eq.(3a) may be identified with eq.(2) in ref./10/ in which the excess surface free energy is also explained by a decreas in the entropy of chain portions remaining non-crystalline. However, in contrast to eq.(2) in ref./10/ eq.(3a) indicates that the specific edge surface energy in the orientational crystallization of polymers is not a constant value but should depend not only on the extent of defects in a monocrystals and the changes in conformational entropies of regions on its surface but also on the parameter λ. This may account for a wide range of the calculated values of σ_e obtained by different experimental methods. For example, for polyethylene (PE) the values of σ_e from 50 to 150 erg/cm^2 have been reported /11/.

Comparing in eq.(3a) the σ_e value to σ_{e0} in ref. /12/ the former, probably can be determined not only as the edge surface free energy in the absence of deformation /12/ but, rather, as the edge surface free energy of a nucleus of an infinitely small diameter as folliws directly eq.(3a) at $\Delta S_i(\ell,\lambda) \rightarrow 0$.

Taking into account the previous results of a numerical analysis of the above equations for PE /5,7/, the values of $\sigma_e'(\ell,\lambda,T)$ were calculated for the two cases of nucleation considered here (Fig.2). When the parameter λ increases, the value of $\sigma_e'(\ell,\lambda,T)$ drastically decreases for bundle-like nuclei and drastically increases for folded-chain nuclei for which the chain packing direction is normal to that of deformation. Figs 1 and 2 show the same type of dependences of these two functions on λ. These results suggest that the value of $\sigma_e'(\ell,\lambda,T)$ determines to a great extent the behaviour of thermodynamic parameters characterizing crystallization processes.



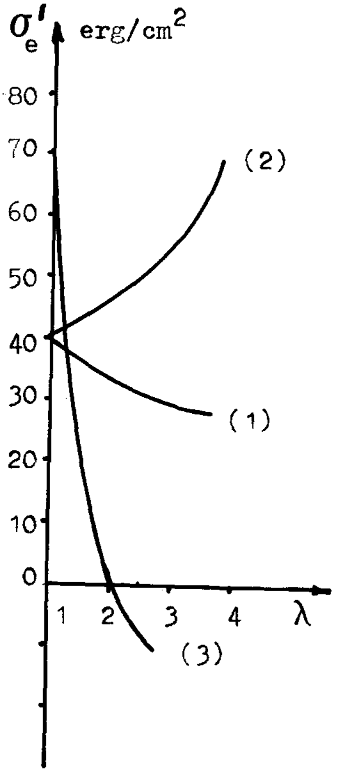


Fig. 1. Changes in potential barriers of molecular deformation λ for varios cases of nucleation. 1. folded-chain nuclei, axis λ is parallel to chain packing, 2. folded-chain nuclei, axis λ is normal to chain packing and 3. bundle-like nuclei

Fig. 2. Changes in surface edge free energy $\sigma_e'(\ell,\lambda,T)$ vs parameter of molecular deformation λ for various cases of nucleation (Designation as in the legened to Fig. 1)

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