$\beta\alpha$-BIFURCATION OF GROWTH DURING THE SPHERULITIC CRYSTALLIZATION OF POLYPROPYLENE

J. Varga, Y. Fujiwara*, A. Ille

Department of Plastics and Rubber,
Technical University H-1521 Budapest

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Abstract

Spontaneous β to α polymorphic transition occurs from pinpoint nuclei on the periphery of the growing β-spherulite of polypropylene at a high crystallisation temperature ($\beta\alpha$-bifurcation of growth), and its relative occurrence frequency increased with rising temperature. This is accompanied by a simultaneous decrease in growth rate. The phenomenon of $\beta\alpha$-bifurcation of growth was interpreted through secondary $\beta\alpha$-nucleation and the necessary energetic conditions and temperature dependence of this have been discussed.

Introduction

It was reported in a previous work [1] that segments of α-modification were forming on the periphery of growing β-spherulites during the stepwise isothermal crystallization of polypropylene when the temperature of crystallization (T_c) was raised above a critical level (designated as $T_{\beta\alpha}$). This α-phase developed from pinpoint nuclei generated on the surface of β-crystallites.

In the present paper a quantitative interpretation is attempted for this $\beta\alpha$-bifurcation of growth during crystallization, utilizing the principles of the kinetic theory of crystal growth (2—10). The quantitative description is based on the assumption that the secondary nuclei of the α-modification are formed on the surface of a β-crystallite (secondary $\beta\alpha$-nucleation). It is known (1, 11) that at lower crystallization temperatures ($T_c < T_{\beta\alpha}$), the reverse phenomena may occur, namely, β-phase forms on the surface of α-spherulites ($\alpha\beta$-bifurcation of growth). This phenomenon is, however, occasional and scarcely reproducible. Nevertheless, quantitative evaluation has also been extended to this case.

In order to quantify both the $\beta\alpha$- and $\alpha\beta$-bifurcations, the growth rate values of both modifications (G_α and G_β) are needed over a wide temperature range. At higher temperatures, however, no G_β values are available in the literature since β-spherulites are formed only below a certain limit temperature

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* Faculty of Science, Shizuoka University, Shizuoka, Japan.

(411 K according to Padden and Keith [12]). In the present work, G_β values were successfully determined over a wide temperature range, almost up to the fusion point of the β-modification, by the *stepwise crystallization* technique.

Results from studies on growth kinetics and the effect of temperature on the course of $\beta\alpha$-bifurcation of growth are also covered in this paper.

Experimental

High-molecular weight PP samples, containing special stabilizer and pigment were studied ($\bar{M}_w = 235\,000$; MFI 190/5=0.6 g/10 min).

The phenomenon of bifurcation during the crystal growth was monitored by a polarization microscope using a primary red filter. Black-and-white prints from the coloured slides are presented here.

G_α and G_β values were determined by observation of changes in size of spherulites with time. For the ascertainment of G_β values at elevated temperatures, β-spherulites of definite size were grown at a lower temperature to $T_{c1}=401$ to 408 K followed by raising the temperature to $T_{c2}=401$—423 K where growth rates were determined.

Experimental results

Investigation of the characteristics of $\beta\alpha$-bifurcation and the determination of growth rates of α- and β-modifications led to the following results:

The ratio of G_β to G_α decreases monotonously with increasing temperature. In contrast to the general opinion found in the literature [11, 12] that the growth rate of the β-modification is always higher than that of the α-modification, it was found in this work that above the temperature of $T_{\beta\alpha}$, $G_\alpha > G_\beta$ (Fig. 1).

Characteristic features of $\beta\alpha$-bifurcation of growth are illustrated by a series of photographs shown in Fig. 2. On the surface of the β-spherulites grown at the lower temperature step ($T_{c1}=408$ K), nuclei of α-phase are formed (Picture a, Fig. 2) that may grow to α-spherulitic segments if the temperature of the second isothermal step exceeds $T_{\beta\alpha}$ (Pictures b and c, Fig. 2). The peculiar shape of the α-spherulite segments on β-spherulites becomes especially noticeable during the fusion process (Pictures d, e, f, Fig. 2). It can be seen that the fusion of spherulites formed in two temperature steps proceeds in two steps again. The fraction of β-modification formed at the lower temperature step fuses first (Picture d, Fig. 2) followed by the fusion of the fraction crystallized at the higher temperature (Pictures e, Fig. 2). It is worth noting

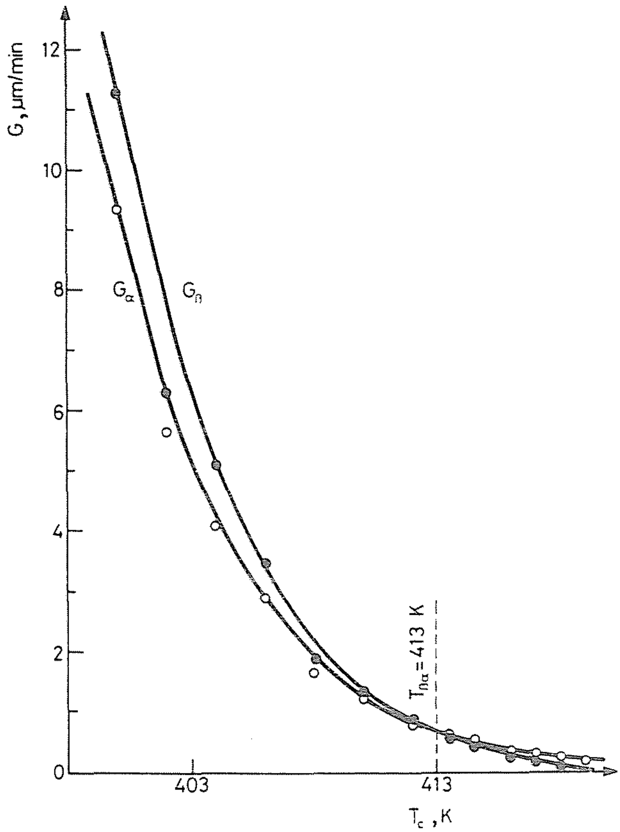
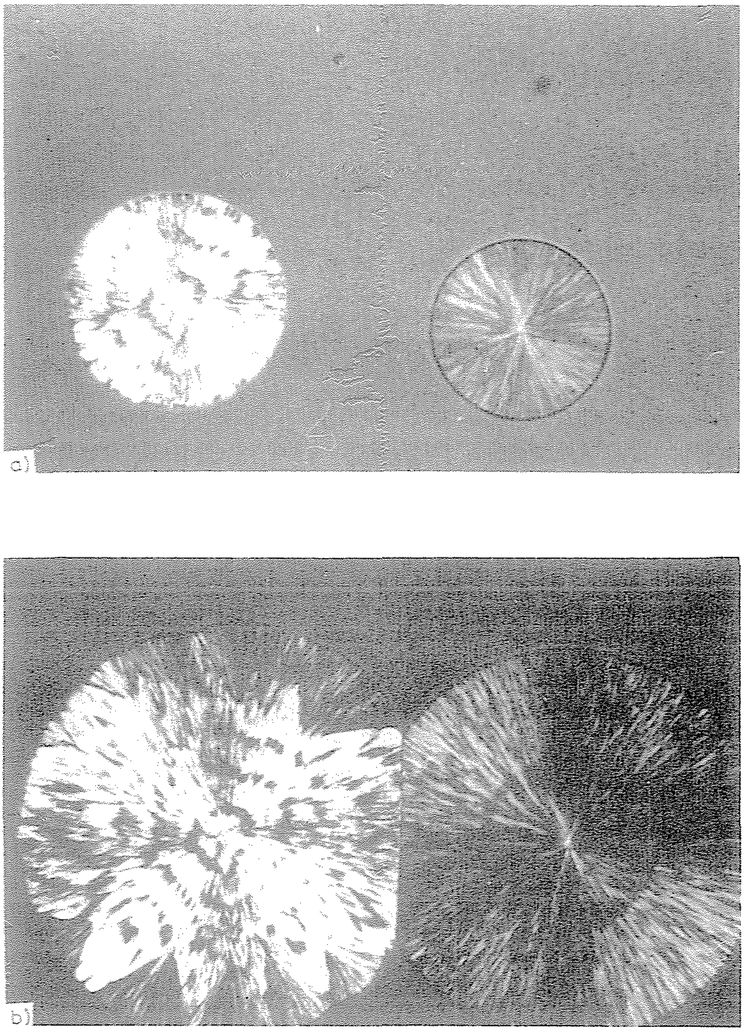


Fig. 1. Temperature dependence of linear growth rates (G_α, G_β) of modifications α and β, respectively

that the individual α-spherulites grown simultaneously during crystallization also fuse in two steps (Picture f, Fig. 2).

Growing segments of α-spherulites have a characteristic shape demonstrating the pinpoint nuclei on the surface of the β-spherulites they have evolved from. This peculiar shape contradict to the idea that they might be α-spherulite inclusions formed separately from the β-spherulites.

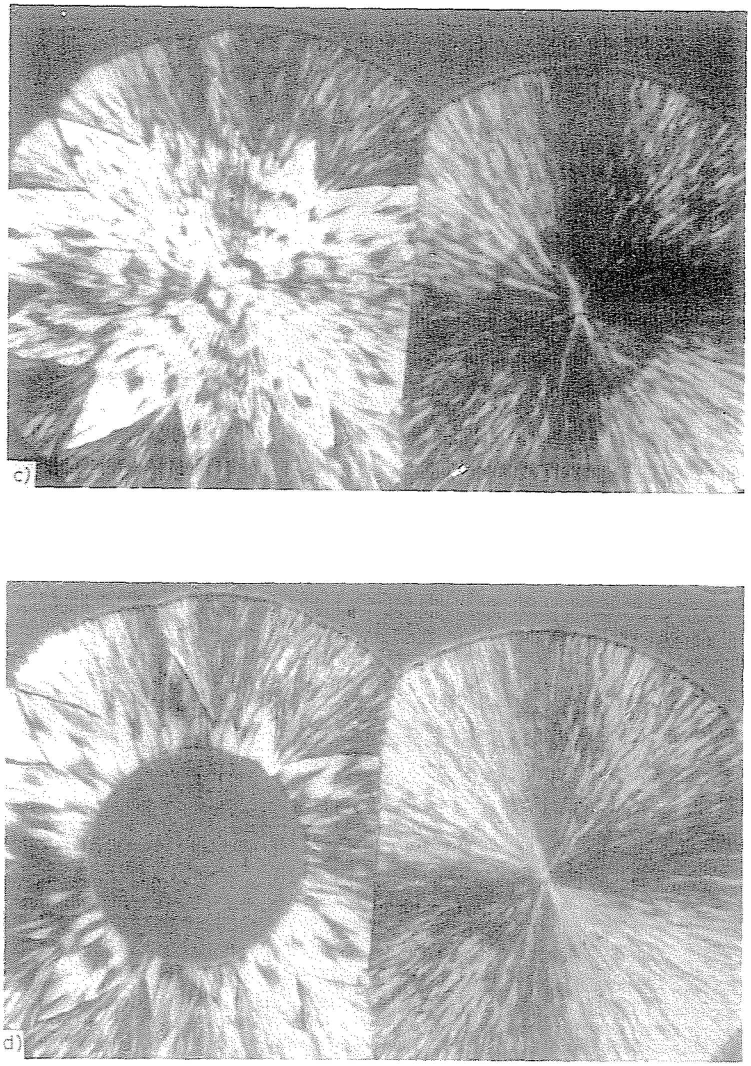
It can be deduced from the feature of fusion that no β to α-recrystallization of the basic spherulites crystallized in the first step is induced by the α-nuclei, in fact, β-spherulites continue to grow where uncovered by the α-modification. Other data demonstrate that a βα-transition in the solid state is not possible since the two modifications are constructed by different helices. Elementary cells of the α-modification consist of alternating right-handed and left-handed type 3_1 helices while in any crystal lattice of the β-modification, only helices



of one hand are present [13, 14]. A simple $\beta\alpha$-transition would, therefore, involve rewinding of helices, a process which is sterically hindered inside the crystalline phase.

The number of α-segments on the periphery of growing β-spherulites increases with rising temperature. As visualized by the series of photographs in Fig. 3, it is clearly noticeable in Picture c that an almost total $\beta\alpha$-transformation has taken place at the second temperature step.

It should be seen that the uncovered growing surface of the basic β-spherulites is becoming completely occupied by segments of α-spherulites



over a period of time. For this reason, the time range of measurement of G_β values is relatively narrow at high T_c. In spite of this fact, the accuracy of G_β determination is still satisfactory.

It must be emphasized when the experimental results are considered that the increase in the number of α-nuclei at elevated temperatures is accompanied by a simultaneous decrease in the growth rate (Fig. 1). The increase in number of α-nuclei can be deduced from the change in the ratio of α to β nucleation. Its quantitative interpretation is discussed below.

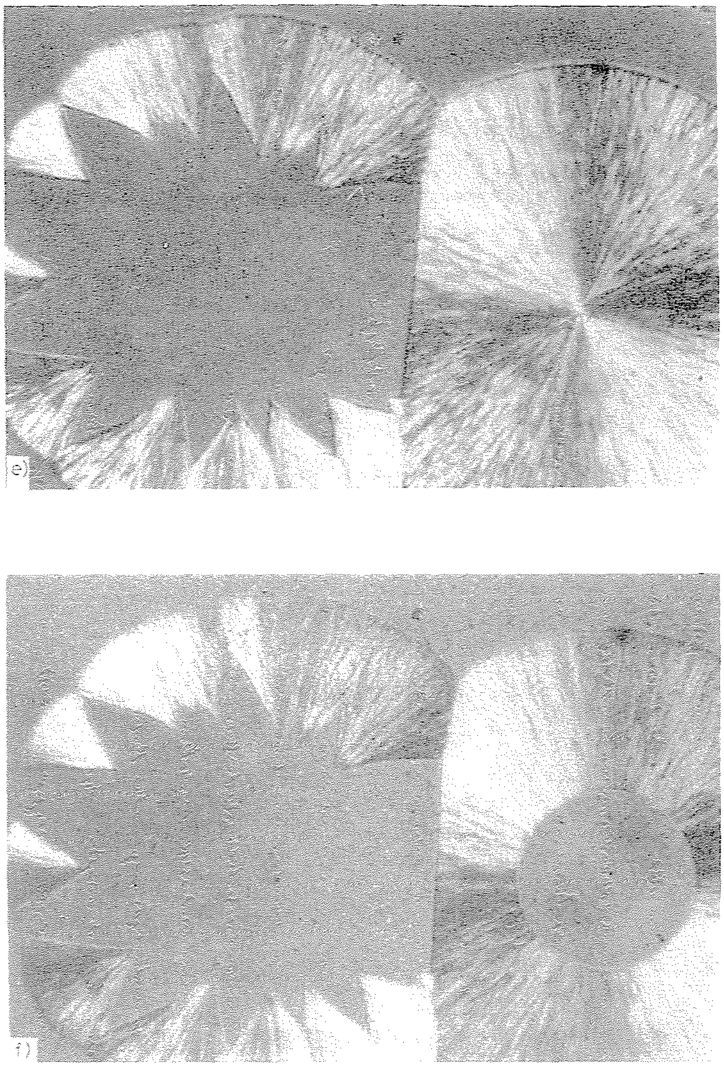
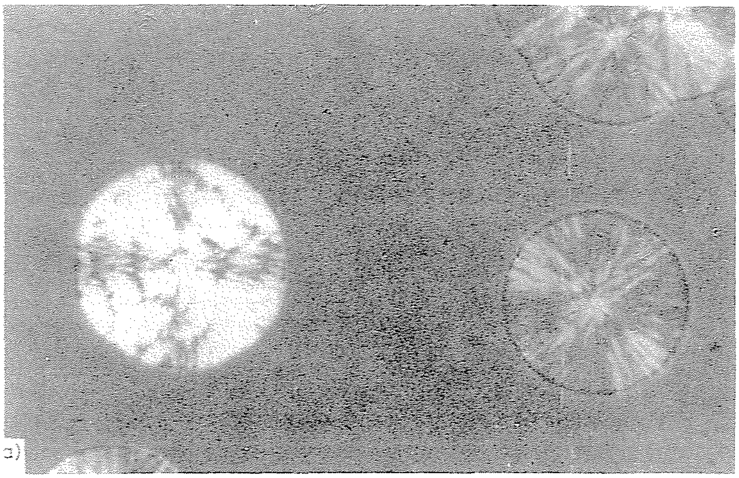
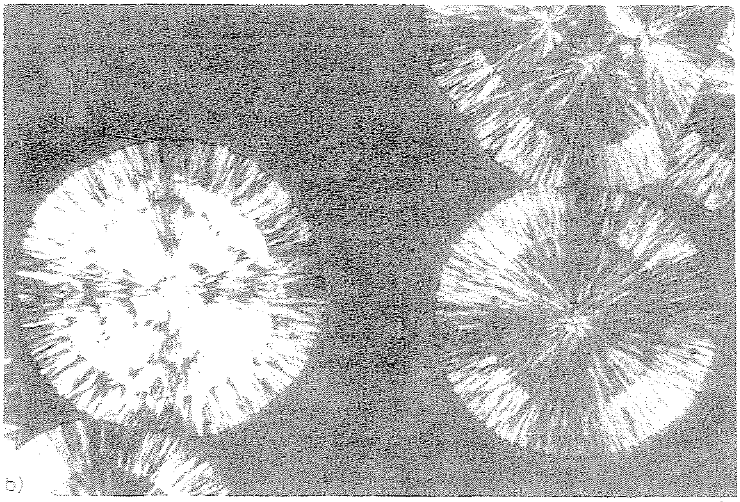


Fig. 2. α- and β-spherulites grown by stepwise crystallization and their fusion characteristics
Picture a: spherulites formed at the first temperature step ($T_{c1}=408$ K)
Pictures b, c: crystal growth and $\beta\alpha$-bifurcation at $T_{c2}=415.5$ K ($t_c=290$ and 510 min),
Pictures d, e, f: stepwise fusion of spherulites at 430.5 K, 436.5 K and 440 K


a)


b)

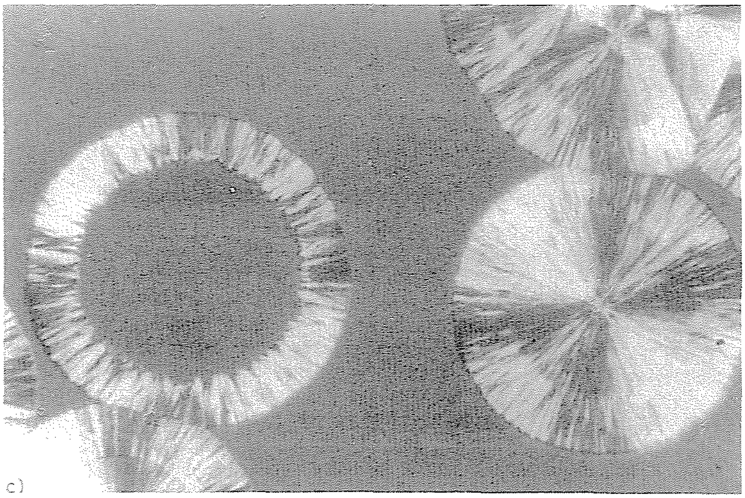


Fig. 3. β-Spherulites grown by stepwise crystallization and their fusion
Picture a: structure formed at he first temperature step ($T_c = 408$ K),
Picture b: growth at $T_{c2} = 418$ K, $t_c = 390$ min,
Picture c: structure at 436.5 K after the complete fusion of β-modification

Interpretation of $\beta\alpha$-bifurcation on the basis of secondary $\beta\alpha$-nucleation

The growth rate is controlled by the rates of secondary nucleation and of transport processes. The growth rate (G) can be described by the following equation:

$$G = G_0 \exp \frac{-Q^*}{RT_c} \exp \frac{-\Delta\Phi^*}{kT_c} \tag{1}$$

where G_0 is the pre-exponential factor (frequency factor),
$\Delta\Phi^*$ is the free energy of formation of secondary nuclei of critical size,
Q^* is the activation energy of transport processes,
k and R are the Boltzmann and the gas constants, resp.

According to the kinetic theory of crystallization of polymers [8—10], the free energy of formation of secondary nuclei of critical size is:

$$\Delta\Phi^* = X \frac{b\sigma\sigma_e T_m^0}{\Delta H_f \cdot \Delta T} \tag{2}$$

where X is a factor depending on the growth regime, as discussed below
T_m^0 is the equilibrium melting temperature,

ΔT is the supercooling ($\Delta T = T_m^0 - T_c$),

ΔH_f is the enthalpy of fusion (J/cm^3),

σ, σ_e are the free energies of surfaces parallel with the polymer chains, and that of fold surface resp.

b is the layer thickness of secondary nuclei.

Secondary nucleation as a principal factor of growth may proceed by three different mechanisms depending on the temperature. On this basis, Hoffman [8—10] described three kinds of growth regimes (I, II, III).

At a high temperature of crystallization, with small supercooling (Regime I), secondary nucleation is the dominant process. A single secondary nucleus on the growing surface generates the new monomolecular layer through rapid lateral growth. At a medium supercooling (Regime II), multiple secondary nucleation is typical, i.e. several secondary nuclei are simultaneously created on the growing surface and the new crystalline layer is formed by their lateral growth. At a high supercooling (Regime III), the secondary nuclei may be formed even on the uncompleted crystal surface. Factor X in Equation (2) is equal to 4 in Regimes I and III but 2 in Regime II.

The temperature dependence of the growth rates of α- and β-modifications was treated using Equations (1) and (2), applying the usual correction by the transport factor [10], resulting in the curves of Fig. 4. It can be established on this basis that growth takes place in Regimes II and III in the temperature range studied. The transition temperature from Regime II to III (T(II—III)) is 408+1 K for the α-modification. This value is close to that obtained by Clark and Hoffman [10]. This temperature is nearly identical for the β-modification, T(II—III)=406+1 K.

In the present work, we searched for the conditions under which an α- or β-extraneous secondary nucleation is possible on the growing crystal

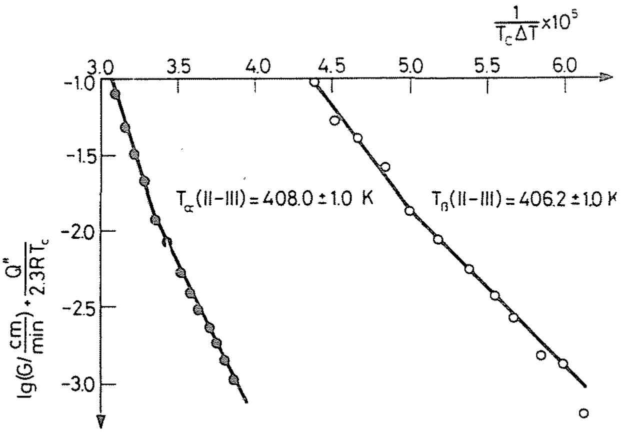


Fig. 4. Processing of G_α and G_β values by Equations (1) and (2)

surface of a given (β or α) modification, respectively (secondary $\beta\alpha$- or $\alpha\beta$-nucleation), in other words, *whether the surface of β-crystallites has an α-nucleating effect*. For this reason, the normal case of secondary nucleation, i.e. when the nucleus has the same modification as the surface of the basic crystallite, will be designated as $\alpha\alpha$- or $\beta\beta$-nucleation for the sake of unanimity.

Obviously, Equations (1) and (2) are equally suitable for description of growth rates of both modifications (α and β). The specific values in the Equations (T_m^0, σ, σ_e, b, ΔH_f, ΔT), however, are different for the two modifications, thus they are distinguished by subscripts.

In this paper it was assumed that the transport factor and frequency factor are equal for the two different modifications. G_0 depends on the molecular length, the crystallographic data, namely the thickness of monolayer and the direction of layer normal to the spherulite radius, as well as the growth regime. Our experiments were made on the same material, and, luckily, the temperatures of regime transition T(II—III) were found to be nearly equal for the α- and β-modifications. The difference due to the crystallographic origin is supposed to be fairly small. Therefore we can assume that $(G_0)_\alpha = (G_0)_\beta$ for the temperature range under consideration. For this reason, the difference between G_α and G_β is attributed essentially to the differences in free energies of secondary nucleation ($\Delta\Phi^*_{\alpha\alpha}$ and $\Delta\Phi^*_{\beta\beta}$).

It has been shown in Fig. 1 that $G_\alpha = G_\beta$ at the temperature $T_{\beta\alpha}$. It can be established from the data in Fig. 4 that growth proceeds according to Regime II at this temperature for both α and β form.

It can be stated on this basis that

$$\Delta\Phi^*_{\alpha\alpha} = \Delta\Phi^*_{\beta\beta} \tag{3}$$

as deduced from the equality of G_α and G_β at the temperature $T_{\beta\alpha}$. This means that

$$\frac{b_\alpha\sigma_\alpha(\sigma_e)_\alpha(T_m^0)_\alpha}{\Delta T_\alpha(\Delta H_f)_\alpha} = \frac{b_\beta\sigma_\beta(\sigma_e)_\beta(T_m^0)_\beta}{\Delta T_\beta(\Delta H_f)_\beta} \tag{4}$$

where

$$\Delta T_\alpha = (T_m^0)_\alpha - T_c \qquad \Delta T_\beta = (T_m^0)_\beta - T_c$$

At the crystallization temperature of $T_c = T_{\beta\alpha}$ Equation (4) can be rearranged as follows:

$$\frac{b_\beta\sigma_\beta(T_m^0)_\beta\dfrac{(\sigma_e)_\beta}{(\Delta H_f)_\beta}}{b_\alpha\sigma_\alpha(T_m^0)_\alpha\dfrac{(\sigma_e)_\alpha}{(\Delta H_f)_\alpha}} = \frac{(T_m^0)_\beta - T_{\beta\alpha}}{(T_m^0)_\alpha - T_{\beta\alpha}} = \frac{\Delta T_\beta}{\Delta T_\alpha} = K \tag{5}$$

The left-hand side of Equation (5) comprises only various specific parameters that are practically independent of the temperature of crystallization, and can thus be designated by a constant K.

Since $(T^0_{\mathrm{m}})>(T^0_{\mathrm{m}})$, it follows that $0<K<1$.

It can be deduced from Equations (3) to (5) that a simple relation exists between the free energies of the secondary $\alpha\alpha$- and $\beta\beta$-nucleation:

$$\frac{\Delta\Phi^*_{\beta\beta}}{\Delta\Phi^*_{\alpha\alpha}}=\frac{\Delta T_\beta}{K\Delta T_\alpha} \tag{6}$$

which can be rearranged into the following form:

$$\frac{\Delta\Phi^*_{\beta\beta}}{\Delta\Phi^*_{\alpha\alpha}}=\left\{1+\frac{\Delta T_{\mathrm{m}}}{\Delta T_\beta}\right\}. \tag{7}$$

Where

$$\Delta T_{\mathrm{m}}=(T^0_{\mathrm{m}})_\alpha-(T^0_{\mathrm{m}})_\beta>0 \tag{8}$$

Let us consider next the conditions of secondary $\beta\alpha$-nucleation using the Equations (5) to (8), as deduced above. The formation of a secondary nucleus of α-modification on the surface of a β-crystallite (secondary $\beta\alpha$-nucleus) is illustrated in Fig. 5.

The free energy of the secondary $\beta\alpha$-nucleation is controlled by volume and surface energies. In accordance with the kinetic theory of crystallization

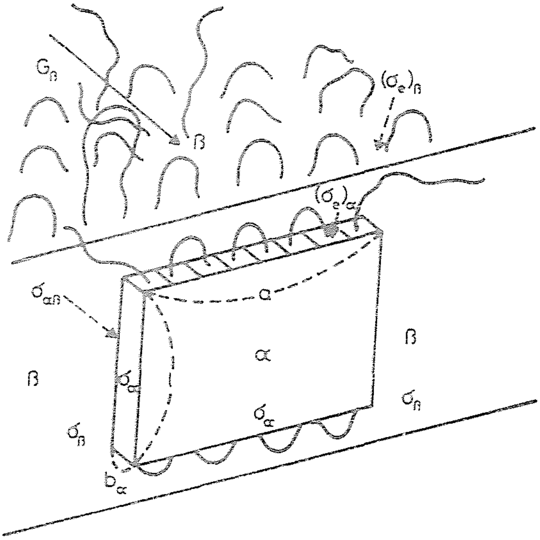


Fig. 5. Outline of the secondary $\beta\alpha$-nucleation: Formation of a secondary α-nucleus with dimensions a, b, l on the surface of a β-crystallite. Free energy values of side and fold surfaces for both modifications, σ_α, σ_β and $(\sigma_e)_\alpha$, $(\sigma_e)_\beta$. Surface energy, $\sigma_{\alpha\beta}$, at the interface between the α- and β-modification

of polymers (7), the following equation can be established by using the symbols shown in Fig. 5:

$$\Delta\Phi_{\beta\alpha} = 2b_\alpha l\sigma_\alpha + 2ab_\alpha(\sigma_e)_\alpha + al\Delta\sigma - ab_\alpha l(\Delta f)_\alpha \tag{9}$$

where

$$\Delta\sigma = \sigma_{\alpha\beta} + \sigma_\alpha - \sigma_\beta \tag{10}$$

Δf is the difference between the free energies of the crystalline and amorphous phase, usually approximated as

$$\Delta f = \frac{\Delta H_f}{T_m^0} \cdot \Delta T$$

$\sigma_{\alpha\beta}$ is the interfacial energy between the crystal surfaces α and β.

Critical dimensions of secondary nuclei (a^*, l^*) and the free energy of their formation ($\Delta\Phi^*_{\beta\alpha}$) can be calculated from the limit values of Equation (9), obtained by a suitable differentiation process as follows:

$$a^* = \frac{2b_\alpha\sigma_\alpha}{b_\alpha(\Delta f)_\alpha - \Delta\sigma} \qquad l^* = \frac{2b_\alpha(\sigma_e)_\alpha}{b_\alpha(\Delta f)_\alpha - \Delta\sigma} \tag{11}$$

$$\Delta\Phi^*_{\beta\alpha} = \frac{4b_\alpha^2\sigma_\alpha(\sigma_e)_\alpha(T_m^0)_\alpha}{b_\alpha(\Delta H_f)_\alpha\Delta T_\alpha - \Delta\sigma(T_m^0)_\alpha} \tag{12}$$

On the basis of Equations (2) and (12), the ratio of free energy of secondary $\beta\beta$-nucleation to that of $\beta\alpha$-nucleation can be established:

$$\frac{\Delta\Phi^*_{\beta\beta}}{\Delta\Phi^*_{\beta\alpha}} = \frac{b_\beta\sigma_\beta\dfrac{(\sigma_e)_\beta}{(\Delta H_f)_\beta}(T_m^0)_\beta\Delta T_\alpha}{b_\alpha\sigma_\alpha\dfrac{(\sigma_e)_\alpha}{(\Delta H_f)_\alpha}(T_m^0)_\alpha\Delta T_\alpha} - \frac{b_\beta\sigma_\beta(\sigma_e)_\beta\Delta\sigma(T_m^0)_\beta}{b_\alpha^2\sigma_\alpha(\sigma_e)_\alpha(\Delta H_f)_\beta\Delta T_\beta} \tag{13}$$

Equation (13) can be reduced as follows:

$$\frac{\Delta\Phi^*_{\beta\beta}}{\Delta\Phi_{\beta\alpha}} = K + \frac{K}{\Delta T_\beta}(\Delta T_m - A_\alpha\Delta\sigma) \tag{14}$$

where

$$A_\alpha = \frac{(T_m^0)_\alpha}{b_\alpha(\Delta H_f)_\alpha} \tag{15}$$

Equation (14) is plotted in a linearized form in Fig. 6. It can be seen that the direction and slope of the straight line depend on the value of $\Delta\sigma$. If $\Delta\sigma$ is lower than a critical $\Delta\sigma^*$ value (Fig. 6):

$$\Delta\sigma < \Delta\sigma^* = b_\alpha(\Delta H_f)_\alpha\frac{\Delta T_m}{(T_m^0)_\alpha} \tag{16}$$

then the ratio of free energies increases with rising temperature and reaches unity at a certain temperature (point Q in Fig. 6). At this temperature, the probability of secondary $\beta\beta$- and $\beta\alpha$-nucleations are then equal. When $\Delta\sigma = 0$, no energy difference exists between the two kinds of secondary nucleations and Equation (14) is reduced to Equation (7) (point P in Fig. 6).

From the experimental observation that the frequency of $\beta\alpha$-bifurcation of growth increases with temperature, it follows that $\Delta\sigma < \Delta\sigma^*$.

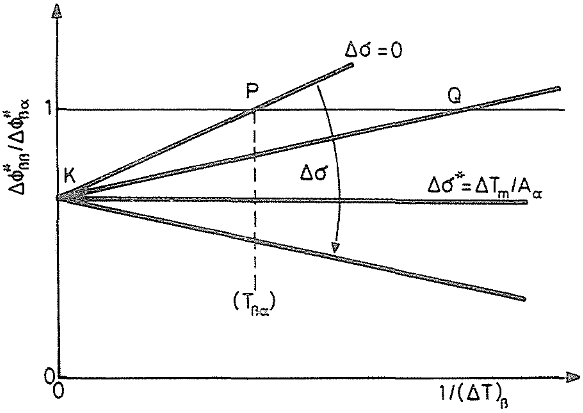


Fig. 6. Linearized plot of Equation (14)

Possibility of secondary $\alpha\beta$-nucleation

The formation of a secondary nucleus of β-modification on the growing surface of an α-crystallite can be interpreted similarly. Thus, Equation (13) can be re-written by the corresponding changes in subscripts as follows:

$$\frac{\Delta\Phi^*_{\alpha\alpha}}{\Delta\Phi^*_{\alpha\beta}} = \frac{1}{K} - \frac{1}{K\Delta T_\alpha}(\Delta T_m + A_\beta \Delta\sigma') \tag{17}$$

where

$$\Delta\sigma' = \sigma_{\alpha\beta} - \sigma_\alpha + \sigma_\beta \tag{18}$$

and

$$A_\beta = \frac{(T^0_m)_\beta}{b_\beta(\Delta H_f)_\beta} \tag{19}$$

Equation (17) is demonstrated graphically in Fig. 7. It can be established that the probability of an $\alpha\beta$-bifurcation of growth increases monotonously with decreasing temperature independently of the magnitude of $\Delta\sigma'$.

It should be noted that a reliable physical meaning can only be assigned to Equations (14) and (17) in the range between the fusion point of the

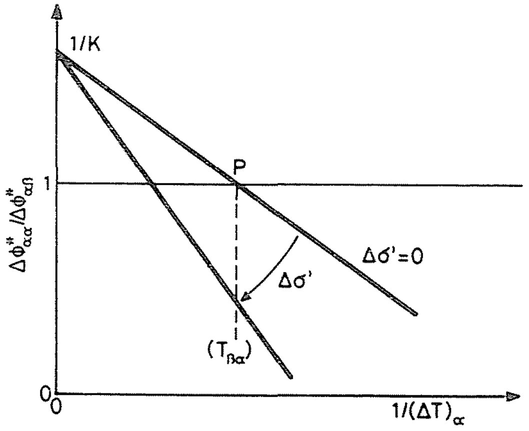


Fig. 7. Linearized plot of Equation (17)

modifications and the glass transition temperature. In fact, the Equations fit correctly only in the temperature range where growth of the modifications proceeds in the same Regime.

Preconditions of $\beta\alpha$- and $\alpha\beta$-modification change

The emergence of an extraneous secondary nucleus of critical size (secondary $\beta\alpha$- or $\alpha\beta$-nucleation) on a growing crystal surface does not lead necessarily to a growth transformation. It also requires some other conditions such as:

1. Extraneous secondary nucleus generated on a growing lamellar surface must grow and complete one monolayer of new modification, either immediately in that layer, or after successive attachment of a number of monolayers.

2. After completion of transformation on the whole surface of the growing lamella, this new modification surface must have larger growth rate than that of surrounding lamellae.

According to Condition 2, $\beta\alpha$-growth transformation is possible to proceed above $T_{\beta\alpha}$ while $\alpha\beta$-growth transformation is only possible below this temperature. Condition 1 is more complex. The actual conditions are determined by the feature of the growth regime and by the lateral growth rate of extraneous secondary nuclei. A monomolecular layer of the new phase may be formed either from a single extraneous secondary nucleus (Regime I) or by successive lamination of increasingly wider layers of the new phase (Regimes II and III).

As a result, only a certain proportion of the extraneous secondary nuclei may generate bifurcation even for the case of Condition 2.

For the determination of $\Delta\sigma^*$ or the semiquantitative evaluation of $\beta\alpha$-bifurcation, the material parameters (ΔH_f, T_m^0, σ and dimensions of the elementary cell) need to be understood. The data available in the literature for the individual constants, however, are highly variable even in the case of the α-modification which is well understood e.g. $(T_m^0)_\alpha$ falls between 456 and 493 K while $(\Delta H_f)_\alpha$ is between 63 and 260 J/g (15). The majority of the data for the β-modification has been found by us (16). The material parameters from the literature are collected in Table 1. Underlined data have been utilized for obtaining the kinetic data of growth (Fig. 4). These data are very close to those obtained in our laboratory.

Table 1

Material parameters of α-and β-modifications of polypropylene

Parameters		α-modification		β-modification	
			Ref.		Ref.
T_m^0	(K)	$\underline{481}$	17	$\underline{457}$	16
		458	20	443	20
		493	21		
ΔH_f	(J/g)	$\underline{146.5}$	17	$\underline{113.0}$	16
		209.3	10		
ϱ	(g/cm³)	0.936	10	0.920	22
a_0	(nm)	0.549	10	0.636	
b	(nm)	0.626	10	0.55	
σ	(J/m²)	8.04×10^{-3}	**	6.17×10^{-3}	16

* Thickness and width per one segment of the monomolecular layer considering the growth planes (110) and (300) for the modifications α and β respectively.

** Calculated from the underlined data.

Employing these values the following constants can be deduced:

$$\Delta\sigma < \Delta\sigma^* = 4.28 \times 10^{-3}\ \mathrm{J/m^2}$$

$$K = 0.647$$

$$A_\alpha = 5.6 \times 10^3\ \mathrm{K\ m^2/J}$$

Considering the σ_α and σ_β values given in Table 1 the interfacial free energy between the α- and β-modifications becomes using Equation (10):

$$\sigma_{\alpha\beta} < 2.41 \times 10^{-3}\ \mathrm{J/m^2}$$

According to optical observations, the temperature of over-all change of $\beta\alpha$-transformation is near the actual fusion point of the β-modification which is about 432 to 435 K (Pictures d, e in Fig. 3), corresponding to ΔT_β a little larger than 22 to 24 K. If we assume here that (a) such over-all $\beta\alpha$-transformation temperature corresponds to the condition

$$\Delta\Phi^*_{\beta\beta} = \Delta\Phi^*_{\beta\alpha} \tag{20}$$

and (b) ΔT_β is practically equal to the above value, by substituting this ΔT_β value and other related quantities from Table 1 into Equation (14) we get

$$\Delta\sigma = 1.96 \text{ to } 2.15 \times 10^{-3}\ \mathrm{J/m^2}$$

Accepting these values and applying them in equation (10),

$$\sigma_{\alpha\beta} = 0.09 \text{ to } 0.28 \times 10^{-3}\ \mathrm{J/m^2}$$

Then the possible values for $\Delta\sigma$ and $\sigma_{\alpha\beta}$ under the above assumptions are in the temperature range between $T_{\alpha\beta}$ and $T_{m\beta}$:

$$\Delta\sigma = 4.28 \text{ to } 1.96 \times 10^{-3}\ \mathrm{J/m^2}$$

$$\sigma_{\alpha\beta} = 0.09 \text{ to } 2.41 \times 10^{-3}\ \mathrm{J/m^2}$$

The small differences between the free energies of the two modifications σ_α, σ_β and that of $(\Delta H_f)_\alpha$ and $(\Delta H_f)_\beta$ provides the thermodynamic condition for the $\beta\alpha$-growth transformation.

Synopsis

During the stepwise crystallization of polypropylene, $\beta\alpha$-bifurcation of growth was observed on the periphery of growing β-spherulites if the temperature of the second crystallization step was above $T_{\beta\alpha} = 413$ K. The relative frequency of $\beta\alpha$-bifurcation of growth increased with rising temperature. The phenomenon of $\beta\alpha$-bifurcation of growth was interpreted by considering secondary $\beta\alpha$-nucleation, based on the kinetic theory of crystallization, and an analysis of energetics for this was carried out. Kinetic growth data necessary for the quantitative evaluation of $\beta\alpha$-bifurcation of growth were determined over a wide temperature range. It was established that above $T_{\beta\alpha} = 413$ K the growth rate of the α-modification exceeded that of the β-modification. In the range studied, crystallization took place in Hoffman's Regimes II and III. Cross-over temperatures between the two Regimes were 408 ± 1 K and 406.2 ± 1 K for modifications α and β, respectively.

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Dr. József VARGA } H-1521, Budapest
A. ILLE }
Y. FUJIWARA Faculty of Science, Shizuoka University
Shizuoka, Japán