

Character of Crystallization Nuclei in Isotactic Polypropylene

FRANTIŠEK RYBNIKÁŘ, *Technical University, Faculty of Technology, 762 72 Gottwaldov, Czechoslovakia*

Synopsis

Examination of the isothermal crystallization and the effect of melting conditions on samples of isotactic polypropylene and its composite with talc, combined with electron-microscopic observation, has shown two types of heterogeneous nuclei effective in the crystallization process: (1) metastable nuclei, representing the unmelted crystalline phase of polypropylene, stabilized by solid heterogeneities, and operating after melting at relative low melting temperature and/or short melting time; and (2) stable crystallization nuclei, associated with solid heterogeneities, being probably catalyst residues. On the surface of these nuclei isotactic polypropylene tends to crystallize in an ordered fashion.

INTRODUCTION

Although most crystallization of polymers is initiated by heterogeneous nucleation, little is known concerning the nature of these nuclei and of the mechanism of heterogeneous nucleation.¹ In the case of isotactic polypropylene (iPP), the situation is particularly complicated, as it was shown that nucleation was exhibited not only by solid substances but also by liquids and gases^{2,3} and that the same substance did not exert the same nucleation effect in various commercial iPP types.⁴ A general discussion of heterogeneous nucleation on a solid substrate was given by Binsbergen.⁵ He states that most inorganic substances show little nucleation activity in polyolefins and he doubts the decisive role of polymerization catalyst residues, left in the polymer after inactivation of the catalyst and after the usual washing procedures, in heterogeneous nucleation, because these residues are several orders larger in number than the number of spherulites observed. On the other hand, Boon et al.⁶ proved that heterogeneous nucleation in isotactic polystyrene was prompted by catalyst residues containing Ti and Al.

On the basis of our own results obtained with some polyolefins filled with solid inorganic fillers, we decided to investigate the possibility that heterogeneous nucleation particles in iPP are also catalyst residues. The argument on the difference in the number of catalyst residues and spherulites observed is not substantial, since not every particle is required to possess the surface structure necessary for effective heterogeneous nucleation. The aim of this article was to examine the character of nucleation particles effective in iPP by investigating the influence of melting conditions on the crystallization process and also by electron-microscopic observation.

EXPERIMENTAL

Materials. The isotactic polypropylene used in our experiments is an unfractionated commercial product, Tatren PD 140 (Slovnaft Bratislava, Czechoslovakia) in the shape of 2-mm-thick pressed sheets. As an active nucleating agent, commercial talc type Micro Talc IT extra (AS Norwegian Talc) was used. Powdered iPP and 10% talc were homogenized by hand mixing and shaking. Sheet pressing was performed at 210°C and 10 MPa.

Measurement of crystallization characteristics. The course of the isothermal crystallization was followed by a thermo-optical method on equipment of our own construction. Samples in the form of microtomed slices about 30 μm thick were inserted between two cover slips and placed in the heating stage of a polarizing light microscope. The temperature of the heating stage was kept constant within $\pm 0.1^\circ\text{C}$. Prior to the crystallization, the samples were melted under chosen conditions and then cooled down to the desired crystallization temperature T_c . During the isothermal crystallization, the intensity of depolarized light was registered continuously as function of the crystallization time. From such crystallization isotherms, the value of the crystallization half-time r was evaluated. Also an analysis of the crystallization mechanism according to the Avrami equation was carried out. Concurrently with the registration of the crystallization isotherm, visual measurements of spherulite size and number were performed for the evaluation of the radial spherulite growth rate v and of the number of nucleation centers N . At the end of the crystallization process, the sample was cooled to the laboratory temperature, and its melting point T_m was determined from the temperature dependence of the intensity of depolarized light registered at a heating rate $14^\circ\text{C}/\text{min}$.

Determination of number of nuclei. When the number of nuclei was relatively small, their determination was made visually in a polarizing light microscope. Otherwise, the N value was determined on the basis of overall crystallization rate characterized by the crystallization half-time r , and the spherulite growth rate v . In a spherulitic crystallization process controlled by heterogeneous nucleation, where the Avrami exponent n is 3,

$$N = \frac{3 \ln 2}{4\pi v^3 r^3}$$

The N values determined both ways agreed within $\pm 5\%$.

Electron microscopy. Sample morphology was studied via replication of the free, fracture, and etched surfaces. Fracture surfaces were prepared in liquid nitrogen. For selective etching, a mixture of 7% KMnO_4 and concentrated H_2SO_4 was used. Etching was performed for 30 min at room temperature in a similar manner, as described by Olley et al.⁸ For sample shadowing, Pt or Au-Pd was used. Replication was done by poly(acrylic acid) and the replica was backed by a thin C film.

RESULTS AND DISCUSSION

The data relating to the evaluation of crystallization and structure characteristics of the investigated iPP sample are collected in Figure 1. The samples were melted in a standard manner 14 min at 220°C and crystallized in the T_c range 137 – 150°C . The plots of the crystallization half-time r , growth rate v ,

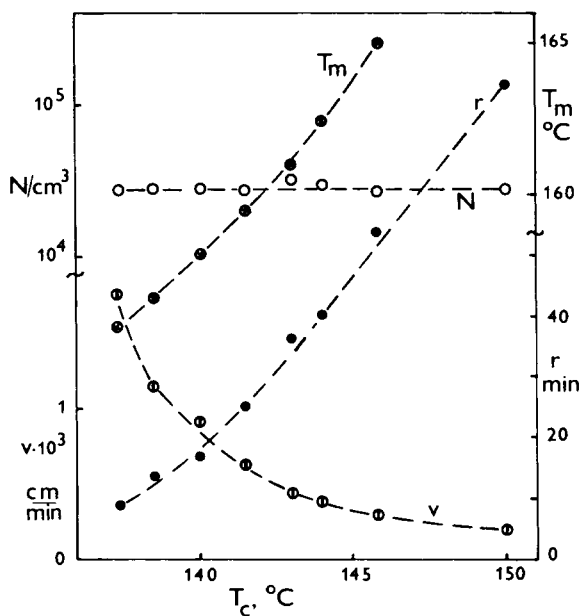


Fig. 1. Dependence of some crystallization and structure characteristics of iPP on crystallization temperature T_c . Before crystallization, the samples were melted 14 min at 220°C.

and melting temperature T_m vs. crystallization temperature have the expected shape. In all cases the crystallization mechanism was identical, since the value of the Avrami exponent n was practically the same and approached 3, which is in agreement with direct microscopic determination of heterogeneous nucleation and spherulitic growth. On the other hand, the fact that N did not depend on T_c is very important. According to the kinetic theory of polymer crystallization,⁹ the critical dimension of growth nuclei increases markedly with increasing T_c . This dimension of growth nuclei lies in the order of tens of nanometers for most practical conditions of polymer crystallization. It follows that heterogeneous nucleating particles in our iPP sample must have larger dimensions. According to Binsbergen,⁵ the situation may correspond to nucleation on relative long surface steps of a solid substrate, which is in accord with our assumption of the nucleation substrate being relatively large inorganic particles. The fact that N does not depend on T_c in the investigated T_c range enables us to perform further investigation of the crystallization nuclei only at one crystallization temperature.

We then examined the effect of the melting temperature T_t and melting time t_t on the number of heterogeneous nuclei which is active at $T_c = 144^\circ\text{C}$. When the T_t effect was investigated at 185, 220, and 250°C, t_t was 14 min. X-ray measurements have shown that already after 2 min melting at 185°C, all traces of orientation retained in iPP disappeared. This fact excludes the possibility of N values being affected by orientation-induced nucleation.

Figure 2 shows that the number of heterogeneous nuclei decreases sharply with increasing T_t to 220°C and then remains practically constant at a value of about $4.5 \times 10^7/\text{cm}^3$. Such a dependence of N on T_t means that in the crystallization process two different kinds of nucleation centers are operative. The first kind represents metastable nuclei that undergo easy fusing at a higher melting tem-

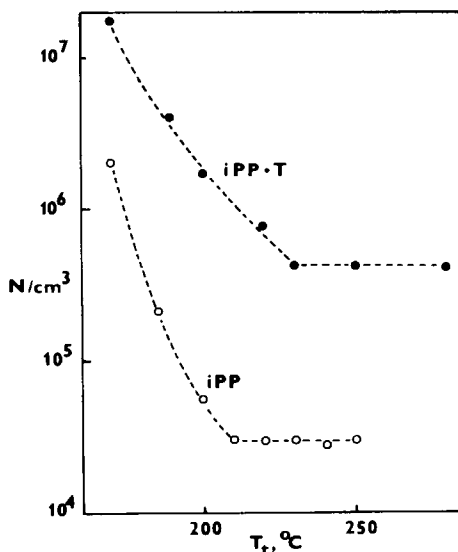


Fig. 2. Effect of melting temperature T_t on the number of heterogeneous crystallization nuclei N in iPP (O) and in iPP filled with 10% talc (●). Melting time was 14 min.

perature. They may represent the remnants of the polymer crystalline phase, surviving above the polymer melting point as a consequence of surface stabilizing action of the second kind of stable heterogeneous nucleation particles or other solid heterogeneities. Such a situation was described by Turnbull,¹⁰ who showed that in pores, crevices, and surface steps of solid heterogeneities the crystal fragments may survive far above the bulk polymer melting temperature and serve as nuclei on subsequent cooling.

The measurement of the t_t effect demonstrated the speed of fusing of metastable nuclei at various melt temperatures (Fig. 3). The dominant effect of melt temperature is clearly apparent, since at $T_t = 185^\circ\text{C}$ the fusing of nuclei was slow

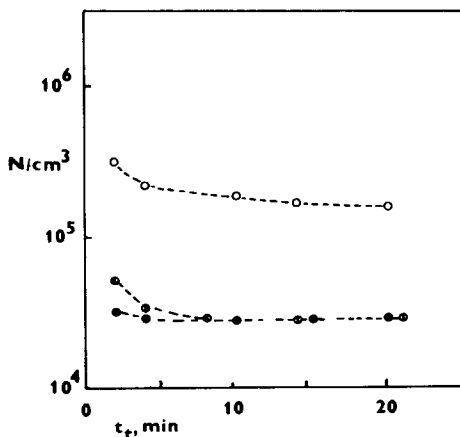


Fig. 3. Effect of melting time t_t at melting temperatures $T_t = 185^\circ\text{C}$ (O), 220°C (◊), and 250°C (●) on the number of heterogeneous crystallization nuclei N active at $T_c = 144^\circ\text{C}$.

and after 20 min was far from being complete. The increased T_t resulted in markedly accelerated fusing of metastable nuclei. At $T_t = 220^\circ\text{C}$ all metastable nuclei were destroyed in less than 8 min, at 250°C , even in about 2 min. All results shown confirm that in the given iPP sample, after fusing of metastable nuclei, a constant concentration of stable heterogeneous nuclei remains which can be reduced neither by a higher melt temperature nor by a longer melting time. One might speculate that stable heterogeneous nuclei originate from polymer chains firmly attached to the polymerization catalyst surface.

Typical electron micrographs in Figure 4 show etched surfaces of the central region of heterogeneously nucleated iPP spherulite, crystallized in the stable monoclinic form. It may be easily observed that the spherulite central region is composed of an interwoven array of short lamellae, stacked edge-on, and the spherulite periphery of long radially oriented lamellae with short lateral branches oriented approximately perpendicular to the radial lamellae. The disclosed heterogeneous nuclei show mostly lamellar morphology and average dimensions of 1–5 μm . We assume that they represent inorganic crystalline substances. Deep etching of the polymer, necessary for disclosing the surface of the nucleus, prevented in most cases detailed information on the character of the interaction of the polymer–nucleation substrate. Only occasionally, dense piling of short lamellae edge-on at the nucleus surface could be observed, as shown in the insert in Figure 4.

Investigating polymer–solid filler systems, we have found that some sheet silicates, such as kaolin and talc, are nucleation active in polyolefins and that under favorable conditions the polymer–filler interaction has the character of

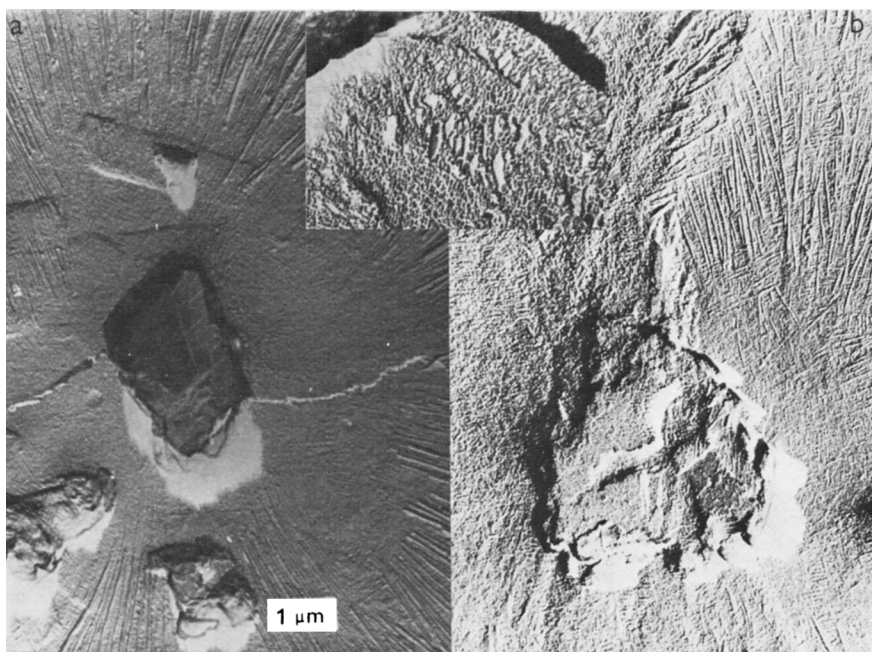


Fig. 4. Electron micrographs of etched iPP surfaces showing the central spherulite region. Insert shows orientation of polypropylene lamellae edge-on on the nucleus surface.

an epitaxial crystallization.⁷ The epitaxial polymer overgrowth was very well formed in the composite polyethylene–talc (Fig. 5). In the iPP–talc composite, it was not so well developed; nevertheless, the basic regular polymer deposition on the talc surface was apparent (Fig. 6). Therefore, we decided to examine the crystallization behavior of iPP filled with talc, following melting at various T_t values, as a model system for iPP with heterogeneous nuclei. Results of this examination are included in Figure 2. Due to the talc nucleation activity, the overall crystallization rate of the iPP–talc composite was much higher than that of iPP alone, therefore for the investigation of the T_t effect on N , a higher $T_c = 150^\circ\text{C}$ was chosen.

Comparing the $N-T_t$ plots of iPP and of the iPP–talc composite, one can see that though they exhibit a similar shape, they do markedly differ in two points. First, in the case of filled iPP, the concentration of stable heterogeneous nuclei is higher by an order than in the unfilled one, in accord with the nucleation activity of talc. However, taking into account the relative high talc concentration in the composite, it is clear that only a small fraction of talc particles is nucleation active. This is a similar situation we have anticipated in the case of catalyst residues in iPP. The qualification necessary for a solid particle to become nucleation active in iPP still remains to be determined. Second important observation from $N-T_t$ plots is the increased stabilizing action of talc on metastable nuclei, since the decrease in their number with growing T_t is slower than in iPP alone. Also, the limiting T_t necessary for their complete fusing within 14 min is about 10°C higher than in the case of iPP. All these circumstances indicate

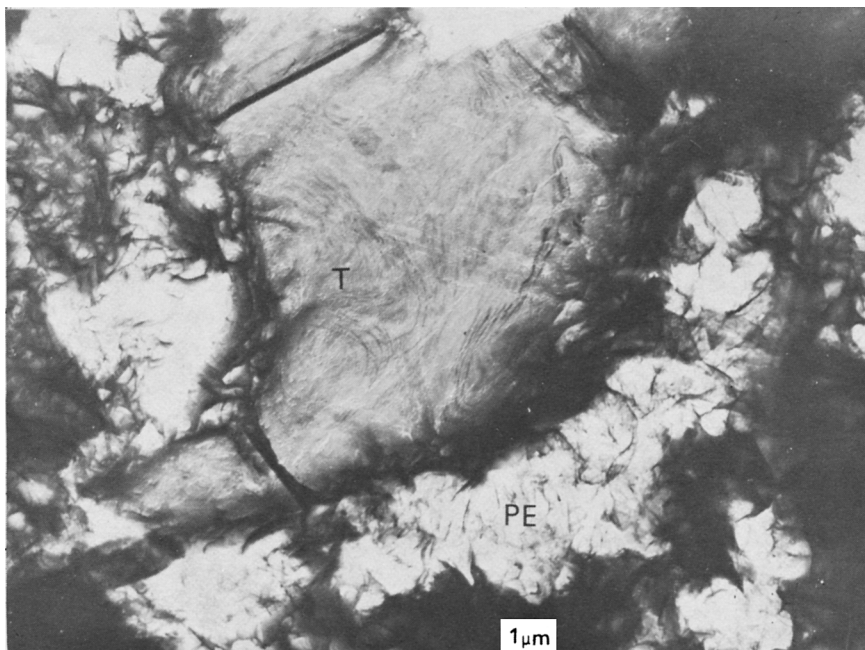


Fig. 5. Electron micrograph of the free surface of linear polyethylene filled with talc. The surface of the talc particle (T) in the polyethylene matrix (PE) is covered by an epitaxial polyethylene layer.

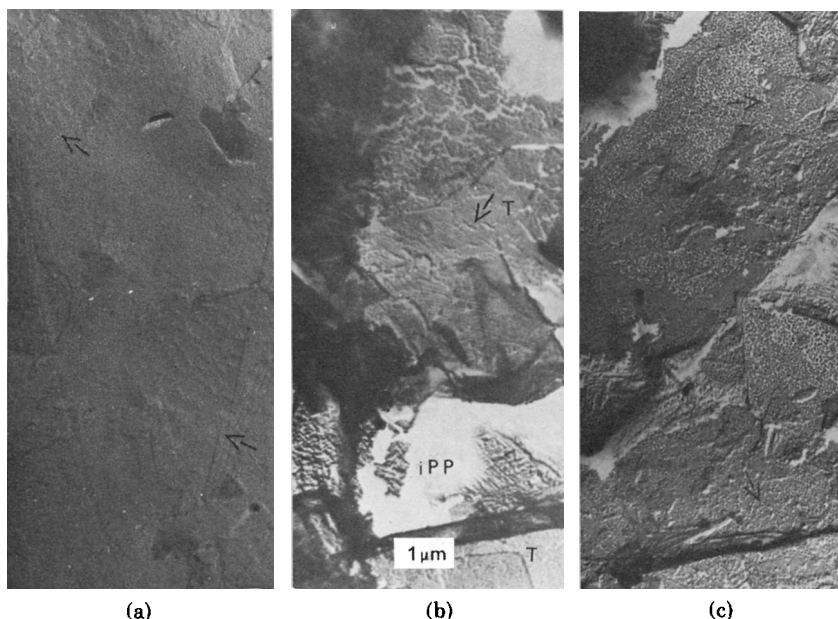


Fig. 6. (a) Fracture surface of iPP-talc composite, showing talc particle partly covered by an oriented iPP overgrowth. (b) Free surface of the iPP-talc (T) composite. (c) Etched surface of iPP-talc composite. Arrows show places with the tendency of iPP to regular deposition on the talc surface.

a close analogy in behavior of the original stable heterogeneous nuclei in iPP and a nucleation active inorganic substance.

CONCLUSIONS

The study of the crystallization behavior of iPP at various T_c values and of the effect of melting conditions on the crystallization nuclei number, together with electron microscopy, disclosed information on the character of heterogeneous nuclei active in the bulk crystallization of iPP from the melt. Depending on the melting conditions, two kinds of heterogeneous nuclei initiate the crystallization. At low melting temperatures and/or short melting periods, the metastable nuclei dominate, representing the remnants of the polymer crystalline phase, stabilized above T_m by the action of heterogeneities. The second kind of stable heterogeneous nuclei is most probably associated with the nucleation substrate, characterized by a lamellar structure with overall dimensions in the order of several microns. It is assumed that the nucleation substrate represents essentially residues of polymerization catalysts. The character of the interaction of iPP with the nucleation substrate lies between crystallization on the substrate surface steps and epitaxial crystallization, similarly to what was established in polyolefins filled with talc.

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