

## HIGH-PRESSURE CRYSTALLIZATION OF POLYPROPYLENES

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### ABSTRACT

*The aim of the work is to prove and describe the crystallization technique based on synergy application of high pressure and  $\beta$ -nucleation during isothermal crystallization. High-pressure crystallization equipment pvT100 was employed for sample preparation. Samples were characterized by wide-angle X-ray scattering. Multi-component crystalline structures  $\beta/\gamma$  and  $\alpha/\beta/\gamma$  were obtained in the research. An increase of crystallization pressure inhibited the effect of the low amount of  $\beta$ -nucleant. The amount of  $\gamma$ -phase increased with rising crystallization temperature and pressure; at the highest pressures and temperatures  $\gamma$ -phase became predominant. In the samples crystallized at high pressures, the amount of  $\beta$ -phase rapidly decreased on the expense of  $\gamma$ -phase with rising crystallization temperature.*

**Keywords:** isotactic polypropylene, beta nucleation, high-pressure crystallization

### 1. INTRODUCTION

Isotactic polypropylene (iPP) is a widely used commodity polymer mostly processed by high pressure techniques. Due to its versatility, polypropylene is one of the most commonly used thermoplastics. Moreover, isotactic polypropylene is an important material not only from a commercial point of view, but also from the scientific perspective because of its specific morphological behavior.

As a result of various conditions, isotactic polypropylene can crystallize in several forms denoted  $\alpha$ ,  $\beta$ ,  $\gamma$  and smectic [1 to 3]. Each of these forms is observed with specific preparation procedures and is identified with specific peaks in the X-ray pattern. The  $\alpha$ -phase is the predominant crystalline phase and as such it always occurs in commonly prepared iPP articles. On the contrary, the  $\beta$ -phase is less common and its higher amounts are prepared only under special crystallization conditions or using nucleating agent addition, which is, actually, the most reliable preparation procedure [3 to 6]. Other ways include crystallization in shear field or in temperature gradients. The previous work of Obadal et al [7], which focused on the specific  $\beta$ -nucleation effect of the nucleator based on N,N'-dicyclohexyl-2,6-naphthalenedicarboxamide (NU100), revealed that the concentration of 0.03 wt.% of the nucleator can be rated as a "boundary range", since the application of this amount leads to rapid increase of  $\beta$ -phase content.

The  $\gamma$  form of iPP was first reported in 1960s and was generated by either crystallization at high pressures of the homopolymer or by crystallization at atmospheric pressure of low molecular weight fractions or copolymers [1, 2, 8]. The  $\gamma$ -phase crystal structure was first identified as triclinic with the unit cell similar to that of  $\alpha$  form. However, recent studies led to a reassignment of the structure as orthorhombic [9].

Many papers have reported two-phase crystalline systems of iPP ( $\gamma/\alpha$  and  $\beta/\alpha$ ), their preparation, transformations and properties, but papers discussing the coexistence of three crystalline phases have rarely appeared. Kalay et al [10] obtained such a crystalline system using the SCORIM injection-molding technique, by which the formation of  $\beta$ -phase was favored by shear fields during solidification of the polymer melt, and a high pressure in the mould supported the creation of the  $\gamma$ -

phase. The crystallization of ethylene-propylene copolymer with a small amount of ethylene modified by NU100 nucleating agent led to the coexistence of all crystalline phases, as reported by Busse et al [11]. The three-phase iPP crystalline system was also prepared by crystallization of photo-degraded  $\beta$ -nucleated iPP, as evident from our recent work [12]. However, using the mentioned experimental methods, the proportion of  $\alpha$ ,  $\beta$ , and  $\gamma$  phases cannot be controlled accurately.

As written above, the resulting structure of the material is affected by crystallization conditions, thus understanding of the relations between pressure, nucleation and polypropylene crystallization is of considerable interest from both scientific and industrial points of view, and is also the topic of this paper.

## 2. EXPERIMENTAL

### 2.1. Materials

Commercially available isotactic polypropylene MOSTEN 58412, produced by Chemopetrol Litvinov a.s., Czech Republic, is homopolymer with average molecular weight  $M_w$  of about 170000. In order to increase the  $\beta$ -phase content in the samples, specific  $\beta$ -nucleating agent (NJ Star NU100), produced by RVI International, was used. Chemically, it is *N,N'-dicyclohexyl-2,6-naphthalenedicarboxamide*.

A Brabender DSK 42/6D twin-screw extruder was used for the preparation and homogenization of blends containing PP Mosten 58412, NU100 nucleating agent and 0.3 wt.% of paraffin oil (for better dispergation of the nucleating agent). Three types of materials were prepared: neat iPP, iPP with 0.01 wt.% and iPP with 0.03 wt.% NU100.

### 2.2. Sample preparation

The pressure-volume-temperature (pvT) technique was used for sample preparation (i.e. high-pressure crystallization). The experiments were carried out on a pvT100 apparatus manufactured by SWO Polymertechnik GmbH (Krefeld, Germany).

Approx. 0.75 g of the mixed material was put into the measurement cylinder and melted at the temperature of 240°C and pressure 20 MPa for 7 minutes. Then, the crystallization pressure was introduced and the material was cooled down at the rate of 5 °C/min to a given crystallization temperature,  $T_c$ . After reaching these conditions, monitoring of isothermal and isobaric crystallization process started. The end of crystallization was signalized by the piston holding the same position for 5 minutes. Then the sample was quickly cooled to the temperature of 50°C and the pressure was decreased to ambient.

The crystallization process was monitored by a computer recording time, temperature and piston position. The resulting sample was a cylinder with a diameter of 7.8 mm and length approx. 18 mm.

For isothermal isobaric crystallization of samples the following sets of conditions were used:  $p_c = 100$  MPa and  $T_c = 140, 150, 160, 170$  °C;  $p_c = 200$  MPa and 160, 170, 180, 190 °C.

### 2.3. Wide angle X-ray scattering

Wide angle X-ray scattering (WAXS) experiments were performed in the reflection mode with a URD 6 diffractometer equipped with  $\text{CuK}\alpha$ . Radial scans of intensity vs. diffraction angle,  $2\theta$ , were recorded in the range of 10° to 30° by steps of 0.04° and length of step scan 5 s. Specimens for WAXS were cut out from the central part of the samples prepared by high-pressure crystallization. Then, the specimen surface was ground and polished using cooled disk-type grinder with sand papers to rectangular shape. The specimen dimensions were 2 x 7 x 19 mm (thickness x width x length). The quantification of polymorphic composition was calculated by equations according to Obadal et al [13].

## 3. RESULTS AND DISCUSSION

### 3.1. Polymorphic compositions

Figure 1 shows composition of the tested samples for crystallization pressure  $p_c = 100$  MPa. Under elevated pressure during iPP crystallization the  $\gamma$ -phase content in all samples increases with rising  $T_c$  and becomes predominant at the highest  $T_c$  (170°C).

In the neat iPP samples the  $\alpha$ -phase content decreases most in the temperature range between 140 and 160°C (from 52 % to 12 %). Quite the same situation occurs in the samples nucleated by a minute amount of the nucleant (i.e. 0.01 wt.%) - from 44 % to 10 %. What can be seen in the Figure 1 is a unique 3-phase crystalline system in iPP; however, first two systems contains very similar  $\alpha$ -phases content – it follows that  $\beta$ -phase in the sample with 0.01 wt.% NU100 is formed at the expense of  $\gamma$ -phase.

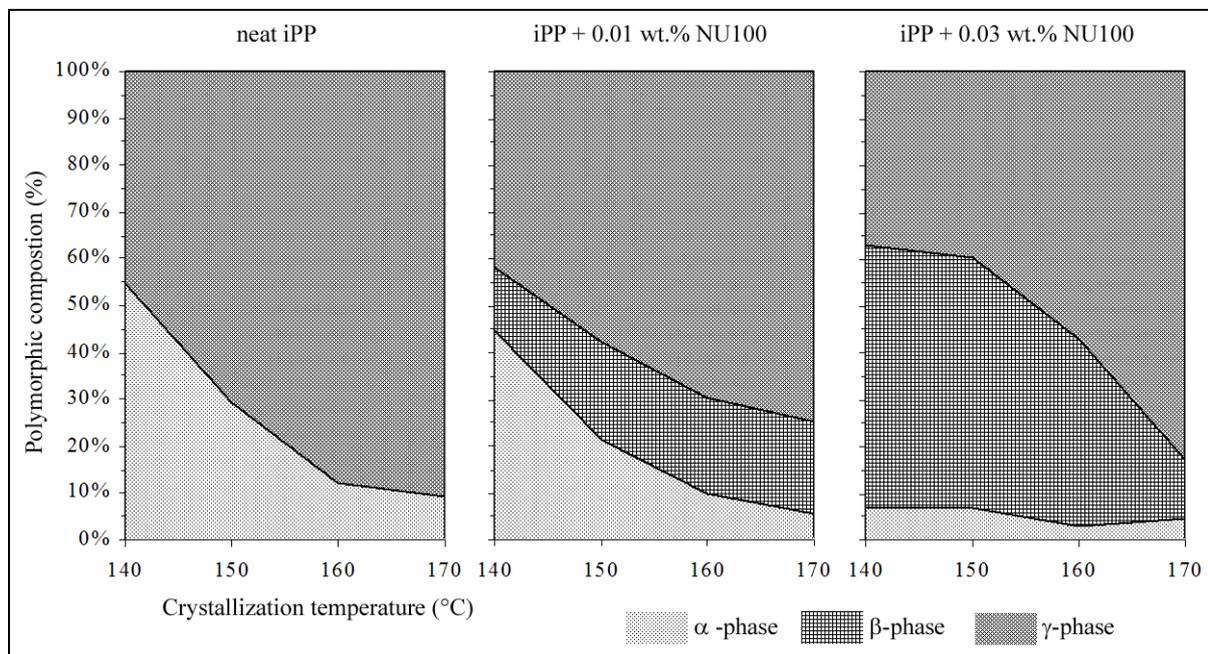


Figure 1. Polymorphic compositions in the samples crystallized at different crystallization temperatures under 100 MPa pressure.

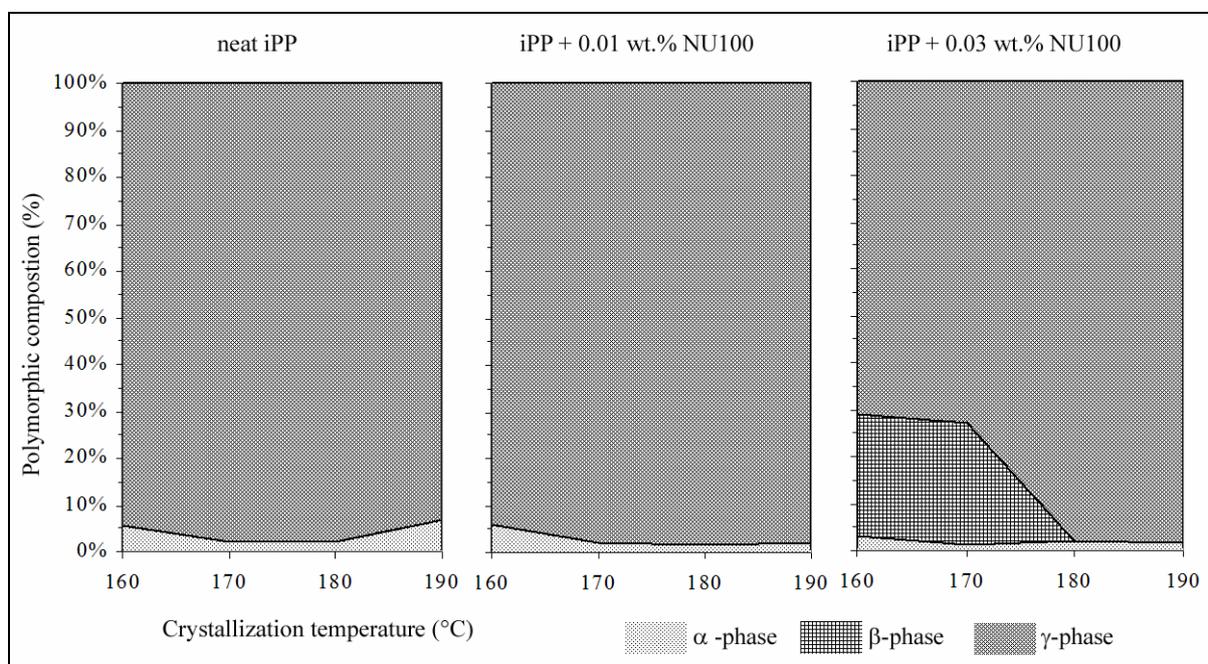


Figure 2. Polymorphic compositions in the samples crystallized at different crystallization temperatures under 200 MPa pressure.

In the samples containing 0.03 wt.% NU100 the content of  $\alpha$ -phase is low (4 – 7 %), but constant in the whole temperature range. The volume of  $\gamma$ -phase rises with increasing temperature of crystallization and becomes predominant at  $T_c = 170^\circ\text{C}$ . The strong effect of  $\beta$ -nucleant is dominant only at low crystallization temperatures (140 and  $150^\circ\text{C}$ ), at it is constant (approx. 55 %); at higher temperatures the  $\beta$ -phase content notably decreases to 12 %, on the contrary to the rising  $\gamma$ -phase content.

The higher crystallization pressure ( $p_c = 200$  MPa) illustrated in Figure 2., causes predominant formation of  $\gamma$ -phase, especially in neat and iPP nucleated with 0.01 wt.% NU100. This corresponds with theoretical predictions. In the samples with very low amount of nucleating agent the effect of  $\beta$ -nucleant is entirely inhibited by the strong impact of high pressure on crystallization. The polymorphic behavior is quite the same as that of neat iPP.

An interesting phenomenon can be seen in polymorphic variation of iPP samples with 0.03 wt.% NU100. Only a small amount of  $\beta$ -phase (approx. 25 %) was obtained at low  $T_c$ ; with increasing temperature, namely  $180^\circ\text{C}$ ,  $\beta$ -phase disappears totally. Less than 2 % of  $\alpha$ -phase are insignificant, thus predominant pure  $\gamma$ -phase was obtained at high  $T_c$ . In contrast to samples with 0.01 wt.% NU100, this is another conclusive proof of the strong effect of high pressure on the crystallization of isotactic polypropylene.

#### 4. CONCLUSION

The method based on synergy of a specific  $\beta$ -nucleating agent and high pressure during crystallization specifically affects the crystallization of iPP. The applications of the two factors allow the tailoring of three-phase crystalline systems in iPP.

The following point can be drawn from the research:

WAXS provides quantification of polymorphic composition in all samples. In conditions of isothermal crystallization, the amount of  $\gamma$ -phase in all cases increases with rising crystallization temperature and pressure; at the highest pressures and temperatures  $\gamma$ -phase becomes predominant. The amount of  $\beta$ -phase in the samples crystallized at 200 MPa rapidly decreases with rising temperature, and at the highest temperature  $\beta$ -phase disappears on the expense of  $\gamma$ -phase. At high pressures, the effect of a small amount of nucleant was totally inhibited; its influence could be only seen in the samples crystallized at 100 MPa. In the neat iPP samples, the amount of  $\alpha$ -phase decreases with rising crystallization temperature and pressure to an insignificant portion.

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