

Induced Orientation of Isotactic Polypropylene by Magnetic Orientation of β -phase Linear *trans*-Quinacridone as the Nucleating Agent

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Effect of the nucleating agent on the magnetic orientation of isotactic polypropylene (iPP) during the melt crystallization was investigated by means of transmitting light intensity measurement under crossed polars (TLM) and wide-angle X-ray diffraction (WAXD). IPP with various amounts of β -phase linear *trans*-quinacridone (LTQ), which is known as an organic pigment, was melt-crystallized under magnetic fields ranging from 0 to 8 Tesla. Although a high molecular weight iPP did not undergo magnetic alignment because of the formation of large spherulites, it does undergo alignment if LTQ is mixed. The degree of orientation increased with both the amount of LTQ and the field strength. The mechanism of the orientation was explained by the epitaxial growth of the iPP on the LTQ crystal aligned by the applied magnetic field.

Key words: magnetic orientation, isotactic poly(propylene), β -phase linear *trans*-quinacridone, nucleating agent, crystallization

1. INTRODUCTION

Materials with diamagnetic anisotropy can undergo alignment under external magnetic fields. It has been reported that some crystalline polymers including poly(ethylene-2,6-naphthalate) (PEN)[1], isotactic poly(styrene) (iPS)[2], poly(ethylene terephthalate) (PET)[3], low molecular weight isotactic poly(propylene) (iPP)[4], and poly(carbonate) (PC) [5] show the magnetic orientation during the crystallization from melt.

Recently, we reported a novel method for the orientation control of polymers under the magnetic field. Namely, the alignment of polymers induced by magnetic orientation of nucleating agents[6]. It is well known that some organic and inorganic materials, called the nucleating agents, promote the crystallization of crystalline polymers. They reduce the size of spherulite and enhance mechanical properties. According to Lotz et al [7], the nucleating effect, in some cases, is based on the epitaxial relationship, i.e. the lattice matching, between the crystal of nucleating agent and the polymer crystal. Combination of the epitaxy and the magnetic alignment of the nucleating agent leads us to an idea of a novel method of orientation control of polymers as shown schematically in fig.1. As reported in the literature [8], a single crystal can align in a low viscosity environment under the magnetic field. This environment is satisfied in polymer melts. If a nucleating agent, oriented magnetically, has an epitaxy with respect to a crystalline

polymer, the polymer nucleation occurs at a specific surface of the "oriented" nucleating agent (epitaxial crystallization), resulting in crystallization with the orientation (transcrystallization). Our new finding [6] that a high molecular weight isotactic polypropylene shows a strong orientation by addition of N,N'-dicyclohexyl-2,6-naphthalenedicarboxamide is based on this mechanism shown in fig.1.

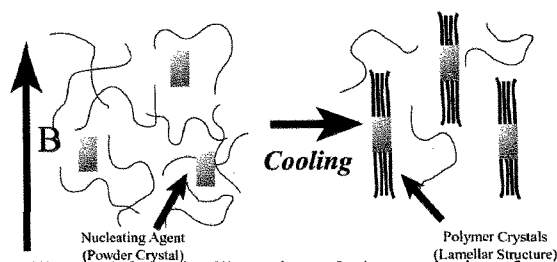


Fig.1 Schematic illustration of the mechanism for orientation control of polymer induced by the magnetic orientation of the nucleating agent

Our method is of industrial importance by two reasons. First, a high degree of orientation is easily attained even for high molecular weight polymers that are difficult to align by themselves under the magnetic field during the melt crystallization. Second, since the orientation of the polymer is induced by the magnetic orientation of the nucleating agent and the orientation of the nucleating agent occurs in the polymer melt, it is enough to apply

the magnetic field just for a short period when the polymer is melted. In this study, we report another example of the orientation of iPP induced by the magnetic orientation of β -phase linear *trans*-quinacridone as the nucleating agent.

2. EXPERIMENTAL

2.1 Materials

Commercial isotactic polypropylene (JHH grade, $M_w=30.3 \times 10^4$, supplied by Mitsui Chemicals. Co) and linear *trans*-quinacridone pigment were used in this study as a crystalline polymer and a nucleating agent, respectively. The crystalline form of LTQ was β -phase, determined by wide-angle X-ray diffraction, although it is known that LTQ has polycrystalline phase [9]. IPP was mixed with various amounts of LTQ (0~10wt%). The samples were vacuum dried and heat-pressed at 200°C for 10 min, then allowed to quench in ice water to obtain a film of 100 μm thick. The film was heated at 5°C/min from room temperature to 200°C, held for 5 min, followed by isothermal crystallization at 135°C. This heat treatment was carried out under the magnetic field ranging from 0 to 8 tesla. It should be noted that the melting point of β -LTQ is about 390°C, far above that of iPP: it keeps crystalline state during the heat treatment.

2.2 Differential Scanning Calorimetry (DSC)

The kinetics of crystallization was studied using DSC. Measurement were carried out under nitrogen atmosphere on a Seiko DSC 200 system equipped with SSC5200H analysis system. The film of iPP with various amounts of LTQ were heated at 5°C/min from the room temperature to 200°C and held for 5min, followed by isothermal crystallization at 125°C.

2.3 Optical Measurement

Home-built optical apparatus [2] was used to carry out *in-situ* magnetic birefringence measurement under the crossed polar condition. Transmitting light intensity obtained with this apparatus is described as

$$I^2 = I_0^2 \sin^2 2\theta \sin^2 (\pi d \Delta n / \lambda) \quad (1)$$

where I_0^2 is the incident light intensity, θ , the angle of the magnetic field with respect to the analyzer, fixed at 45° in the present case, d , the sample thickness, Δn , birefringence, λ , wavelength of the He-Ne laser beam (632.8nm). This equation indicates that the transmitting light intensity changes sinusoidally when the change in Δn , associated with chain orientation, is large.

2.4 Wide-angle X-ray Diffraction (WAXD)

Orientation analysis for the samples prepared in the magnet were carried out using a Mac Science, M18XHF equipped with imaging plate.

3. RESULTS AND DISCUSSION

3.1 Effect of LTQ on the crystallization of iPP

Fig.2 shows the DSC thermograms of iPP with various amounts of LTQ isothermally crystallized at 135°C. The measurement was carried out without magnetic field. The elapsed time 0 means the time at which the temperature reaches 135°C. Although the half crystallization time $t_{1/2}$ is longer than 300 s in the case of iPP without LTQ, it drastically decreases with increasing the amount of LTQ, which means that LTQ promotes the crystallization of iPP. It is clearly demonstrated that LTQ has a strong nucleating effect for iPP.

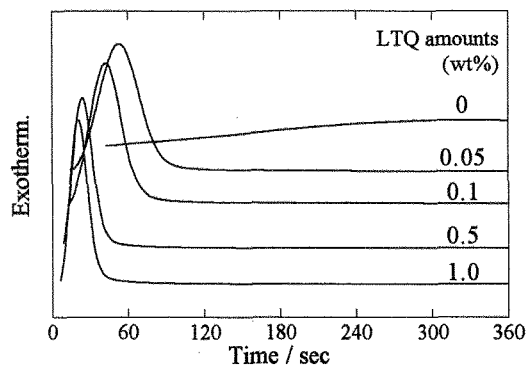


Fig.2 DSC thermograms of iPP with various amount of LTQ during the crystallization at 125°C.

Table I Crystallization data of iPP with various amount of LTQ

LTQ amounts (wt%)	0	0.05	0.1	0.5	1.0
$t_{1/2}$ (sec)	325	53	42	24	21
Avrami exponent, n	3.0	4.3	4.5	4.7	4.4

Table I shows the $t_{1/2}$ and Avrami exponent n for the various samples. The kinetics of the isothermal crystallization from the melt of iPP/LTQ have been analyzed on the basis of the Avrami equation:

$$X_T = 1 - \exp(-K \cdot t^n) \quad (2)$$

where X_T is the volume fraction of material crystallized at time t , K is the overall kinetic rate constant, n is the Avrami exponent depending on the type of nucleation and on the geometry of growing crystals. According to the theory, $n=3$ means the spherulitic growth of the crystal under the condition of heterogeneous nucleation or two dimensional crystallization under homogeneous nucleation. Since commercial iPP contains small amount of residual catalyst or stabilizer, the growth dimension of iPP without LTQ is attributed to the spherulitic growth under the heterogeneous condition. For iPP with LTQ, however, the exponent is over 4, which is not interpreted within the usual scheme. Stein et al reported an extended method using the sector model [10], where crystal growth with the conic shape gives the value of 5 in Avrami exponent. When the epitaxial

crystallization occurs on a pair of specific surfaces of the nucleating agent, the polymer crystal must grow with twin conic shape because of the lamellar branching. Therefore, the observed larger exponents are attributed to the epitaxial nucleation of iPP on LTQ.

3.2 Effect of LTQ on the magnetic orientation of iPP

Fig.3 shows the change in the transmitting light intensity under crossed polars observed for iPP with 0.05% LTQ during the crystallization at 135°C in and outside the magnet. The increase in the transmitting light intensity observed in the case of 0 tesla is attributed to the formation of crystallites. Even though they are not aligned, crystallites contribute to the increase in intensity. On the other hand, the sinusoidal behavior is observed when the crystallization is carried out under the magnetic field of 4 tesla. Under the magnetic field, the initial increase in the intensity occurs in an earlier stage of the crystallization, and the magnitude of the intensity is larger than that for the corresponding intensity in the absence of magnetic field. This unique behavior has been found for PEN [1], iPS [2], and PET [3], and described by eq. (1). The second sine square factor including Δn explains the sinusoidal behavior when the increase in Δn is sufficiently large. Above results strongly suggest that the macroscopic orientation occurs in the iPP/LTQ mixture crystallized in the magnet.

Orientation analysis was carried out by wide angle X-ray diffraction measurement. Fig. 4 shows the WAXD patterns of (a) iPP and (b) iPP/1% LTQ crystallized in the magnet (8 T). The arrow indicates the direction of the magnetic field. All of the samples exhibit crystalline diffractions assignable to the α -modification. Only the Debye-Scherrer ring, indicating the absence of the macroscopic orientation, is observed for iPP without LTQ. Optical microscope observation shows the formation of large spherulites, because of which the magnetic orientation at the early stage of crystallization is made invisible. On the other hand, we can find an intense orientation in the sample of iPP/1% LTQ. It is

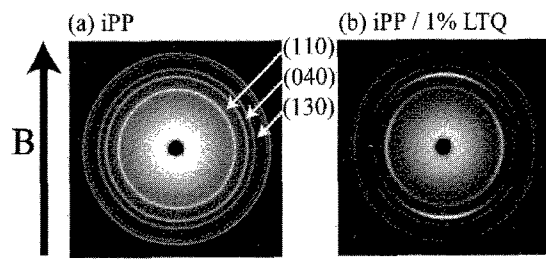


Fig. 4 WAXD patterns of the samples crystallized in the magnet (8 Tesla).

concluded from the orientation analysis that the orientation of the iPP with LTQ is that the *b*-axis is uniaxial aligned along the magnetic field, thus iPP chains align perpendicular to the field direction. The orientation coefficient $\langle P_2 \rangle$ was determined using the data of azimuthal scan along (040) plane of iPP from the following equation:

$$\langle P_2 \rangle = \frac{3 \langle \cos^2 \phi \rangle - 1}{2} \tag{3}$$

$$\langle \cos^2 \theta \rangle = \frac{\int_0^\pi I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_0^\pi I(\phi) \sin \phi d\phi}$$

where ϕ is the azimuthal angle and zero degree is defined as the field direction. $I(\phi)$ is the diffraction intensity of (040) at the azimuthal angle ϕ , and θ , the angle between the orientation axis (*b*-axis) and the direction of the magnetic field. Fig.5 shows the plots of orientation coefficient $\langle P_2 \rangle$ against the LTQ content. As shown in fig.4(a), irrespective of the field strength, $\langle P_2 \rangle$ is zero for the samples without LTQ. Also, no orientation is observed irrespective of the LTQ content when the crystallization is carried out without magnetic field. On the other hand, in the presence of the magnetic field, the degree of orientation shows a sharp increase with increase in the LTQ content. The orientation of iPP is appearing even at very small amount of LTQ (0.05%) and at weak field strength of 2 tesla. It is evident that $\langle P_2 \rangle$ is dependent on both the LTQ content and the field

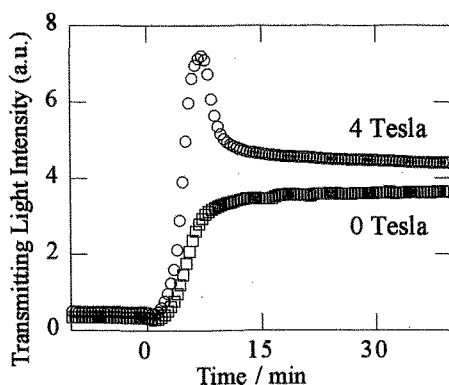


Fig.3 Change in the transmitting light intensity of iPP/0.05% LTQ during the crystallization at 135°C from the melt.

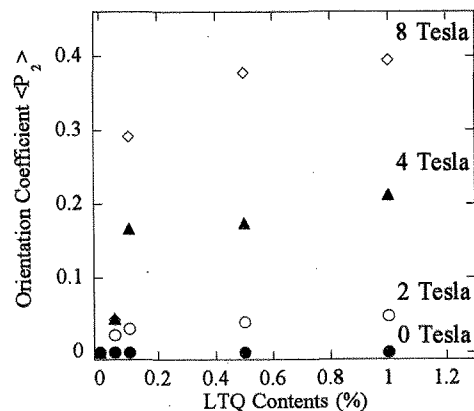


Fig.5 Plots of orientation coefficient $\langle P_2 \rangle$ against the amount of LTQ.

strength. About 40% out of the whole iPP crystal is subjected to the magnetic orientation at maximum. The degree of orientation, however, seems to be saturated above 0.5% of LTQ. $\langle P_2 \rangle$ of the sample with 10% LTQ is almost the same as that of 0.5% LTQ. It conflicts with the orientation mechanism illustrated in fig.1. The reason may be attributed to the aggregation of LTQ crystallites in the melt of iPP. Polarized optical microscope observation supports this reason.

Fig.6 shows the WAXD profiles of iPP/10%LTQ crystallized under the magnetic field of 8 tesla. The meridional direction corresponds to the magnetic field. Note that the diffraction peak at $2\theta=5.5^\circ$, assigned to (100) of LTQ, show a strong orientation. The diffraction intensity along the meridional direction is much larger than that of equatorial direction. It means that the LTQ crystal is oriented with its a^* -axis lied parallel to the field. We previously found that β -LTQ, suspended in an epoxy resin, shows the magnetic orientation with the a^* -axis aligned parallel to the field by its own diamagnetic anisotropy. Since this orientation manner of LTQ is exactly the same as that in fig.6, we can therefore conclude that the orientation of LTQ in iPP matrix is due to the diamagnetic anisotropy of LTQ.

It is shown that the magnetic orientation of LTQ and epitaxial crystallization of iPP is responsible for the alignment of iPP under the magnetic field. Since the analysis of the LTQ crystal including the atomic coordinate is not available at present, the detail analysis on the epitaxy between iPP and LTQ can not be made. However, considering that $(100)_{\text{LTQ}}$ is parallel to $(040)_{\text{iPP}}$, which are both perpendicular to the magnetic field, we might assume that there is an epitaxy between $(100)_{\text{LTQ}}$ and $(040)_{\text{iPP}}$.

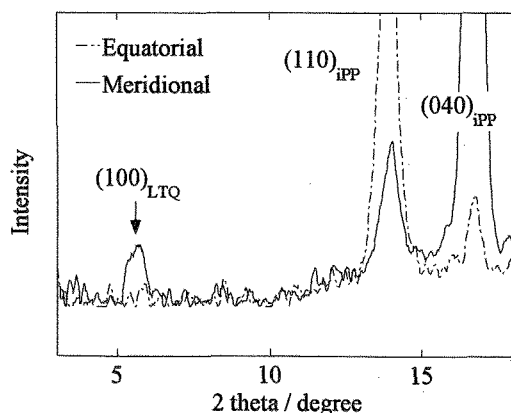


Fig.6 WAXD profiles of iPP / 10%LTQ crystallized in the magnet (8 T).

4. CONCLUSION

Orientation of the iPP induced by the magnetic orientation of LTQ was observed during the crystallization from the melt. Crystallization kinetics measurement showed that LTQ promoted the

crystallization of iPP and changed the geometry of the crystal morphology. By adding LTQ powder into iPP matrix, followed by melt crystallization in the magnet (> 2 tesla), strong orientations were observed by the transmitting light intensity measurement and the wide angle X-ray diffraction. The degree of orientation increased both with increase in LTQ content and the field strength. The mechanism for the orientation of iPP is summarized as follows: due to its diamagnetic anisotropy, the LTQ crystallites undergo magnetic orientation in the melt of iPP. When the iPP melt is cooled, the nucleation of iPP occurs upon the specific "oriented" surface of LTQ. Since iPP lamellar crystal grows with the shape of cone, induced orientation of iPP is realized.

5. ACKNOWLEDGEMENT

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