

Magnetic orientation of isotactic polypropylene

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Abstract

Magnetic orientation of a low molecular weight isotactic polypropylene (iPP) is reported. Unlike other crystalline polymers for which the magnetic orientation has already been reported by our group, iPP was less expected to undergo the magnetic orientation because its repeating unit does not contain aromatic rings which are the main source of the diamagnetic anisotropy. The magnetic orientation was observed for samples melted in a magnetic field (6 T) in the temperature range between 180 and 240°C followed by cooling. This temperature range is well above the melting point (168°C). The X-ray and crystallization kinetics measurements indicated that some ordered structure exists in this temperature range. The samples obtained by quenching exhibited the orientation of crystals with the *b*-axis aligned parallel to the magnetic field. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Magnetic orientation; Isotactic polypropylene; Ordered structure

1. Introduction

We have recently reported that crystalline polymers including poly(ethylene-2,6-naphthalate) (PEN) [1,2], isotactic polystyrene (iPS) [3], and PET [4,5] undergo magnetic orientation during crystallization from melt. In this article, we demonstrate another example, that is, the magnetic orientation of isotactic polypropylene (iPP). A main difference in the chemical structure of iPP in comparison to the other three polymers is that the repeating unit of the iPP does not contain aromatic rings which provide large diamagnetic anisotropy. Though the aromatic ring is not the only source of the diamagnetic anisotropy, the lack of this chemical unit might be unfavorable to the magnetic orientation. Another aspect of iPP is that it has a strong tendency to form large spherulites which are not favorable for the built-up of the orientation. However, the following nature of the iPP might be in favor of magnetic orientation: when a melt of iPP is quenched in ice water, it forms mesophase [6–8]. An isotropic glass of iPP, prepared by quenching a melt of iPP in isopentane, transforms into a liquid crystalline structure upon heating above the glass transition temperature [9]. These phenomena suggest that the iPP has a strong tendency to form mesophase including liquid crystalline phase and/or condensation crystal phase. This nature of the iPP is in favor of the

magnetic orientation since the liquid crystallinity is one of the important factors for the magnetic orientation [10].

In this study, the magnetic orientation of a low molecular weight iPP is reported. The orientation is observed to occur above the melting point (168°C). This is in contrast to the condition of the magnetic orientation of the other three polymers. These polymers undergo the magnetic orientation below the melting point during the isothermal crystallization. Experimental results obtained by X-ray and crystallization kinetics measurements suggest the existence of some ordered structure above the melting point. The orientation direction of the crystallites obtained is discussed.

2. Experimental

2.1. Sample preparation

Pellets of isotactic polypropylene (SA002V) supplied by Japan Polychem, melt flow index: 240 g/10 min, density: 0.91 g/cm³ were pressed at 200°C for 10 min and allowed to quench in ice water. The thickness was ca. 200 μm. By using the furnace, whose detail is reported elsewhere [2], the pressed film is heated at 5°C/min and quenched in ice water as soon as the temperature reaches a maximum heating temperature (T_{\max}) (referred to as the quenching process). In the case of the sample preparation in the magnet, the quenching was performed by taking out the heating cell from the furnace located in the magnet. Alternative process for the sample preparation is as follows: the pressed film is

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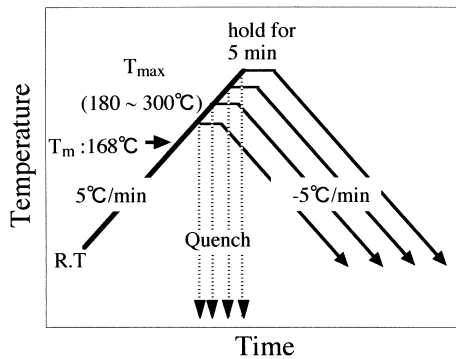


Fig. 1. Thermal history applied for the preparation of samples.

heated at 5°C/min and held at T_{\max} for 5 min, followed by a slow cooling at 5°C/min to the room temperature (referred to as slow cooling process). Both processes are carried out inside as well as outside the magnet. Each of the T_{\max} s is all located above the melting point, 168°C, determined by the differential scanning calorimetry. Fig. 1 shows a diagram for the heat treatment process.

2.2. Wide angle X-ray measurements

Wide angle X-ray diffraction (WAXD) measurements for the heat treated samples were carried out at room temperature using an MAC Science MXP system operating at 40 kV and 200 mA to generate Ni-filtered $\text{CuK}\alpha$ X-ray beam. The X-ray azimuthal scans for these samples were made, with the zero azimuthal angle corresponding to the direction perpendicular to the magnetic field. High temperature WAXD measurements were carried out outside the magnet by using an MAC Science heating unit on the same system operating at 40 kV and 280 mA at the heating rate of 5°C/min in nitrogen atmosphere.

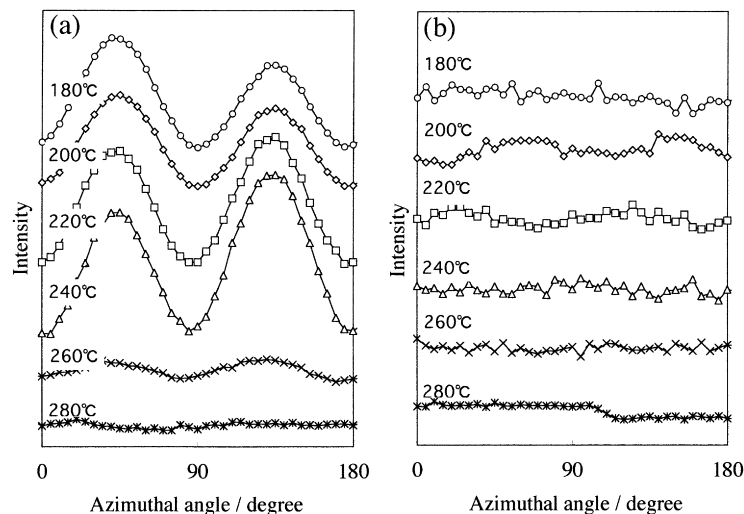


Fig. 2. Optical azimuthal scans obtained for the samples quenched at various highest melting temperatures T_{\max} s indicated in the figure. At zero azimuthal angle, the direction of the applied magnetic field coincides with the direction of the analyzer. Each curve is shifted vertically by an arbitrary amount. The quenching process was carried out: (a) in the magnet (6 T) and (b) outside the magnet.

2.3. Optical measurements

The azimuthal angle dependence of the intensity of transmitting light passing through the heat treated samples was measured at room temperature using an Olympus BH-2 microscope equipped with a photomonitor. By rotating the sample under the crossed polar condition, the transmitting light intensity changes as $I^2 \approx \sin^2 \phi$, enabling the detection of the orientation. Here, ϕ is taken as the film direction to which the magnetic field was applied during the heat treatment, and is measured with respect to the analyzer. When $\phi = 0$, the direction of the applied magnetic field coincides with that of the analyzer.

High temperature measurements for the change in transmitting light intensity under the crossed polars were carried out using a home-built apparatus whose details are reported elsewhere [2]. With the occurrence of the anisotropy, the transmitting light intensity changes according to $I^2 \approx \sin^2 \pi d \Delta n / \lambda$, where d , Δn , and λ are the sample thickness, the birefringence, and the wavelength of the light, respectively.

3. Results and discussion

3.1. Magnetic orientation by quenching from above the melting point

Fig. 2 shows the optical azimuthal scans for the samples heated to different highest heating temperatures (T_{\max} s) followed by quenching (quenching process). The orientation is clearly observed for the samples heated in the magnet up to T_{\max} s between 180 and 240°C (Fig. 2(a)). Above 260°C and below 168°C (the melting point), the orientation is not observed. It is known that oriented spherulites [11] occur under the temperature gradient. Also, transcrystalline

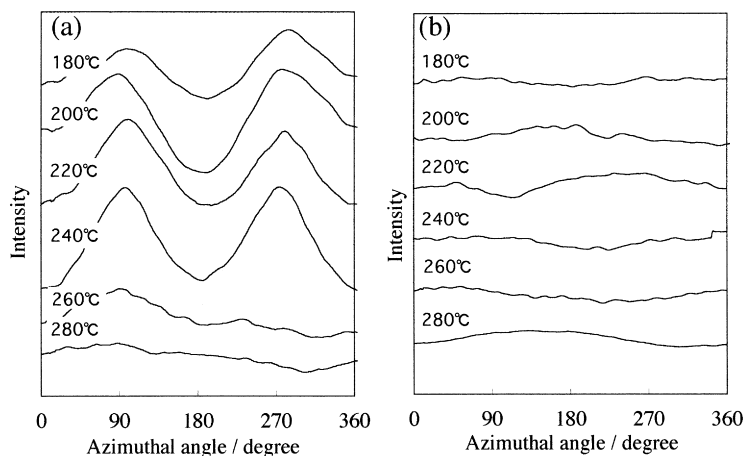


Fig. 3. X-ray azimuthal scans on the (040) plane obtained for the samples quenched at various highest melting temperatures T_{\max} s indicated in the figure. The samples examined are the same as used in the optical measurements (Fig. 2). The quenching process was carried out: (a) in the magnet (6 T) and (b) outside the magnet.

structures develop from the interface [12,13]. All these structures may contribute to the macroscopic orientation. However, the samples prepared without the magnetic field, with all other controlling parameters as the same, evidently do not exhibit any orientation over the whole range of T_{\max} s (Fig. 2(b)). Therefore, the orientation observed is attributed solely to the magnetic field.

It seems that the built-up of the magnetic orientation occurs in the molten state. The possibility of the magnetic orientation during the quenching might be ruled out because the heating cell is taken out from the magnet so rapidly that there would not be enough time for the built-up of the orientation in this period. We are therefore led to an assumption that some ordered structure exists between 180 and 240°C since ordered domains with anisotropic magnetic susceptibility are necessary for the magnetic orientation to occur [14]. In this view, this ordered structure disappears upon heating above 250°C since no magnetic orientation

occurs above this temperature. The existence of the ordered structure will be discussed later.

The same samples as used for the optical azimuthal measurements described above are also subjected to the X-ray azimuthal measurements. All these samples exhibit crystalline peaks assignable to the α -modification. Fig. 3 shows the X-ray azimuthal scans carried out for the (040) plane. Peaks at 90 and 270° indicate the orientation of crystallites. Fig. 3(a) is the result for the samples prepared in the magnet. Orientation is obviously observed for the samples prepared with T_{\max} lower than 240°C. No orientation is observed for the samples prepared outside the magnet (Fig. 3(b)).

In order to see the effect of the cooling rate, we also carried out cooling at slower cooling rates, 1, 5, and 20°C/min (slow cooling process), in addition to the quenching (quenching process). Cooling was carried out in the magnet. For all the cooling rates examined, the results indicated the orientation. We could therefore say that the magnetic orientation occurs irrespective of the cooling rate if the pressed film is heated up to the highest heating temperatures ranging between 180 and 240°C and then allowed to cool.

3.2. Analysis of the crystal orientation

The analysis was made for the sample prepared through the quenching process: The sample is prepared by heating the pressed film at 5°C/min up to 200°C and allowed to quench in ice water. The crystal type was of α -modification. This modification is monoclinic with $a = 6.65 \text{ \AA}$, $b = 20.96 \text{ \AA}$, and $c = 6.50 \text{ \AA}$, and $\beta = 99.3^\circ$ [15].

Fig. 4 shows the X-ray azimuthal scans at $2\theta = 14.1$, 16.9, and 18.6, corresponding to the (110), (040), (130) planes, respectively. The azimuthal angles of 90 and 270° correspond to the direction of the magnetic field. A strong orientation is observed for the (040) plane. The maxima at 90 and 270° indicate that the b -axis aligns parallel to the

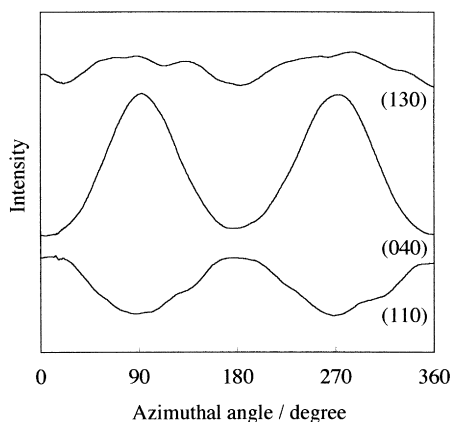


Fig. 4. X-ray azimuthal scans for the (110), (040), (130) planes. Zero azimuthal angle corresponds to the direction perpendicular to the magnetic field.

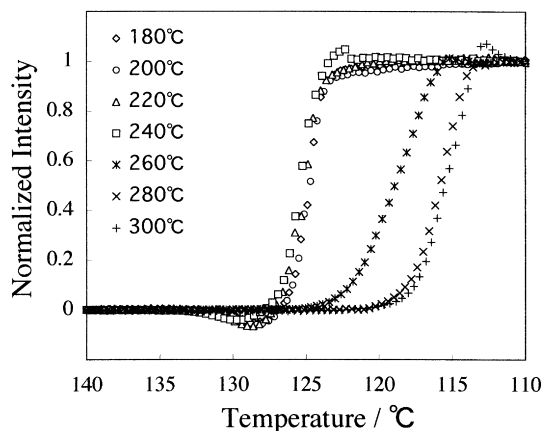


Fig. 5. Transmitting light intensities measured under the crossed polars upon cooling at 5°C/min of the samples melted at different highest melting temperatures, T_{\max} , indicated in the figure. The intensity is normalized by the value at the lowest temperature. The increase in the intensity is due to the formation of crystals.

magnetic field. This is in marked contrast to the orientation attained by the mechanical stretching, where the c -axis aligns in the stretching direction. This assignment of the orientation direction of the b -axis could reasonably explain the azimuthal profiles for other planes: Granted that the b -axis is in the direction of the magnetic field with an axial symmetry along the magnetic field, a calculation shows that the (110) plane exhibits the maxima at the azimuthal angles of ± 17.4 and $180 \pm 17.4^\circ$, and the (130) plane exhibits the maxima at ± 43.2 and $180 \pm 43.2^\circ$. The calculation is consistent with the experimental azimuthal profiles for these planes shown in Fig. 4.

Though the anisotropic diamagnetic susceptibility of iPP fibers is reported [16], full information on the principal axes of the diamagnetic susceptibility of iPP crystal is not yet known. Therefore, we cannot analyze the orientation of the

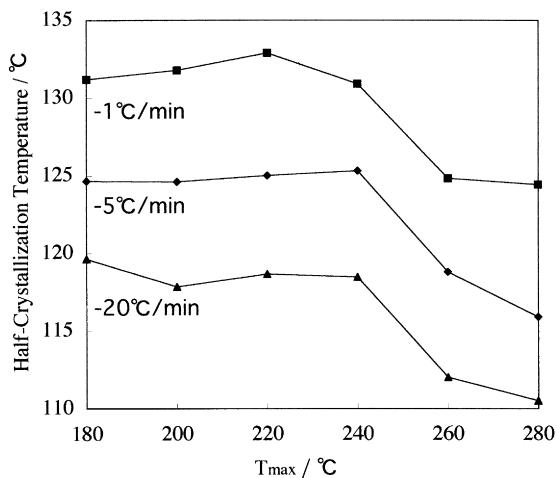


Fig. 6. T_{\max} dependence of half-crystallization temperature which is defined as the temperature at which the half of the crystallization is completed and is determined from the plot as shown in Fig. 5. The results obtained for the different cooling rates are also shown.

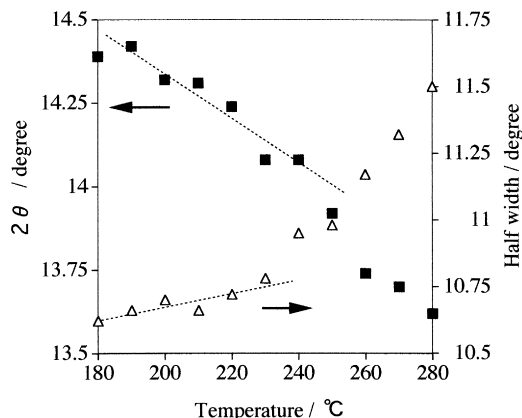


Fig. 7. Peak position and half-width of X-ray diffraction of the melt of iPP plotted against the temperature. Heating rate is 5°C/min.

b -axis in terms of the anisotropic diamagnetism. In addition, the ordered structure responsible for the magnetic orientation may be different from the crystal structure, and hence the magnetic anisotropy of the ordered structure could be different, accordingly. Further study is required to clarify these points.

3.3. Evidence for ordered structure above the melting point

So far, we have observed that the magnetic orientation occurs at the temperature range between 180 and 240°C, but it does not occur above 250°C. This observation seems to indicate that some residual orientation order remains up to 240°C and it disappears upon further heating. The residual order might originate from the crystals existing originally in the pressed film. Though there is no direct evidence, the following results seem to imply the ordered structure.

Evidence supporting some residual order existing above the melting point is provided by the kinetic study of the crystallization from the melts. (The measurements here are carried out without the magnetic field.) A pressed film, which contains crystals, was heated from room temperature and melted at a highest melting temperature, T_{\max} , for 5 min, and then cooled at 5°C/min down to the room temperature. The change in transmitting light intensity measured under crossed polars during the cooling process is shown in Fig. 5. The increase in the intensity indicates the formation of crystals. The onset temperature of the crystallization is about 128°C when the T_{\max} is below 240°C, but it shifts to lower temperatures drastically when the T_{\max} exceeds 240°C. This situation is well demonstrated in Fig. 6 where the half-crystallization temperature (the temperature at which the half of the crystallization is completed, determined from the plot as shown in Fig. 5) is plotted against T_{\max} . In Fig. 6, the results obtained for different cooling rates are also plotted. Irrespective of the cooling rates, it is observed that the half-crystallization temperature decreases drastically toward lower temperatures if the initial melting temperature (T_{\max}) is higher than 240°C.

The observation above might be interpreted as follows: In the case of $T_{\max} < 240^{\circ}\text{C}$, some residual order is still remaining and could serve as nuclei upon cooling, resulting in higher onset temperatures of crystallization. However, in the case of $T_{\max} > 240^{\circ}\text{C}$, this residual order disappeared probably by the completion of melting, and hence lower temperatures are needed for the onset of crystallization. The residual order that we are discussing here is most likely imperfectly-melted crystals, which could be referred to as mesophase [17–19].

X-ray measurements might provide another evidence supporting the ordered structure. High temperature WAXD measurement shows that above the melting point, the diffraction does not exhibit crystalline peaks, but it just exhibits a broad peak suggesting an amorphous melt. Fig. 7 shows that the peak top of this broad peak shifts to lower $2\theta_{\max}$ values when the temperature is increased. The shift is steeper above 240°C . Since the peak top reflects the average distance between the chains, the steep decrease in $2\theta_{\max}$ around 240°C could suggest an appreciable decrease in density around this temperature. This decrease might be caused by the transformation of the residual order into the isotropic melt. A steeper change around 240°C is also observed for the half-width of the peak. The half-width exhibits a steeper increase as shown in Fig. 7. These observations seem to support the discussion made above in terms of crystallization kinetics.

A few studies have been reported regarding the structures existing in melts. These include the Brillouin spectroscopy of paraffin and polymers [20,21] and the magnetic birefringence measurement of polyethylene [22]. Our observation on iPP might be related to the phenomenon observed in the literature, but further investigation should be necessary to fully understand the melt structure of the iPP.

4. Conclusions

The magnetic orientation of a low molecular weight iPP is reported. The iPP aligns in the magnetic field (6 T) in molten states at the temperature range between 180 and 240°C , which is above the melting point. This condition for the orientation is different from those for PEN [1,2], iPS [3], and PET [4,5]. The magnetic orientation of these latter polymers has been found to occur during the induction

period of crystallization from melts. Irrespective of this apparent difference of the orientation condition, it seems that the mesophase is most likely involved in this phenomenon in any case. Since we know little about the structure and the formation dynamics of the mesophase of crystalline polymers except the cold crystallization process of PET [23], the hypothesis that we have made to explain the magnetic orientation of the iPP should be examined in the future study.

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