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Crystal orientation of β-phase isotactic polypropylene induced by magnetic orientation of *N*,*N*′-dicyclohexyl-2,6-naphthalenedicarboxamide

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Abstract

Melt crystallization of isotactic polypropylene (iPP), containing crystallites of *N*,*N*′-dicyclohexyl-2,6-naphthalenedicarboxamide (DCNDCA) as a nucleating agent of the the β-phase iPP crystal, is carried out under a magnetic field (6 T) to obtain the alignment of the iPP crystal induced by magnetic alignment of DCNDCA. In a previous paper, DCNDCA was reported to undergo magnetic alignment in a liquid suspension. The obtained iPP sample exhibits alignment of the β-phase crystal with the *c*-axis aligned perpendicular to the magnetic field. The comparison of this alignment of iPP with the reported magnetic alignment of DCNDCA indicates that the β-phase crystal grows epitaxially on the DCNDCA crystal. The $(330)_\beta$ plane of the iPP crystal lies on the *bc*-plane of the DCNDCA crystal in which the direction of the *c*-axis of the iPP coincides with the direction of the *b*-axis of the DCNDCA crystal. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Magnetic alignment; Poly(propylene); Epitaxial crystal growth

1. Introduction

In a series of papers, we reported that crystalline polymers, including poly(ethylene-2,6-naphthalate) [1,2], isotactic polystyrene [3], poly(ethylene terephthalate) (PET) [4], and low molecular weight isotactic polypropylene (iPP) [5], align when they are crystallized from the melt under a high magnetic field (6 T). As the magnetic orientation does not occur in an isotropic phase, it is evident that anisotropic phases appearing during crystallization are involved in this phenomenon.

Recent discussions have been made on mesophases and their formation mechanism [6–9]. Understanding of mesophases in crystalline polymers would be important to elucidate the anisotropic phases responsible for the magnetic orientation, and vice versa. The detail of the mesophases in view of magnetic orientation, however, is not fully clarified yet. In fact, a low molecular weight iPP undergoes magnetic alignment, while those with higher molecular weights do not [10]. Paraffin aligns [11,12] but polyethylene does not seem to align. In addition, PET and low molecular weight iPP do not align if they once are heated above their equilibrium melting point [13].

In contrast to the magnetic alignment of crystalline polymers, the alignment of polymer fibers and organic and inorganic crystals in a liquid suspension is simple because their size, shape, crystallinity, etc. are fixed and do not change during the alignment. They are simply described in terms of the rotation of a particle in a viscous medium under a magnetic torque [14].

The third route to the magnetic alignment is to use an alignment of a low molecular weight crystal by which an alignment of a polymer could be induced. In this paper, an attempt is made to achieve the alignment of a larger molecular weight iPP induced by the magnetic alignment of one of its nucleating agents [15]. A number of studies have been reported on the nucleating agents of iPP [16,17], among which we are interested in those that induce the epitaxial growth [18,19]. The induced alignment is possible if the iPP chains grow epitaxially on the nucleating agent. Though the detail has not been fully established yet, our preliminary study suggests that iPP chains grow epitaxially on the nucleating agent used in this study [20]. In addition, we already reported [15] that the nucleating agent used in this study undergoes magnetic alignment in a liquid suspension. In this paper, it is reported that the alignment

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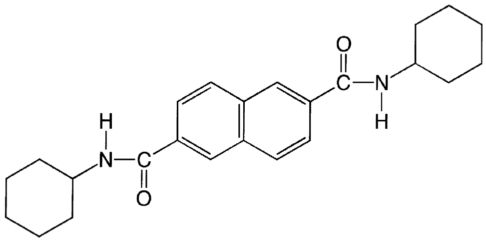

Fig. 1. Chemical structure of *N*,*N*′-dicyclohexyl-2,6-naphthalenedicarboxamide (DCNDCA).

of the β-phase iPP is induced by the magnetic alignment of a nucleating agent. Also, the epitaxial growth of iPP is discussed.

2. Experimental

2.1. Materials

Nucleating agent used in this study is a powder of *N*,*N*′-dicyclohexyl-2,6-naphthalenedicarboxamide (DCNDCA) (Fig. 1) purchased from Kankyo Kagaku Center Co. and was used as received. Isotactic polypropylene (iPP) used was a Mitsui Chemical JHH grade with nominal molecular weight of $M_n = 60,000$ ($M_w = 300,000$). The pellet of iPP was mixed with the DCNDCA crystalline powder (0–3 wt%) using an Imoto Co. Ltd. laboratory mixer at 220 °C for 5 min. The obtained mixture was hot-pressed at 200 °C for 10 min, followed by quenching in ice water to obtain a film of ca. 100 μm thickness.

2.2. Sample preparation

The thermal treatment of the film was carried out in a home-built furnace [3] placed in a vertical magnetic field (6 T) generated by an Oxford superconducting magnet. The film was heated in the magnetic field at 200 °C for 5 min, crystallized at 135 °C (Fig. 2) for 2 h, and then brought to the room temperature.

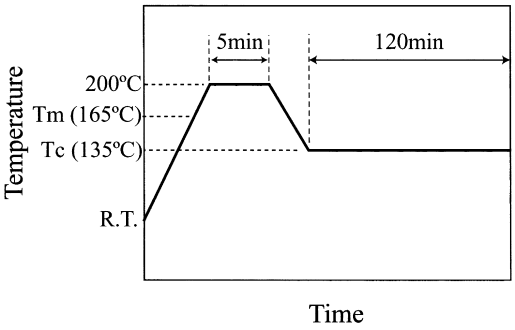

Fig. 2. The thermal history applied for the sample preparation under the magnetic field of 6 T.

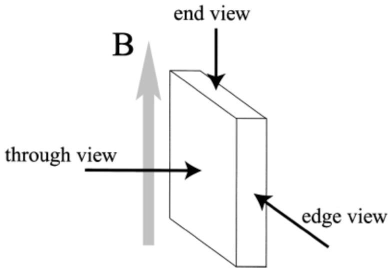

Fig. 3. Definition of three views of X-ray measurement with respect to the film surface and the magnetic field.

2.3. Wide-angle X-ray diffraction

A MAC Science X-ray M18XHF equipped with IP system was used. Measurements from three directions (through, end, and edge views) were carried out as shown in Fig. 3.

3. Results and discussion

3.1. Magnetic orientation of iPP induced by DCNDCA

Fig. 4(a) and (b) show the X-ray diffraction patterns obtained for the iPP sample without DCNDCA, heat-treated

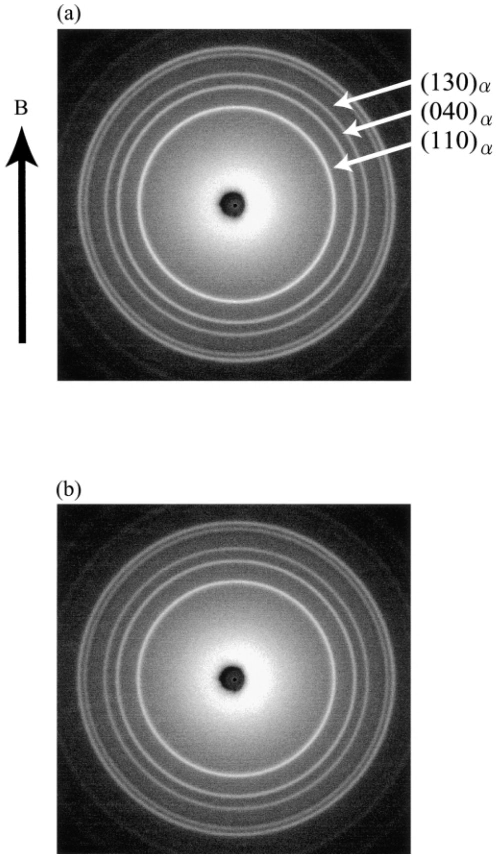

Fig. 4. Wide-angle X-ray diffraction patterns of iPP film samples crystallized without DCNDCA (a) in and (b) outside the magnet.

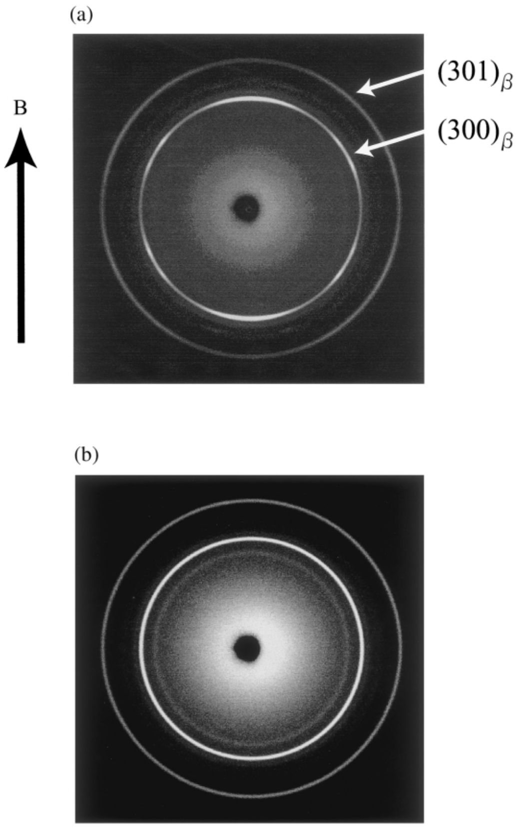

Fig. 5. Wide-angle X-ray diffraction patterns of iPP/3 wt% DCNDCA crystallized (a) in and (b) outside the magnet.

in the magnet (a) and outside the magnet (b) following the thermal history displayed in Fig. 2. It should be noted in Fig. 2 that iPP is molten at 200 °C while DCNDCA crystallites remain in solid state (melting point is 400 °C). The DCNDCA crystallites align in this period. Both X-ray patterns give several rings corresponding to the α-phase iPP [21]. No magnetic orientation is observed. This result is consistent with the previous result [10]. Namely, a high molecular weight iPP (the same sample as used in this study) does not undergo magnetic alignment, while a low molecular weight iPP exhibits magnetic alignment of the α-phase crystal under the same thermal history [5] shown in Fig. 2.

Upon addition of the nucleating agent, entirely different patterns are observed. Fig. 5 shows the X-ray diffraction patterns obtained for the iPP with DCNDCA (3 wt%), heat-treated in the magnet (a) and outside the magnet (b) following the thermal history displayed in Fig. 2. The diffraction appearing in both (a) and (b) is attributed to the β-phase iPP. The sample prepared outside the magnet exhibits two rings. The inner one corresponds to $(300)_\beta$ and the outer one corresponds to $(301)_\beta$ [22]. Clearly, no orientation is observed. In contrast, the sample prepared under the magnetic field exhibits intense arcs for the $(300)_\beta$ diffraction. Though the intensity is weak, the arcs are also observed for the $(301)_\beta$ diffraction.

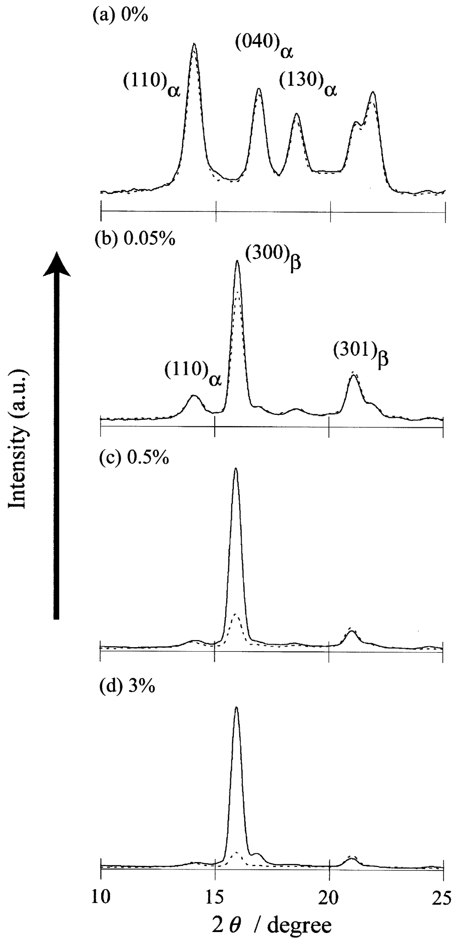

Fig. 6. X-ray diffraction profiles of iPP with various amounts of DCNDCA crystal. The isothermal crystallization at 135 °C was carried out in the magnet (6 T). The meridiaonal (solid line) direction corresponds to the field direction.

Fig. 6 demonstrates the concentration dependence of DCNDCA on the degree of orientation. At zero concentration, the α-phase is formed, and magnetic alignment is not observed. Addition of DCNDCA encourages the formation of the β-phase. Even at a concentration as low as 0.05 wt%, the formation of the β-phase is dominant over the α-phase. Magnetic alignment of the β-phase is clearly observed at a concentration of 0.05 wt% and the alignment is enhanced upon increase in concentration. This concentration dependence indicates that the nucleating agent is responsible for the observed orientation of the β-phase iPP.

3.2. Orientation analysis of iPP β-phase

In order to analyze the orientation manner of the iPP β-phase induced by DCNDCA, the X-ray diffraction was measured from three different views including the through, edge, and end views (Fig. 7). The through and edge views are identical, exhibiting arcs. On the other hand, the end view exhibits rings. This is due to the cylindrical symmetry along the direction of the magnetic field. Fig. 8 shows the pole figure for the $(300)_\beta$ plane, where the RD coincides

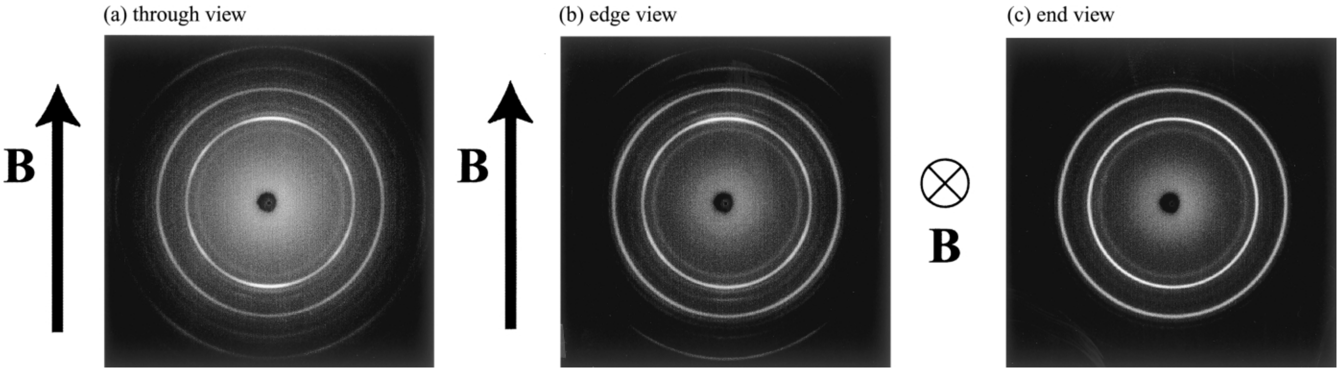

Fig. 7. Wide-angle X-ray diffraction patterns of iPP/3 wt% DCNDCA measured from three different views.

with the field direction. The pattern exhibits the diffraction both in the north and south poles, in association with two broad diffraction bands at 60° from the poles, which is in agreement with the observation in Fig. 7.

For the further analysis, the azimuthal scans on the $(300)_\beta$, $(301)_\beta$, $(330)_\beta$, and $(112)_\beta$ planes were carried out (Fig. 9). Since the β-phase is hexagonal, we may have 6-point patterns for the $(hk0)_\beta$ planes such as the $(300)_\beta$ and $(330)_\beta$ planes, depending on the orientation manner. However, the azimuthal profiles for these planes are more complicated, exhibiting 12-point patterns. The $(330)_\beta$ plane, which is normal to the a-axis, exhibits diffraction at azimuthal angles of $60°n \pm 5.5°$ $(n = 1, 2, \ldots)$. Since the field direction is at 90 and 270°, it is concluded that one of the a-axes lies inclined by 35.5° with respect to the field direction, with the c-axis aligned perpendicular to the filed. Accordingly, the diffraction for the plane $(300)_\beta$ should appear at $60°n \pm 5.5° + 30°$ $(n = 1, 2, \ldots)$ because this plane makes an angle of 30° with respect to the $(330)_\beta$ plane. This is satisfied as seen in Fig. 9. The diffraction patterns for the other planes shown in Fig. 9 are consistent with this orientation manner summarized schematically in Fig. 10.

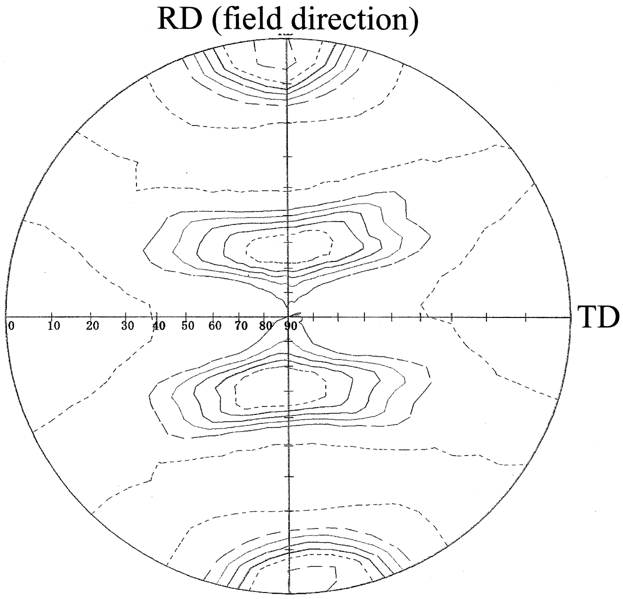

Fig. 8. X-ray pole figure for $(300)_\beta$ of iPP/3 wt% DCNDCA crystallized in the magnet.

From the crystal symmetry of the hexagonal form, we know that among three principal axes of the diamagnetic susceptibility tensor, one (referred to as $\chi_{\|}$) is in the direction of the c-axis, and the other two (referred to as $\chi_{\perp}$) directing normal to the c-axis have the same value. Incidentally, the same consideration applies to the trigonal crystal form (one $\chi_{\|}$ and other two $\chi_{\perp}$s with the same value) including isotactic polystyrene reported previously [3]. Therefore, hexagonal crystals should align exactly with the c-axis parallel or perpendicular to the magnetic field. Since $\chi_{\|} < \chi_{\perp} < 0$ for iPP at molecular level, the precise perpendicular alignment is expected for the β-phase of iPP when this phase is subjected to the magnetic field. However, this orientation manner is not what is shown in

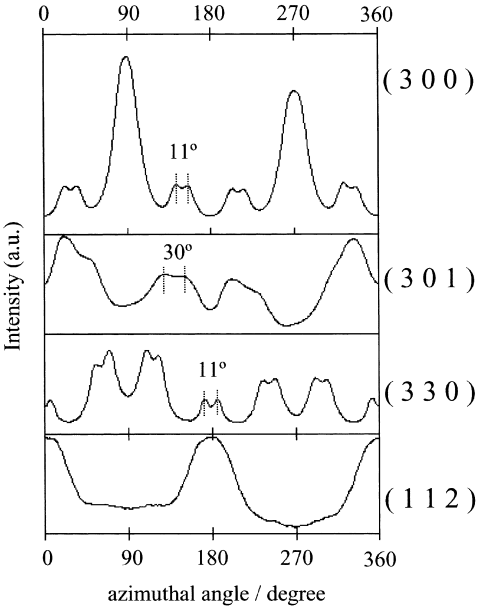

Fig. 9. X-ray azimuthal scans for various lattice planes of iPP/3 wt% DCNDCA crystallized in the magnet. The incident X-ray beam is perpendicular to the magnetic field (through view).

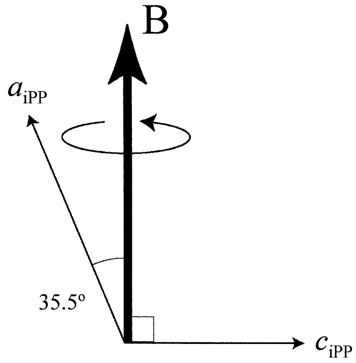

Fig. 10. Crystal orientation of β-phase iPP with respect to the magnetic field.

Fig. 10. This discrepancy strongly suggests the effect of epitaxial growth of the β-phase iPP on the nucleating agent.

3.3. Epitaxial relationship between iPP and DCNDCA

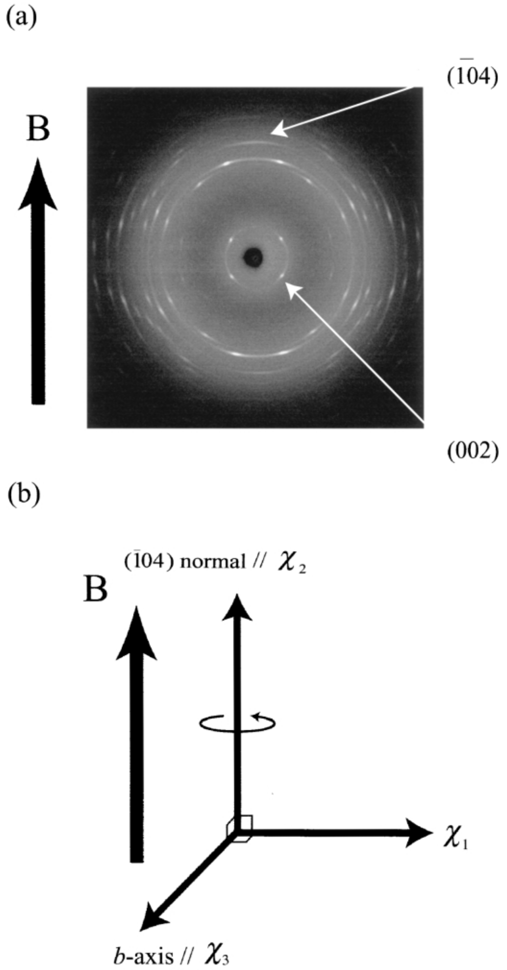

Fig. 11. X-ray diffraction pattern (a) and the schematic illustration of the crystal orientation (b) of DCNDCA as reported in Ref. [15].

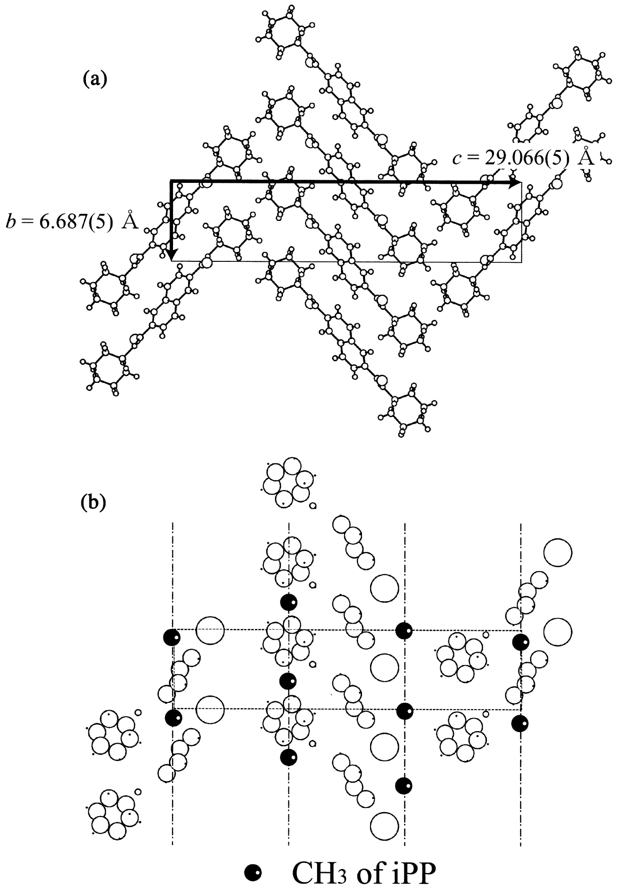

Fig. 12. Surface structure of the contact face of DCNDCA drawn in wire model (a) and the space-filling representation of the same surface along with the methyl units in β-phase iPP on the contact face.

We now examine the epitaxial relationship between DCNDCA and the β-phase iPP on the basis of the anisotropic diamagnetic property of the DCNDCA characterized in the previous study [15]. We reported in the previous paper [15] that the $(\bar{1}04)$ normal and the *b*-axis of the DCNDCA crystal align in the direction parallel and perpendicular, respectively, to the magnetic field. Fig. 11 is a schematic representation of this alignment. It should be noted in this figure that the a^*-axis makes an angle of 35.5° with respect to the magnetic field. The value of this angle coincides with the angle of the *a*-axis of the iPP against the field as shown in Fig. 10. Namely,

$$a^*_{\mathrm{NA}} \| a_{\mathrm{iPP}}, \tag{1}$$

where the suffixes indicate the nucleating agent (DCNDCA) and the β-phase iPP, respectively. In other words, $(100)_{\mathrm{NA}} \| (110)_{\mathrm{iPP}}$. In addition, it is concluded from Figs. 10 and 11 that both the *b*-axis of the DCNDCA and the *c*-axis of the iPP are perpendicular to the field. Combining with Eq. (1), we conclude that

$$b_{\mathrm{NA}} \| c_{iPP}. \tag{2}$$

The epitaxy defined by Eqs. (1) and (2) reasonably explains the orientation giving rise to the azimuthal profiles shown in Fig. 7. It should be noted that there is not a frustration on the β-phase iPP epitaxially grown on the magnetically aligned

DCNDCA because the perpendicular alignment of the *c*-axis of iPP is favorable in terms of magnetic energy.

Mechanism of the alignment of the β-phase iPP induced by the magnetic orientation of the DCNDCA crystal is summarized as follows. The DCNDCA crystal suspended in an iPP melt undergoes magnetic alignment with its *b*-axis oriented perpendicular to the field and the a^*-axis inclined by 35.5° against the field direction. Upon cooling, nucleation starts on the $(100)_{\mathrm{NA}}$ surface which is normal to the a^*-axis. On this surface, the iPP chain undergoes crystal growth in a manner so that $b_{\mathrm{NA}} \| c_{\mathrm{iPP}}$ is satisfied. Both of these axes are perpendicular to the field. This growth does not contradict the magnetic nature of the iPP, that is, the perpendicular alignment of the *c*-axis is most favorable in terms of magnetic energy.

Epitaxy between two surfaces occurs when the geometrical matching of these two surfaces is satisfied at molecular level. In the present study, it should therefore be clarified whether aforementioned epitaxy relationship is valid at molecular level. It should be also clarified why the DCNDCA crystal does not cause the epitaxy of the α-phase but it does the epitaxy of the β-phase even though both phases are composed of the same 3_1 helical moieties. Here we discuss about these points.

Fig. 12(a) shows a projection of the DCNDCA crystal onto the *bc*-plane (i.e. $(100)_{\mathrm{NA}}$). As indicated in Eq. (2), the *c*-axis of the iPP lies parallel to the *b*-axis of the DCNDCA. The epitaxy is expected if there are periodic cavities on the *bc*-plane to which the methyl groups of iPP helix are fitted. The length of the *c*-axis corresponding to the period of the 3_1 helix of iPP is 6.49 Å, while the length of the *b*-axis of the DCNDCA is 6.687 Å. These two values are fairly close. Quantitative estimation of the matching between a period PA of a substrate and a period PB of a polymer crystal is made in terms of the misfit factor, $f_{\mathrm{m}} = 100 \times (PB - PA)/PA$. Empirically, if $f_m < 15\%$, the epitaxy is regarded as good. The f_{m} between the b_{NA} and the c_{iPP} is 2.9%, indicating excellent epitaxy.

In addition to the matching along the c_{iPP}, the lateral matching should be checked. The interchain spacing on the $(110)_{\mathrm{iPP}}$ plane is 11.02 Å, while the length of the *c*-axis of the DCNDCA is 29.066 Å. The misfit factor between the latter and the triple of the former is 13.7%. This indicates that three helices are packed in one span of the *c*-axis of the DCNDCA. A possible packing of the methyl group on the *bc*-plane is shown in Fig. 12(b). In the case of the α-phase iPP, it is reported [18] that the epitaxal plane is $(040)_\alpha$ on which the adjacent helices have the same sense. The interchain distance in this case is 6.65 Å that does not fit on the *bc*-plane of the DCNDCA.

4. Conclusion

A high molecular weight iPP that contains DCNDCA as a nucleating agent for the iPP β-phase was subjected to the melt crystallization in a magnetic field (6 T). The obtained sample exhibited crystal alignment. The observed orientation manner was not consistent with that expected from the magnetic anisotropy of the hexagonal symmetry of the β-phase, but strongly suggested the epitaxial growth of iPP on a specific surface of the DCNDCA crystal. On the basis of the magnetic anisotropy of the DCNDCA crystal already reported, the detail of the epitaxy was examined. It was concluded that the *bc*-plane of the DCNDCA crystal is the epitaxial surface onto which the $(330)_\beta$ plane of the β-phase iPP grows. On these specific surfaces, the *c*-axis of the iPP aligns parallel to the *b*-axis of the DCNDCA. Analyses of the molecular packing of the iPP helix onto the epitaxial surface determined in the present study revealed that the β-phase exhibits a good fitting to this surface, while the α-phase does not.

Acknowledgements

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