

## CRYSTALLIZATION OF POLYPROPYLENE: APPLICATION OF DIFFERENTIAL SCANNING CALORIMETRY

### PART II. CRYSTAL FORMS AND NUCLEATION

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**Abstract:** The influence of homogeneous and heterogeneous nucleation on crystallization processes of isotactic polypropylene (iPP) and its kinetic and thermodynamic parameters is summarized and discussed, as evaluated by DSC measurements.

**Key words:** polypropylene; isotactic; crystallization behavior; crystal forms; nucleation effects; differential scanning calorimetry (DSC).

#### 1. INTRODUCTION

Polypropylene is one of the most important commercial polymers because of its relatively low cost, versatility, recyclability and good mechanical performance in engineering applications. The polypropylene chain exhibits three different configurations, the regular isotactic and syndiotactic and the irregular atactic configurations, which are defined by the position of methyl group in the relation to the polymer backbone. The position of the methyl groups determines not only the configuration but also the preferred conformation of the polymer chain, which affect the crystallization and crystal form of the polymer [1, 2–7]. This polymer exhibits three different crystalline phases:  $\alpha$  (monoclinic),  $\beta$  (hexagonal), and  $\gamma$  (triclinic). During high undercooling, a mesophase, usually called ‘smectic’ is formed instead of crystalline phase.

One of the major goals of nucleation is to modify the crystallization kinetics and the crystallization temperature  $T_c$ , which is important in processing

because an increase in the crystallization temperature due to nucleation enables shortening of the process cycle time, with obvious advantages for extrusion and injection molding. For some crystalline polymers, the addition of nucleator is significant for modifying the fine structure and improving the physical properties of the product. Particularly for iPP which normally forms large spherulites from melt, it is a benefit that the increase in the density of nuclei, and hence the decrease in the diameter of spherulites below the wavelength of visible light, improves the transparency of the moulds [8].

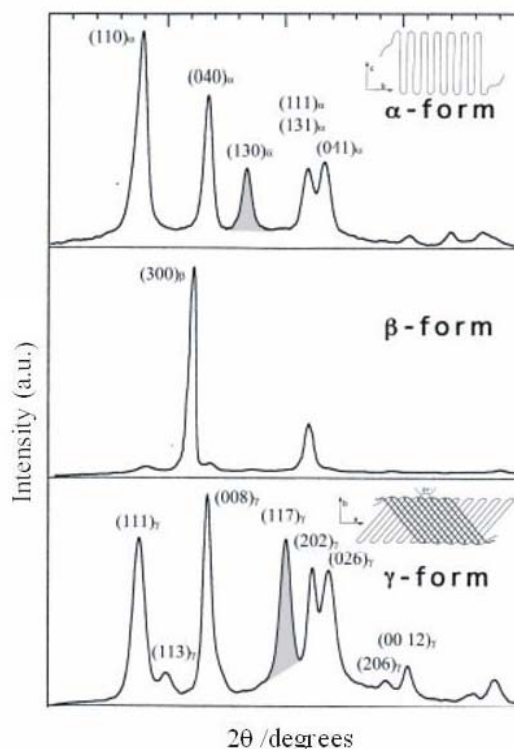
In the first part of our article the theoretical aspects of crystallization of iPP and application of DSC analysis were analyzed. The aim of this work is to discuss the influence of homogeneous and heterogeneous nucleation on crystallization processes of isotactic polypropylene and its kinetic and thermodynamic parameters, as evaluated by DSC measurements.

## 2. CRYSTAL FORMS OF ISOTACTIC POLYPROPYLENE

iPP is a semicrystalline thermoplastic polymer with high tendency to crystallization due to its regular chain structure, having a low specific weight, excellent dielectric properties, chemical inertia and damp resistance typical of the olefin polymers. Investigation of iPP has contributed considerably to the understanding of the crystal structure, the kinetics of crystallization, the melting characteristics and the different supermolecular structures (spherulites, cylindrite, hedrite, quadrite) of polymers.

### 2.1. Polymorphism of iPP

The structure and morphology of iPP have provided for fascinating studies and have reached a stage where the understanding is near completion. A particular characteristic of iPP is its polymorphous behavior, as it is known that this polymer has various forms of iPP crystals:  $\alpha$ -,  $\beta$ -,  $\gamma$ - and mesomorphic forms. In all of these structures, the chain conformation of each individual molecular chain is believed to be identical with a 3/1 helical conformation [1, 8]. This allows crystallization of chains. The different crystal structures are distinct due to the different chain packing geometries of the helices, which depend upon crystallization conditions and molecular characteristics (Fig. 1). It has been proved that the crystallization behavior of the semi-crystalline phase in PP has a significant influence on mechanical properties i.e. the  $\beta$ -form PP exhibits much higher impact toughness than the  $\alpha$ -form PP [1, 9].



**Fig. 1.** The WAXS patterns of the different PP phases and their crystal structures. (Salamone, 1996. Diagnostic reflections are shaded. Courtesy F. Auriemma and C. DeRosa, Naples University)

**$\alpha$ -form.** The monoclinic  $\alpha$  form is the best known and the most common crystalline state of iPP, being formed in melt-crystallized and solution-crystallized iPP. The crystal unit cell dimensions of the  $\alpha$ -form with a crystallographic symmetry of P21/c, is reported by Turner-Jones et al. [10], which represents a small change from those originally reported by Natta and Corradini [11].

The  $\alpha$  form of iPP also has two isomeric helices as a result of different positioning of the methyl groups within the polymer. This form in iPP can be recrystallized or thermal treated from a less ordered  $\alpha_1$  form (with random distribution of methyl groups) to more ordered  $\alpha_2$  form with strong-defined deposition of these groups in the crystal unit cell. The monoclinic  $\alpha$ -form in different temperature range has different respective birefringence values [1].

**$\beta$ -form.** The hexagonal  $\beta$ -form occurs much more rarely in iPP and is thermodynamically less stable than  $\alpha$ -form under normal crystallization conditions. In most cases, the  $\beta$ -form can only be partially formed in samples mixed with  $\alpha$ -form. The hexagonal lattices of the  $\beta$ -form are characterized by a strong negative birefringence.

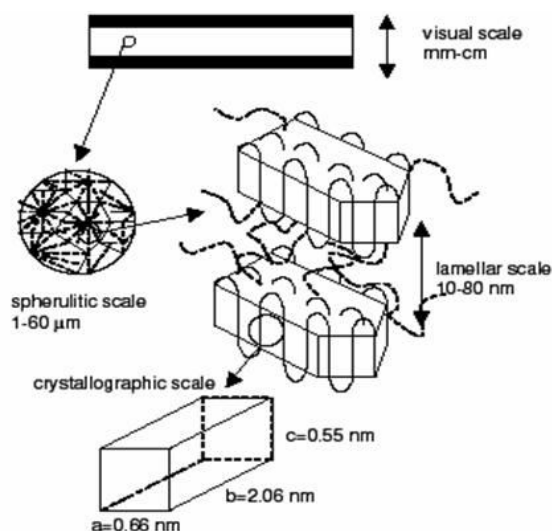
A high content of the  $\beta$ -form in iPP can be achieved under special conditions such as rapid quenching, zone solidification, crystallization under a temperature gradient [12, 13] or in the presence of selective  $\beta$  nucleating agents [14–27]. During deformation, the  $\beta$ -form in iPP can be transformed into  $\alpha$ -form at high temperature or by melt recrystallization at elevated temperature close to the melting temperature of bulk samples.

**$\gamma$ -form.** Conformation of macromolecules in  $\gamma$ -form is analogous to  $\alpha$ -form. The  $\gamma$ -form can be obtained as a result of crystallization under elevated pressure above 200 MPa and from iPP samples with a low molecular weight. Random copolymers of propylene with other olefins can crystallize in the  $\gamma$ -form. According to Zannetti and coworkers, the content of the  $\gamma$  form in copolymer increases as the amount of the comonomer in the chain increases, which is in a good agreement with the observation of Turner-Jones [28].

## 2.2. Morphological scales in iPP

As a semicrystalline polymer iPP shows a hierarchic morphological ordering (Fig. 2). The isotactic molecular chain arranges in a helical conformation forming a monoclinic unit cell. The unit cell dimensions for  $\alpha$ -crystalline are of the size of a few nm and can be observed by wide-angle X-ray diffraction (WAXD). These small unit cell form lamellae can be observed by small angle X-ray diffraction (SAXD). The next higher morphological step is formed by spherulites consisting block of lamellae-shaped crystals. The dimensions are in order of 1 to 50  $\mu\text{m}$  and can be accessed by polarizing light microscopy (PLM). The morphological biggest scale reveals finally visually i.e. skin-core morphology [29, 30].

From several literature reports on morphology of melt-crystallized iPP, it was clearly stated that the crystalline morphology of iPP is dominated by a highly characteristic lamellar branching (crosshatching), with radial and tangential lamellae (chains perpendicular, and parallel to spherulitic radius, respectively) [31, 32].



**Fig. 2.** Morphological scales in iPP with indicated size of dimensions for  $\alpha$ -crystalline form [33]

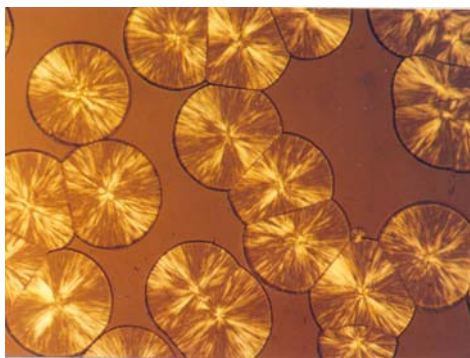
The ratio between the number of radial and tangential lamellae determines the sign of birefringence. Early studies by Padden and Keith suggested the formation of five different types of spherulites consisting of crystals in  $\alpha$ - and  $\beta$ -modification ( $\alpha$ - and  $\beta$ -spherulites) during melt crystallization [34–36]. In particular, they demonstrated that three types of  $\alpha$ -spherulites might be formed depending on crystallization temperature: positive ( $\alpha_I$ ) below 134 °C, negative above 137 °C ( $\alpha_{II}$ ), and mixed-type spherulites in the intermediate temperature range ( $\alpha_{III}$ ).

The different optical characteristics of  $\alpha$ -spherulites have been linked to lamellar morphology through the balance of crosshatched radial and tangential lamellae. In this way, negatively birefringent  $\alpha_{II}$  spherulites are dominated by radial lamellae, whereas  $\alpha_I$  positively birefringent spherulites contain increased quantities of tangential lamellae. Increasing the temperature of crystallization leads to a reduction in the proportion of tangential lamellae and simultaneously, to a transformation of the birefringence from positive to negative. Transition between negative and positive birefringence occurs when approximately one-third of lamellae are tangential [31, 32]. No tangential fibrils form above 155 °C. It was also revealed that the thickness of tangential fibrils was lower than that of radial ones.

It has been observed that  $\beta$ -form iPP lamellar crystals exhibit neither the peculiar lath-like form nor the crosshatched lamellar morphology of  $\alpha$ -form iPP crystals.  $\beta$ -form iPP lamellar crystals are consistently observed to show an extended sheet morphology characterized by frequent giant screw dislocation [37–39].

This crystal structure difference leads to an approximately 10 °C difference in the melting points of  $\alpha$ - and  $\beta$ -form crystals, which can be easily discriminated by either differential scanning calorimetry (DSC) or hot stage PLM [40, 41]. Normally, the melting point of the  $\beta$ -form lamellae is near 152 to 164 °C, while the melting of the  $\alpha$ -form lamellae occurs above 164 °C. Moreover, the  $\alpha$ -form lamellae can still grow in the temperature range from 152 to 164 °C. Suppose now that  $\alpha$ -crystals grow from the melt of a newly melted adjacent  $\beta$ -crystal. The  $\alpha$ -crystal requires an equal mixed of right- and left-handed helices, while the newly created melt of the  $\beta$ -crystal will have only one of these types [42–44].

The morphology of iPP crystallized from the melt has been studied extensively over the past few decades using PLM [45–47], transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) [48]. From investigation carried out by polarizing microscopy, dynamically and isothermally, on the analysis of nucleation morphology of iPP, a lot of information concerning the induction period, nucleation density, growth-rate of the spherulites, and distribution of the dimension of the spherulites can be obtained (Fig. 3) [49].



**Fig. 3.** Spherulitic morphology of isothermally crystallized iPP from melt (COST Action P12-Borealis) at  $T_c = 124$  °C [49]

Results showed that iPP could crystallize in a wide range of spherulite dimensions (from 10–50  $\mu\text{m}$  to 280–370  $\mu\text{m}$ ) depending on the temperature of crystallization and crystallization conditions as well as the presence of nucleating agents [45–47, 50–52]. The presence of maleic grafted PP (PP-g-MA) used as a modifier for PP split films leads to alteration of the crystallization kinetics, although a spherulitic morphology similar to neat PP was developed [45].

### 2.3. Nucleation and its experimental evaluation

Nucleating agents are low molecular mass organic or inorganic substances added to polymers, before or during processing, in very low quantities. The effect of the addition of nucleating agents are usually decrease in crystallite size compared with that of the pure polymer, more uniform morphology, and sometimes an improvement in mechanical properties including increased transparency. Used in low concentration, these agents, acting as heterogeneous nuclei, usually increase the crystallization rate during isothermal crystallization. During nonisothermal crystallization from melt, the temperature of crystallization of the nucleated polymer is shifted towards higher temperature.

Derivatives of sorbitol (known as DBS, MDBS and EDBS) are the most effective known nucleating agents of iPP, leading exclusively to the creation of the monoclinic  $\alpha$ -form [53–55]. The best-known  $\beta$ -nucleating agents are the trans-quinacridone Permanent Red [56] and a bicomponent mixture consisting of equivalent amounts of pimelic acid and calcium stearat [57]. The amount of the  $\beta$ -phase in iPP depends on the concentration of the additives and on the cooling conditions during crystallization from the melt. The  $\beta$  content in the iPP (and thus the efficiency of  $\beta$ -nucleators) can be quantified by WAXD or qualitatively detected by DSC and PLM, which produce difference in spherulite morphologies between  $\alpha$ - and  $\beta$ -crystallites. Also, the DSC melting thermograms (heating rate 10 K/min) are different from these of  $\alpha$ -phase with maximum of the melting curve at lower temperatures from 145–155  $^{\circ}\text{C}$  and lower value of  $T_m^{\circ}$ , values obtained according to Varga et al. [45–47, 57].

Two particular structural effects are usually observed if nucleating agents are introduced into semi-crystalline polymers: an increase of crystallization temperature  $T_c$ , and a modification of mechanical properties. The first effect is characterized by the creation of a larger number of smaller spherulites, related to an increase of the  $T_c$ , and the shortening of the crystallization time. Such effects are especially useful for the industrial application, where the economic benefit is related to shorter cycle's time (about 30% shorter injection

molding cycle). Nucleation efficiency strongly depends on its intrinsic crystallization rate and on the super cooling expressed as  $\Delta T = T_m - T_c$  [58].

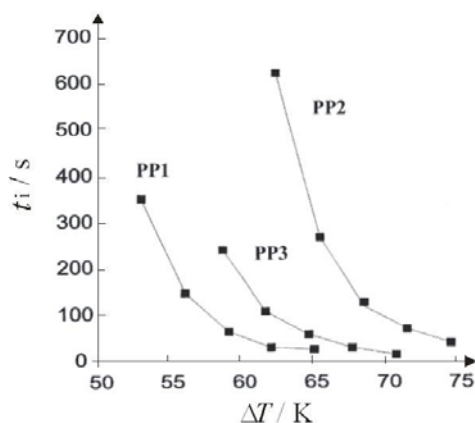
The specific structural  $\alpha$ - and  $\beta$ -form modification of an iPP may lead to significant changes in the end-use properties. There is particular interest in adjustment of the optical properties, a so-called clarifying effect achieved by the use of the derivatives of sorbitol [59–60]. One can also affect mechanical properties, namely enhance the impact strength and lower the stiffness for  $\beta$ -nucleated iPP [56].

Fillon et al. [41, 61, 62] have suggested that macromolecules of the same polymer are the most effective nucleating agents. Such a situation occurs if the crystallization takes place in partly molten semi-crystalline polymers, a process called self-nucleation. The process allows the highest possible crystallization temperature for a given polymer to be achieved.

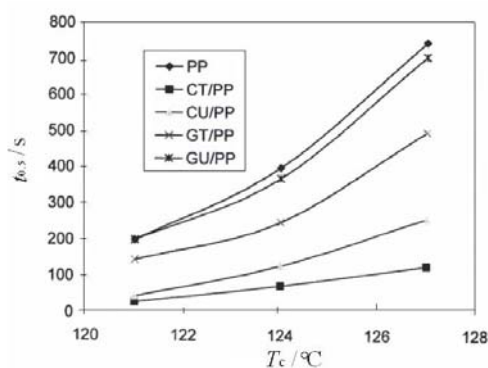
The effects of various additives on the crystallization of iPP have also been investigated. These additives include different nucleating agents, mineral fillers (talc,  $\text{CaCO}_3$ , sepiolite, mica), various pigments, carbon black, and certain flame retardants and other ingredients. Numerous results are also reported on fiber/iPP composites where fiber surface generally favors heterogeneous nucleation. During the crystallization of fiber-reinforced polymers, fibers have dual effect, which depends on the interplay between their enhancing impact on nucleation and their depressing effects on spherulitic growth caused by an impingement mechanism [63]. The nucleation activity of glass fibers and PET yarns used to produce the composite preforms was also analyzed and it was shown that differently treated and sized fibers might exhibit different nucleating ability toward isotactic PP, resulting in lower energy for formation of a stable nucleus and its lower critical dimensions. Predominant nucleating effects, evaluated by induction time of crystallization, crystallization onset temperature as well as half-time of crystallization in composites, exhibited glass fibers with thermoplastic's compatible dispersion containing polyurethanes, pointing out the possible reactive coupling effects between the components of sizing used and the functional groups of maleic anhydride modified PP (MAH modified PP). The presence of the carbonyl groups of MAH in PP is believed to promote heterogeneous nucleation, and correspondingly, the shorter  $t_i$  for the studied modified PPs is observed (Fig. 4) [47].

The half-time of crystallization  $t_{0.5}$  is decreased increasing the presence of fibers in composites. This effect is obviously fibers surface specific: treated and sized fibers have shown lower values for  $t_{0.5}$  (Fig. 5) [64].





**Fig. 4.** Induction time of crystallization versus  $\Delta T$  for PP1 (PP-g-MA), PP2 (homo-iPP) and PP3 (MA-modified PP) [47]



**Fig. 5.** Half-time of crystallization,  $t_{0.5}$  versus  $T_c$  for composites with carbon and glass fibers: CT-treated sized carbon fibers, CU-unsized carbon fibers, GT-sized glass fibers, GU-unsized glass fibers (50 % mas. fibers); PP-fiber grade

The resulting crystal structure of PP in this type of fiber/PP composites exhibits lower lamellae thickness but is less disposed to recrystallization and is more stable [65–67]

Recently, much attention has been paid to PP-nanocomposites, produced by different techniques and containing mainly carbon nanotubes/nanofibers or layered silicates [68–79]. Numerous reports describe the fabrication of a range of PP-nanocomposites, and, in particular, the impact of nanofillers on the

crystallization of a matrix. In general, the results obtained by DSC analysis, applying the known theoretical approaches of polymer crystallization (Avrami, Ozawa, Jezorny, Mo and coworkers) demonstrate nucleation ability of nanofillers resulting in a change of polymer morphology as well [80, 81].

### 3. CRYSTALLIZATION AND TRANSCRYSTALLIZATION OF IPP

For polymers, crystallization consists of two processes, primary and secondary crystallization, which are generally consecutive and well separated.

Primary crystallization is the transition of amorphous molten substance into a crystalline phase. The structure formed during a primary crystallization is in a non-equilibrium state, and the crystallization is never completed. This structure may be improved by post-crystallization and recrystallization processes, which are collectively, designated secondary crystallization.

Primary crystallization consists of two elementary processes: nucleation and growth. In the nucleation process, centers of new phase are formed. Under isothermal conditions, their number is either constant (athermal nucleation) or increasing linearly in time (thermal nucleation). Three types of nuclei can be identified: homogeneous, heterogeneous and self-nuclei.

During crystal growth, new crystal layers are deposited on the primary nuclei, extending the dimensions of the crystalline phase. An important quantitative characteristic of growth is the linear growth rate. Other essential features of growth are the secondary and tertiary nucleation processes.

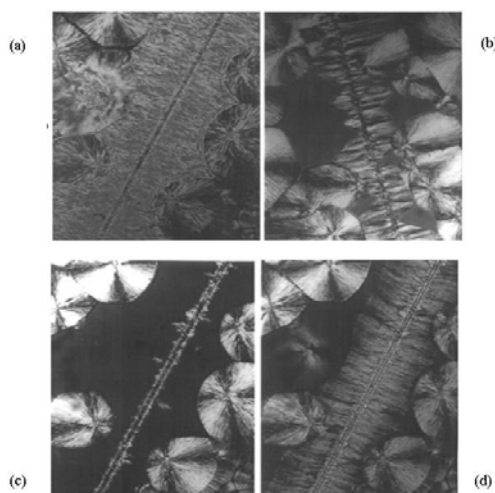
Secondary nucleation is the rate-controlling step of growth, and may follow one of three different mechanisms depending on the extent of supercooling, as described by the kinetic theory of crystallization [82]. These growth regimes are designated I, II and III in order of increasing supercooling ( $\Delta T$ ).

iPP is a favorable model substance, because its linear growth rate,  $G$  can be determined with high precision in a wide temperature range ( $T_c$ ) in term of changes in the radii of spherulites with time. Under isothermal conditions,  $G$  is constant up to high degrees of conversion [1].

It is worth noting that during industrial-scale crystallization of iPP, the addition of heterogeneous nucleating agents and the formation of a characteristic type of self-nuclei, known as row nuclei, may play an important role. In presence of additives with heterogeneous nucleating activity (fibers) transcrystallization (TCR) may occur when the nucleation density at the fiber surface is

much higher and the spherulites can grow up only in perpendicular direction. Transcrystallization, as a nucleation controlled process, depends on thermodynamic conditions, such as crystallization temperature,  $T_c$  and cooling rate. According to the literature, TCR could be initiated by several factors: topography of the substrates, shear induced crystallization, surface energy of the substrate, adsorption of small molecules, thermal gradients [83–85]. Different authors have compared  $\sigma_e$  values and nucleation activity of various fibers and have made their gradation, ranging from  $62.5$  to  $122 \cdot 10^{-3} \text{ J m}^{-2}$ , lower than  $178 \cdot 10^{-3} \text{ J m}^{-2}$  determined for pure iPP [86]. Data for  $\sigma_e$  of iPP reported in the literature range from  $40 \cdot 10^{-3} \text{ J m}^{-2}$  [87] to  $230 \cdot 10^{-3} \text{ J m}^{-2}$  [88], and the differences are usually related to different constants used, including  $T_m^0$ .

TCR development of polypropylene, initiated by melt-shearing and fiber-pulling during crystallization have been followed by many authors in the presence of various crystalline/semicrystalline substrates/fibers, such as talc, PET, polyamide-6, polyamide-66, aramide, carbon, cellulose, cotton and some other polymeric fibers, which are selective  $\alpha$ -nucleating agents [89–92]. Transcrystalline bands of  $\beta$ -modification are formed in their vicinity, as proved by optical micrographs (Fig. 6) [67, 93].



**Fig. 6.** Cross-polarized optical micrographs of iPP/GT model composites: a)  $\beta$ -transcrystalline layer formation by pulling glass fibers in the  $\alpha$ -iPP isothermally crystallized melt under condition  $T_c = 127 \text{ }^\circ\text{C}$ ,  $T_{\text{pull}} = 138 \text{ }^\circ\text{C}$ ; b, c) Texture after the selective melting of the  $\beta$ -form at  $T = 145 \text{ }^\circ\text{C}$  and d) at  $T = 148\text{--}150 \text{ }^\circ\text{C}$ . Negative radial  $\alpha$ -spherulites are clearly discernable

Cylindritic forms have been formed at smaller shearing during crystallization. This type of TCR was found in the presence of glass, polyamide, polyester, aramide and carbon fibers [90, 91]. Varga and Karger-Kocsis have considered that the cylindritic microstructure is a row-nucleated structure and they described the difference between TCR and cylindritic crystallization [91, 92].

### 3.1. Nucleation of polypropylene and DSC

The concept of primary nucleation is based on the assumption that fluctuation in the undercooled phase can overcome the energy barrier caused by the surface free energy of the crystal (developed by Gibbs and modified by Kossel and Volmer) [1]:

$$I^* = (NkT/h) \exp[-(\Delta G^* + \Delta G_\eta)/kT] \quad (1)$$

where  $I^*$  is the nucleation rate,  $N$  is the number of crystallizable elements,  $h$  is the Planck's constant,  $k$  is the Boltzmann's constant,  $\Delta G^*$  is the energy of formation of a nucleus of critical size, and  $\Delta G_\eta$  is the activation energy for the chain transport.

*Homogeneous primary nucleation* and for rectangular shape of the nucleus the free enthalpy of the formation of a nucleus of critical size can be described by the following equation:

$$\Delta G^* = (32\sigma\sigma_e)/(\Delta g_f)^2 = [32\sigma^2\sigma_e(T_m^0)^2]/[(\Delta h_f)^2 f^2 (\Delta T)^2] \quad (2)$$

where  $\sigma$  and  $\sigma_e$  are the side and end surface free energies of the crystal,  $\Delta g_f$  is the free enthalpy of fusion of the crystal of the chosen geometry,  $T_m^0$  is the equilibrium melting temperature,  $\Delta T = T_m^0 - T$ , and  $f = 2T/(T + T_m^0)$ . The term  $\Delta G_\eta$  is usually approximated by the William-Landels-Ferry (WLF) equation for the viscous flow:

$$\Delta G_\eta / kT = U^* / [R(T - T_\infty)] \quad (3)$$

Binsbergen and De Lange have extensively studied *heterogeneous primary nucleation of crystallization*. According to this theory, the formation of a nucleus on a foreign surface involves creation of a new interface, similarly to

the case of homogeneous nucleation. The pre-existing foreign surface greatly reduces the free enthalpy of the formation of a critical nucleus  $\Delta G^*$ . This lowers the critical size of the nucleus and results in the formation of heterogeneous nuclei at lower undercooling. Assuming rectangular shape of a nucleus lying flat on a foreign surface, the free enthalpy of the formation of a nucleus of the critical size:

$$\Delta G^* = (16\Delta\sigma\sigma\sigma_e)/(\Delta g_f)^2 = [16\Delta\sigma\sigma\sigma_e(T_m^0)^2]/(\Delta h_f f\Delta T)^2 \quad (4)$$

where  $\Delta\sigma$  is the specific interfacial free energy difference for the nucleus-foreign surface interface.

At isothermal conditions, it is evident from the expressions for  $\Delta G^*$  for homogeneous and heterogeneous nucleation that nucleation rate is constant.

The real nucleation process in polymer and particularly in PP is a complicated function of time,  $t$ , not just of temperature,  $T$ :  $I^* = I^*(T(t), t)$ . The theories of homogeneous, heterogeneous and self-seeded nucleation describe the mechanisms and show the tendency but do not predict the real habit of nucleation in polymers. Hence, experimental methods of determining nucleation are of particular importance.

Knowledge of nucleation data is often essential for controlling the physical properties of polymer, mechanical properties depend to a great extent on the average size of spherulites, size distribution and the size of so-called "weak spots"-defects of spherulitic structure including cavities and frozen stresses which result from volume contraction during crystallization.

A method has been developed to estimate iPP nuclei density from growth rate data and from half-time of isothermal crystallization measurements derived from DSC, by tuning Lauritzen and Hoffman equation [95].

Monasse and Haudin have studied the thermal dependence of nucleation and growth rate in iPP by applying DSC at cooling rates ranged from 0.31–80 K/min [96]. The experimental data analyzed with the Ozawa theory showed transition between heterogeneous and homogeneous nucleation at about 122 °C. In the temperature range of heterogeneous nucleation they calculated the surface free energies,  $\sigma$  and  $\sigma_e$  and the reported values ( $9.2 \times 10$  erg/cm<sup>2</sup>; 144 erg/cm<sup>2</sup>) agreed quite well with those obtained previously from isothermal DSC measurements.

*Self-nucleation* is a general term describing nucleation of a melt or solution by its own crystals grown previously. Self-nucleation in polymers is particularly strong because of the large temperature range where crystals do not melt entirely.

Self-nucleation is based on the observation that the critical nucleus size decreases with decreasing temperature. After melting the temperature is reduced below the melting point, preferably 10–15 °C higher than the required crystallization temperature, and maintained for a period of time to produce embryos. The temperature is then lowered to the crystallization time, at which most of the embryos reach the critical size and become stable nuclei. Using this technique one can increase the number of nuclei by a few orders of magnitude and significantly reduce the crystallization time.

### 3.2. Secondary nucleation in isotactic polypropylene

After completion of a folded layer on the surface of the crystal a new surface nucleus must be created for further growth of the crystal. This is called a secondary nucleation process. The most widely accepted expression for the secondary nucleation process predicted by the kinetic nucleation theory with reptation is given by [97]:

$$I = (N_o \beta_g p_i) / (a_o n_s) \exp[-4b_o \sigma \sigma_e T_m^o / (\Delta T \Delta h_f kT)] \quad (5)$$

where  $I$  is the secondary nucleation rate,  $N_o$  is the number of reacting species at the growth front,  $\beta_g$  is the retardation factor due to the melt viscosity,  $n_s$  is the number of stems of width  $a_o$ ,  $b_o$  is the molecular thickness, and  $\Delta h_f$  is the enthalpy of fusion. The temperature dependence of the secondary nucleation rate at low and moderately high undercooling is determined by  $\Delta G$  which is proportional to  $T_m^o / (T \Delta T)$  [1, 97].

The secondary nucleation can be determined from the measurements of the spherulites growth rate based on the knowledge of the basic crystallographic and thermodynamic parameters characteristic of iPP, given in literature by different authors [11, 97, 22, 98].

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Резиме

**КРИСТАЛИЗАЦИЈА НА ПОЛИПРОПИЛЕН: ПРИМЕНА  
НА ДИФЕРЕНЦИЈАЛНА СКЕНИРАЧКА КАЛОРИМЕТРИЈА**

**II. КРИСТАЛНИ ФОРМИ И НУКЛЕАЦИЈА**

Разгледувано е влијанието на хомогената и хетерогената нуклеација врз процесите на кристализација на изотактичен полипропилен и врз кинетичките и термодинамички параметри, определени преку методот на ДСЦ.

**Клучни зборови:** полипропилен; изотактичен; кристализација; кристални форми; ефекти на нуклеација; диференцијална скенирачка калориметрија (ДСЦ)

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