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Crystallisation of isotactic polypropylene with β-nucleating agents under elevated pressure

Abstract

Samples of isotactic polypropylene with β-nucleants (triphenodithiazine and E3B) were melted between a cover slip and a glass slide on a microscopic hot stage, after which pressure was applied by means of special weights and maintained during anisothermal crystallisation whilst the temperature dropped to room temperature. The maximum pressure used was 14×10^4 Pa. The thin foils obtained were investigated by means of the WAXS method.

In samples without additives, polypropylene crystallised in the monoclinic form only. The samples with triphenodithiazine and E3B crystallised without pressure contained 50% and 80% of hexagonal forms respectively.

The elevated pressure during crystallisation of the polypropylene reduces the nucleating activity of β-nucleants, which is manifested by a decrease in the amount of hexagonal phase. This effect differs quantitatively with the additive used.

The results obtained will be discussed in the light of the mechanism of the formation of the β polymorph as well as of the $\beta \rightarrow \alpha$ transition.

Key words: *isotactic polypropylene, polymorphism, additives, pressure, crystallisation.*

1. Introduction

Isotactic polypropylene (iPP) can exist in three polymorphic modifications: α (monoclinic), β (hexagonal) and γ (triclinic) [1,2]. Of these forms, the β only arises in the presence of specific organic compounds of small molecular weight (additives) [3,4,5,6,7,8] or during isothermal crystallisation at various temperatures [9,10], and can also be created by shear forces.

According to our hypothesis, described as a mechanism of β->α transformation, the presence or absence of the hexagonal form depends upon the mobility of polymeric chains during crystallisation [11].

We have also suggested that the formation of β-iPP in the presence of additives is a result of the chains' mobility retardation, which is caused by specific weak interaction between the surface of added crystals (or molecules) and polymer [12].

This suggestion was partly confirmed by the electro-crystallisation of iPP, where we found that the electric field causes a lowering of activity of the additives and, as a consequence, a decrease in the content of β-iPP was observed [13]. The other factor which can strongly influence mobility of chains is pressure. Here, it is worth mentioning that crystallisation of melted iPP at high pressure [386 MPa] [14] leads to formation of the γ-phase.

In this study we used only a slightly elevated pressure during the crystallisation of polypropylene containing β-nucleants. This study was undertaken in order to check the action of β-additives in presence of external weak mechanical forces, which may influence the final structure.

2. Experimental

In our investigations we used isotactic polypropylene (Petrochemistry, Płock, Poland) with a melting temperature of 176°C without stabilisers. 0.5% of additives, triphenodithiazine (TPDT) [15] and Permanent Red E3B (E3B) (Hoechst, Germany) were mixed mechanically with powdered iPP. The samples were heated between a cover slip and a glass slide on a microscopic hot stage up to 205°C, after which the samples were pressed uniaxially by special weights. The pressure was retained during anisothermal crystallisation whilst the temperature dropped to room temperature. The temperature and pressure programme was similar to that previously described [16] (Fig.1). We used pressure from 0 to 14×10^4 Pa. The samples obtained took the form of thin foils. This experiment was repeated three times: A for pure iPP, B for iPP with E3B, and C for iPP with TPDT.
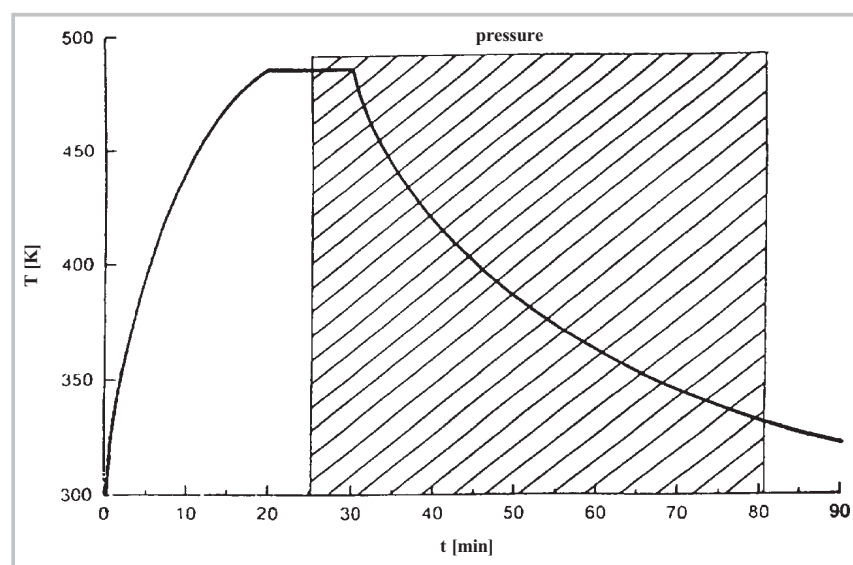

Figure 1. *Temperature and pressure program used during experiments.*

Structural investigations of the samples obtained were carried out by means of a wide-angle X-ray scattering method, using CuKα radiation (λ=1.5418Å). The resolution of superimposed multipeaks was performed by use of a method proposed by Hindeleh and Johnson [17,18] improved and programmed by Rabiej [19]. In this work, the experimental X-ray diffraction patterns are presented as upper curves, and the separated lines of crystalline and amorphous phases are shown below.

On the basis of separated diffraction lines, the β phase content and the degree of crystallinity were analysed. The amount of β-form (k) in samples of iPP was determined by using the Turner-Jones formula [1]. This formula takes into account only one maximum value from the β-form (at $\Theta = 8.06°$) and three from the α-form (at 7.07°; 8.49° and 9.30°). The diffraction maximum at 10.7° is susceptible to various interpretations and common for both forms, but it was not taken into consideration in the Turner-Jones formula [1].

The presence of both the forms were also analysed by means of DSC. The measurements were made in an atmosphere of argon on DSC-200 Netzsch apparatus. The samples were heated in the 323-463K temperature range at the rate of 5 K /min.

3. Results and discussion

In the samples without additives (series A) crystallised both with and without pressure, only the α-phases were presented (Fig.2a).

The samples of iPP with E3B or TPDT, crystallised without pressure, contained 80% and 50% of β-form respectively (Figure 2b and 2c). After crystallisation at elevated uniaxial pressure, the intensity of diffraction peaks from the β-phase dropped significantly (Figure 3.), which indicates a lowering in the amount of hexagonal forms.

On the other hand, this observation raises the question of whether the decrease in the intensity of the peak at Θ=8.06° really corresponds with the disappearance (diminishing) of the β form, or whether it is caused by the effect of the orientation of crystallites perpendicular to the surface of the pressed sample. To exclude the last suggestion, we carried out DSC measurements (Fig.4.), by which it is possible to analyse the amount of both forms [8,20] irrespective of the orien-

tation effect. These measurements were carried out only for samples containing E3B.

We can see that the endothermic peak connected with the melting of the β phase (at 146°C) is much lower in the sample crystallised under pressure (Fig. 4b) than in that crystallised without any external forces (Fig. 4a). However, the intensity of peak in question returns to the previous value (Fig. 4c) after recrystallisation without pres-

sure. This confirms that the specific action of press has an impact on the content of the β modification.

In addition, X-ray and DSC experiments clearly indicated that decrease in the amount of the β-form takes place in the whole mass of the sample, and that the changes observed in the intensity of the X-ray diffraction pattern are connected with the difference in the content of the particular crystalline phase.
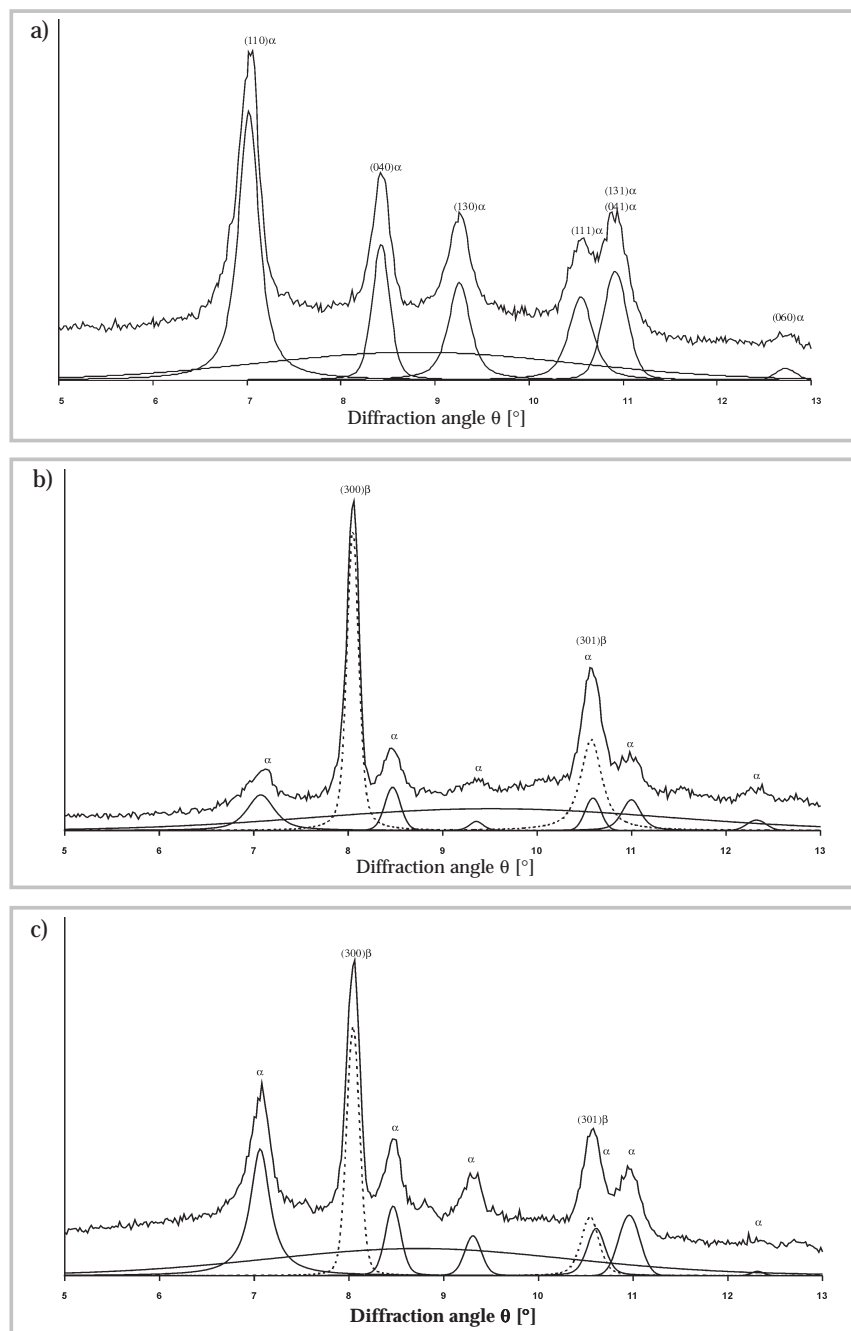

Figure 2. X-ray diffraction patterns of samples crystallised in nonpressure conditions for:
 a) iPP without additives
 b) iPP with E3B
 c) iPP with TPDT
The upper curves are experimental data; the bottom ones are lines after separation. The dotted lines concerns the β-form, and the continuous lines indicate the α-phase and amorphous phase of iPP.

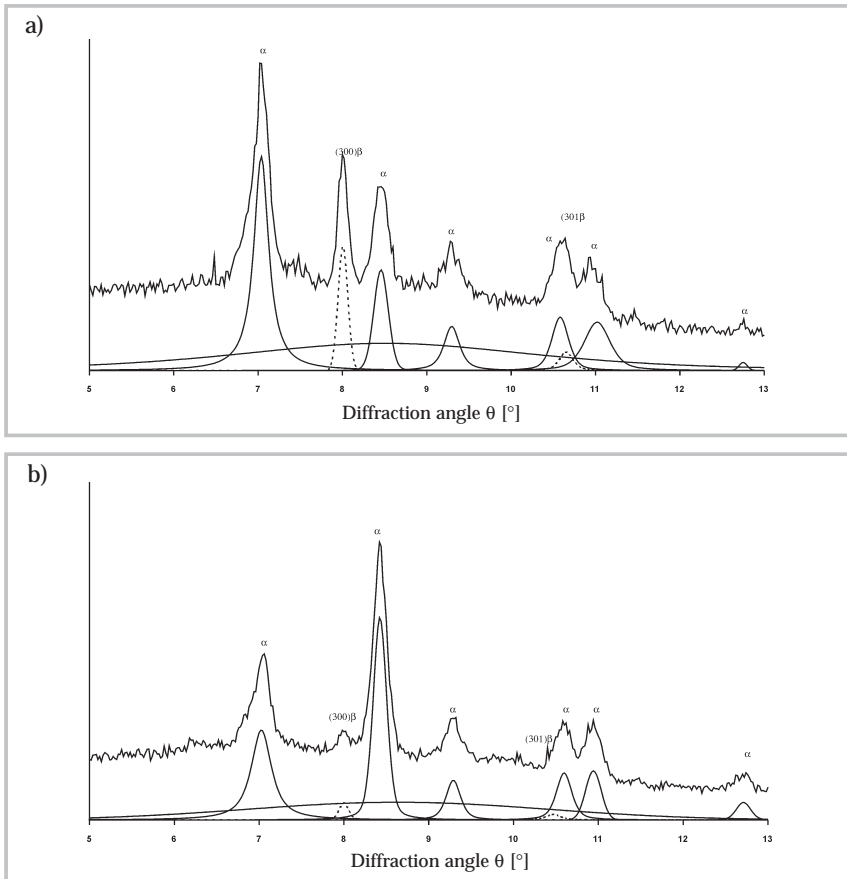The content of the β-phase (k) as a function of uniaxial pressure is presented in Figure 5, where we can see a difference between series B and C. In case of iPP with E3B (series B) the value of k decreases more rapidly (from 80% to 32%) than in the case of iPP with TPDT (series C) (from 50% to 28% at 1.42 x 10^4 Pa).
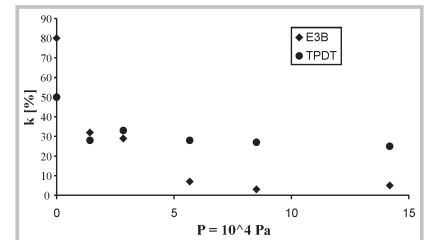

Figure.5. *Changes in the amount of β-phase (k) for samples iPP containing E3B (•) and TPDT (♦) as a function of the pressure applied during crystallisation.*

This suggested that due to the action of pressure, the role of additives as the β-nucleants is reduced. This in turn means that the formation of the monoclinic arrangement of iPP chains is favoured under stress. To explain this thesis, we propose to consider the following model: uniaxial stress (the action of pressure) on the melted iPP sample may force a screw motion of
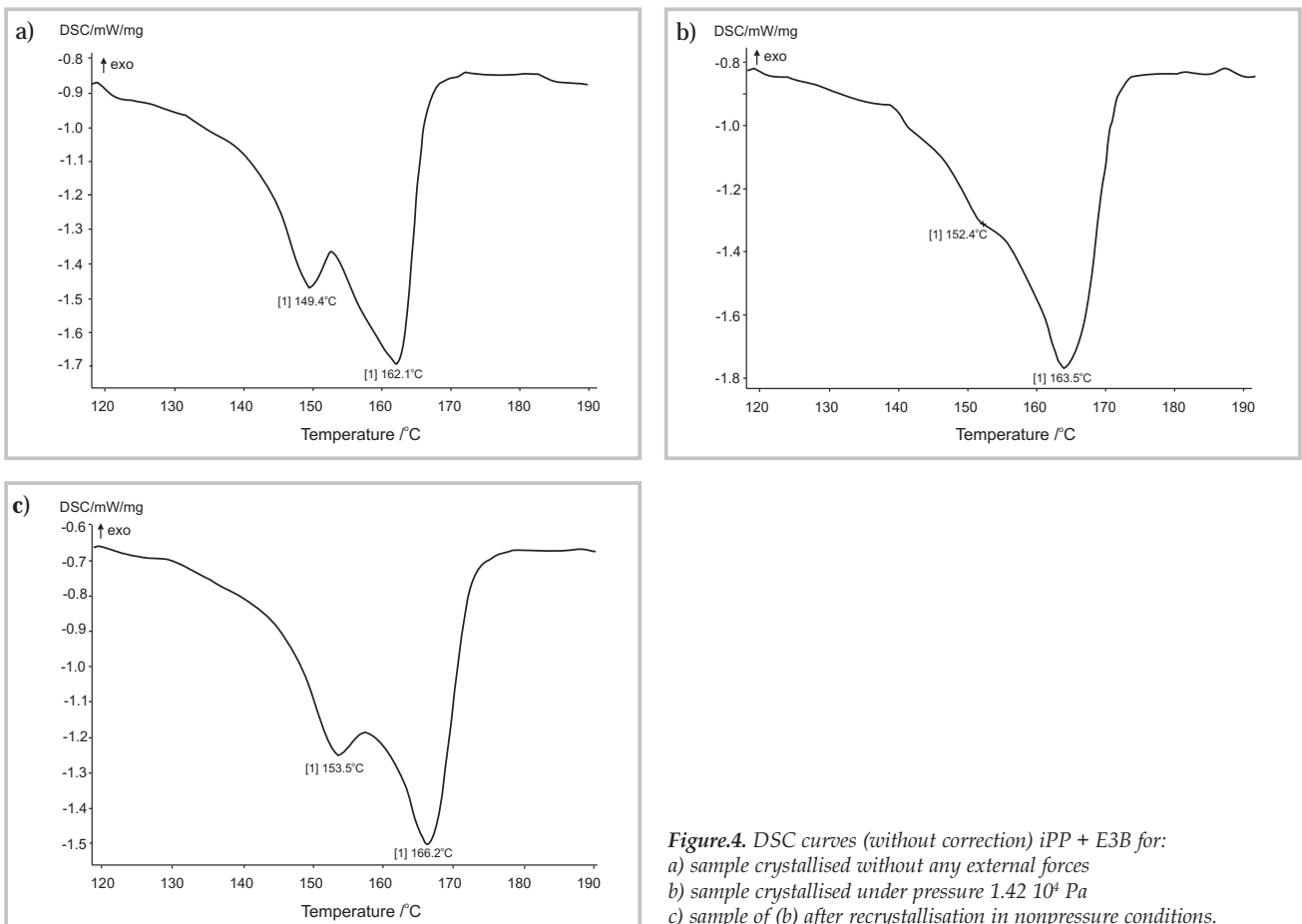
Figure.3. *Wide-angle scattering patterns for samples crystallised with pressure 14 x 10^4 [Pa] for: a) iPP + E3B, b) iPP + TPDT (the bottom and the upper curves as on Figure 2.).*

Figure.4. *DSC curves (without correction) iPP + E3B for:*
a) sample crystallised without any external forces
b) sample crystallised under pressure 1.42 10^4 Pa
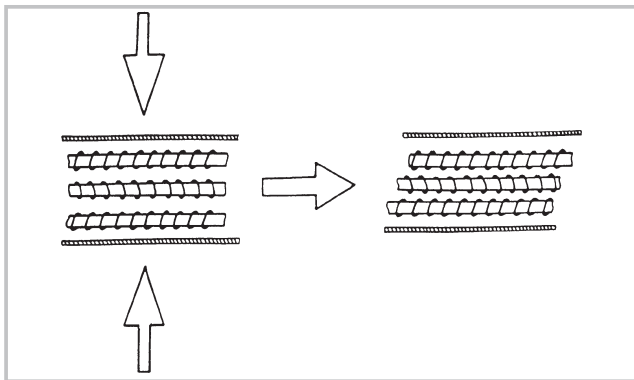*c) sample of (b) after recrystallisation in nonpressure conditions.*

Figure.6. Schematic view of screw motion of one layer of iPP chains caused by uniaxial stress. The black arrows indicate the action of stress.
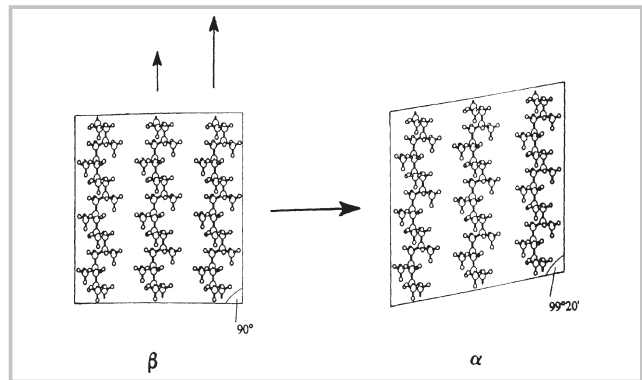

Figure.7. Schematic projection of arrangement of one layer of iPP chain on a,c plane. The left figure presents hexagonal (β) and the right one the monoclinic (α) form (vertical arrows indicate the direction of displacement of the polypropylene chains).

helical chains in a direction perpendicular to the direction of the applied press (Figure 6). As a result of the chains shifting along their axes, the macromolecules could not remain in a hexagonal arrangement, where in the unit cell the x,y plane is at right angle to the c axes, but in the monoclinic phase, this angle is 99°20' [21], (Figure 7).

Therefore, the observed diminishing of β-phase corresponds with the proposed mechanism of formation of this structural modification, according to which the hexagonal form arises when the mobility of chain is retarded during crystallisation. In other words, the pressure causes an increase in kinetic energy, which exceeds the potential energy of interaction between additive and polymer, and as a consequence the macromolecules tend to assume a more stable monoclinic arrangement. This can also confirm that the pressure applied lowers the barrier energy of β→α phase transition.

4. Conclusions

The elevated uniaxial pressure (order 14×10^4 Pa) applied during crystallisation of melted isotactic polypropylene reduces the nucleating activity of β-additives, which is manifested by a decrease in the content of hexagonal β-phase. This effect differs quantitatively with the additive used.

We hope that the present work will throw new light on the mechanism involved in the formation of the β polymorphic form of iPP in the presence of additives, and also that it will help in further explanation and understanding of the mechanism of β→α transformation.

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