Melt Structure of Crystalline Polymers as Studied by Means of Magnetic Orientation

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In a series of papers, we have reported that crystalline polymers including poly(ethylene-2,6-naphthalate) (PEN), isotactic polystyrene (iPS), and poly(ethylene terephthalate) (PET) undergo magnetic orientation in the induction period of isothermal crystallization from the melt. However, we have recently found that isotactic polypropylene (iPP) undergoes magnetic orientation in the molten state. Also it was found that PET aligns in the magnetic field even in its molten state. These findings indicate that the ordered structure responsible for the magnetic orientation could be traced back to the melt before the induction period. In this study, the ordered structure existing in the melt is studied by means of magnetic orientation and the crystallization process. A hypothesis describing the structure and formation mechanism of the ordered structure is presented.

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1. Introduction

With recent advances in superconducting magnets, easy access to high magnetic fields has become possible for chemists and materials scientists. As a result, attention has been drawn to the processing of non-magnetic materials, including diamagnetic and paramagnetic materials, in high magnetic fields.¹⁾ Among many applications to processing, the control of the orientation of materials has been of increasing importance. However, the processing is not the whole issue of magnetic orientation. Observation of magnetic orientation is also useful for the detection and the analysis of anisotropic domains existing in the melt of polymers and metals; These domains are sometimes difficult to detect by conventional methods.

We have reported magnetic orientation of crystalline polymers, including poly(ethylene-2,6-naphthalate) (PEN),^{2,3)} isotactic polystyrene (iPS),⁴⁾ and poly(ethylene terephthalate) (PET).⁵⁾ These polymers exhibit magnetic orientation during the induction period of the isothermal crystallization from melt. In this period, crystal formation is not yet observed in terms of X-ray diffraction. Since it is known^{6,7)} that some ordered structure with anisotropic magnetic susceptibility is necessary for the magnetic orientation to occur, we have concluded that the liquid crystalline like structure could appear in the induction period; resulting in the rotation of this structure under the action of magnetic torque through the externally applied magnetic field.

However, we have recently reported that isotactic polypropylene (iPP)⁸⁾ undergoes magnetic orientation above the melting point T_m . Also, we have found that poly(ethylene terephthalate) (PET),⁹⁾ reported previously to exhibit magnetic orientation in the induction period, undergoes orientation even in the molten state, too. This indicates that the origin of the ordered structure necessary for the magnetic alignment

could be traced back to the melt, that is, before the induction period. This finding could provide a better understanding of the origin and the formation mechanism of the ordered structure responsible for the magnetic orientation. In this study, we will discuss the ordered structure existing in melt by means of magnetic orientation, and attempt to give a picture unifying the observation of magnetic orientation in the induction period and that in the molten state.

2. Experimental

2.1 Magnetic orientation

Pellets of low molecular weight isotactic polypropylene, iPP, (SA002V, melt flow index = 240 g/10 min, supplied by Japan Polychem) were vacuum dried and heat-pressed at 200°C for 10 min, then allowed to quench in ice water to obtain a film of 200 μm thick. The crystallization of iPP is so quick that the obtained film was partially crystallized. Pellets of poly(ethylene terephthalate), PET, (M_w = ca. 10,000, supplied by Asahi Chemical Ind.) were dried and heat-pressed at 290°C for 5 min and quenched in ice water to obtain a film of 50 μm thick. In contrast to iPP, the obtained film was amorphous. The film was vacuum dried for 24 h before the use for experiment.

Thermal treatment of the sample was carried out using a home-build furnace²⁾ in an Oxford superconducting magnet of 6 T. Schemes of the thermal treatment for iPP and PET are shown in Fig. 1. In the case of iPP, the film was heated at 5°C/min in a sample cell placed in the magnet from room temperature to the various melting temperatures T_{max} which are above the melting point (T_m = 168°C). As soon as the temperature reaches T_{max} , the sample cell was pulled out from the magnet and then quenched in ice water. In the case of PET, the amorphous film was heated at 5°C/min from room temperature to the various T_{max} s above the melting point (T_m = 260°C), held at this temperature for 5 min, followed by cooling at 5°C/min to the room temperature. It should be noted that the initial amorphous film undergoes cold crystal-

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Fig. 1 Schematic diagram for the thermal history applied for the preparation of (a) iPP samples and (b) PET samples. All these processes were carried out in the magnetic field of 6 T.

lization during the heating before the temperature reaches the melting point.

Melting time dependence of magnetic orientation was studied as follows: the iPP film was heated up to $T_{\max}$, held for various lengths of melting time in the magnet, followed by a forced cooling, while PET film was heated up to $T_{\max}$, held for various lengths of melting time in the magnet, followed by a cooling at 5°C/min.

2.2 Optical measurements

Optical anisotropy measurements were carried out using an Olympus BH-2 microscope. The transmitting light intensity under crossed polars is given as:

$$I^2 \approx \sin^2 2\phi \sin^2(\pi d \Delta n / \lambda) \quad (1)$$

where ϕ is the azimuthal angle, d , the film thickness, and Δn , birefringence. If the orientation occurs, in association with the change in Δn , the azimuthal angle dependence of the transmitting light intensity shows up.

2.3 Wide angle X-ray diffraction (WAXD)

A MAC science MXP-system was used with Ni-filtered $\text{CuK}\alpha$ beam generated under 40 kV, 200 mA.

2.4 Differential scanning calorimetry (DSC)

Kinetics of crystallization was studied using DSC. Measurements were carried out under nitrogen atmosphere on a Seiko DSC200 system equipped with an SSC5200H analysis system. The films of iPP and PET were heated at 5°C/min from the room temperature to various $T_{\max}$ s and held for 5 min followed by cooling at 5°C/min down to the room temperature.

3. Results and Discussion

3.1 On the size of the ordered structure necessary for magnetic orientation

The energy level of an anisotropic domain which is put in a magnetic field becomes lower if it aligns in a specific direction with respect to the external magnetic field. This decrease in energy is so small that it is difficult for this domain

to align in the magnetic field by overcoming the thermal agitation. However, since the decrease in the magnetic energy is proportional to the volume of the domain, the thermal energy is overcome if the domain volume becomes larger than a certain critical size. This size is estimated as

$$V > \frac{2kT\mu_0}{|\chi_a|B^2} \quad (2)$$

where μ_0 is the magnetic permeability of the vacuum, B the magnetic flux density, V the volume of the anisotropic domain, k the Boltzmann constant, and $\chi_a = \chi_{//} - \chi_{\perp}$ the anisotropic diamagnetic susceptibility of the domain with $\chi_{//}$ and $\chi_{\perp}$ being the diamagnetic susceptibility in the directions parallel and perpendicular, respectively, to the chain axis.

According to literatures, the anisotropic diamagnetic susceptibility χ_a of crystalline fibers of iPP and PET is -2.7×10^{-6} [10] and -2.5×10^{-5} [11] respectively. Figure 2 shows the plot of the minimum size calculated from eq. (2) as a function of the field strength. In the above equation, the melting point of the iPP and PET are used as the temperatures. For the field strength of 6 T of the present study, the minimum sizes necessary for the magnetic orientation of iPP and PET are es-

Fig. 2 Critical size of the ordered domain necessary for the magnetic orientation, calculated by eq. (2) with temperatures taken as 180°C and 270°C, respectively for iPP and PET.

Fig. 3 Optical azimuthal scans for (a) iPP and (b) PET prepared in the magnet under the thermal history illustrated in Fig. 1. Temperatures in the figure indicate $T_{\max}$.

estimated to be 68 nm and 34 nm, respectively, if the domain is assumed to be a sphere. The minimum domain size for PET is smaller because its repeating unit contains an aromatic ring which exhibits a larger anisotropic diamagnetic susceptibility. This estimation is based on the data of the anisotropic diamagnetic susceptibility of the crystalline fibers. However, the orienting domain is not in a crystalline fiber form but is most likely mesophase such as liquid crystalline phase and condensation phase.^{12,13} Therefore, the actual χ_a values for these structures might be smaller. Therefore the estimations for the minimum size might be larger than those given for crystalline fibers. In conclusion, magnetic alignment indicates the existence of anisotropic domains of several tens to hundreds of nanometers depending on the packing manner of polymer chains in the anisotropic domain.

3.2 Magnetic orientation of iPP and PET

Figure 3 shows the results of the optical azimuthal measurements carried out for the samples prepared in the magnetic field (6 T). Peaks at 45° and 135° indicate the orientation. Depending on the melting temperature $T_{\max}$, some samples show these peaks. If the $T_{\max}$ is higher than 240°C and 275°C for iPP and PET, respectively, no orientation is observed. Though not shown here, no orientation is observed for the samples prepared outside the magnet under exactly the same conditions. Here, the difference in the thermal history between iPP and PET (Fig. 1) should be noted. In the case of iPP, the melt is quenched outside the magnetic field. Therefore, the orientation observed below $T_{\max} = 240^\circ\text{C}$ is attributed to the anisotropic structures existing in the melt. On the other hand, in the case of PET, the melt is cooled in the magnet down to room temperature, and therefore we do not know in which stage the orientation occurred.

In order to make this point clear, experiments with a ther-

mal history similar to that applied to iPP were carried out for PET. The amorphous film was heated at 5°C/min in the magnet up to 270°C and 280°C, then allowed to quench in ice water outside the magnet. The quenched film thus obtained was annealed outside the magnet under the condition of cold crystallization. Optical azimuthal scans for as-quenched and annealed samples are compared in Fig. 4. It is clear that no orientation is observed for the as-quenched samples irrespective of the melting temperature $T_{\max}$. In contrast, the an-

Fig. 4 Optical azimuthal scans for the PET samples heated up to (a) 270°C and (b) 280°C. In the figure, 'quench' indicates as-quenched sample, while 'anneal' indicates samples quenched followed by annealing at cold crystallization temperature.

nealed samples exhibit orientation if the $T_{\max}$ is 270°C. This observation is explained as follows. There may be aligned anisotropic domains in the melt at 270°C, but the alignment could not be detected optically because the aligned domains are too small and/or too rare in number to be detected optically. Upon annealing, cold crystallization proceeds starting from these small but aligned domains, resulting in an alignment of crystallites. On the other hand, the sample quenched from 280°C does not exhibit orientation even after the annealing. This is because there are not anisotropic domains in the melt at 280°C.

The above observation strongly suggests that both in melts of iPP and PET there are anisotropic domains of some tens of nanometers in size at the smallest, depending on melting temperature $T_{\max}$. Possibility of aligned domains in the melt of PET at 280°C could not be ruled out. Their size and/or their anisotropic diamagnetic susceptibility is too small for these domains to be detected by magnetic orientation at the field strength of 6 T.

3.3 Annealing time dependence

The time τ required for an anisotropic domain to align in the direction of magnetic field is expressed as

$$\tau = \frac{6\mu_0\eta}{|\chi_a|B^2} \quad (3)$$

where η is the viscosity. The viscosities of iPP and PET used in this study were 500 Pa·s (at 180°C) and 120 Pa·s (at 270°C), respectively, which, combined with the values of χ_a , leads to τ values of 39 s for iPP and 1 s for PET.

Figure 5 shows optical azimuthal scans for the iPP samples heated in the magnet at various melting temperatures $T_{\max}$ s for various melting periods, followed by quenching outside the magnet. For the heat treatment at 180°C which is close to the melting point ($T_m = 168^\circ\text{C}$), the orientation remains de-

spite heating for at least 12 h. This indicates that anisotropic structures are stable at 180°C. Although the monochromatic light source was not used for the qualitative comparison of the birefringence, it seems from the figure that the orientation increases with an increase in the heat treatment time. This built-up time of orientation is far larger than the estimated one, *i.e.*, 39 s. One reason for this discrepancy might be that the actual χ_a value of the anisotropic domain is not as large as that estimated from crystals. Another reason could be that the shape of the anisotropic domain is not a sphere but a prolate ellipsoid. The τ value estimated above is for a domain of the spherical shape. If the shape is a prolate ellipsoid, τ increases drastically with increase in the aspect ratio.¹⁴⁾ From these observations, it seems that the regularity of the anisotropic domain in molten iPP might be much lower than that in crystalline phase and/or the shape of the domain could not be spherical. However, further study is needed to confirm these points.

With an increase in melting temperature $T_{\max}$, the orientation disappears over time. For the heat-treatment at 240°C, no orientation is observed if the sample is heated for 30 min. This indicates that the anisotropic domain observed at this temperature is not stable but exists only in a transient state, which is in contrast to the stable anisotropic domain existing at 180°C. In the case of liquid crystalline polymers, the temperature range for the stable liquid crystalline phase is wide, and hence they are called liquid crystalline polymer. In contrast, crystalline polymers, such as iPP studied here, are not regarded as liquid crystalline polymer because the stable anisotropic phase is formed only in a very limited temperature range above the melting point.

A similar observation is made for the PET. Figure 6 shows the X-ray azimuthal scans of the samples heat treated at various $T_{\max}$ s and various durations of melting time. The samples heat treated at $T_{\max} = 270^\circ\text{C}$ exhibit orientation irre-

Fig. 5 Optical azimuthal scans for the iPP samples prepared by heating at (a) 180°C and (b) 240°C over the time period indicated in the figure, followed by quenching.

Fig. 6 X-ray azimuthal scans along the (010) plane of PET samples prepared by heating at (a) 270°C and (b) 280°C over the time period indicated in the figure, followed by quenching.

spective of the duration of melting, while those heat treated at $T_{\max} = 280^\circ\text{C}$ do not exhibit orientation irrespective of the duration of melting time. This observation is consistent with the observation obtained from Fig. 4.

3.4 DSC evidence for the ordered structure above the melting point

So far we have provided evidence for local ordered domains existing in the melt by means of magnetic orientation. Those domains could be heterogeneous nuclei, when the melt is subjected to crystallization, and could facilitate the crystallization. Therefore, the study of the melt crystallization could provide further evidence for the local ordered domains.

DSC measurements were carried out for the purpose. Figure 7(a) shows the DSC thermogram obtained from iPP. The iPP film was heated from room temperature to the melting temperature $T_{\max}$ and held for 5 min, followed by cooling at $5^\circ\text{C}/\text{min}$. With increase in $T_{\max}$, the exothermic peak position moves to lower temperatures, reaching a constant temperature for $T_{\max} > 260^\circ\text{C}$. Figure 7(b) describes this observation more clearly. Here the peak position T_c and the enthalpy ΔH of crystallization are plotted against the $T_{\max}$. Both T_c and ΔH exhibit a large change at $T_{\max} = 240^\circ\text{C}$. This temperature coincides with the highest possible melting temperature for magnetic orientation. The same experiment was carried out for PET. DSC thermograms are shown in Fig. 8(a). T_c and ΔH are plotted against $T_{\max}$ in Fig. 8(b). Exactly the same tendency as iPP is observed: Peak positions are located at higher temperatures if the $T_{\max}$ falls to the temperature range of magnetic orientation, *i.e.*, 270°C and 275°C .

3.5 Local ordered structures in the melt of crystalline polymers

Wunderlich and Grebowics¹³⁾ proposed that mesophase,

Fig. 7 (a) DSC thermograms for iPP obtained upon cooling at $5^\circ\text{C}/\text{min}$ from various melting temperatures ($T_{\max}$) indicated in the figure. (b) Temperature T_c of the exothermic peak top and the enthalpy of crystallization ΔH are plotted against the melting temperature $T_{\max}$.

Fig. 8 (a) DSC thermograms for PET obtained upon cooling at 5°C/min from various melting temperatures (T_{max}) indicated in the figure. (b) Temperature T_C of the exothermic peak top and the enthalpy of crystallization ΔH are plotted against the melting temperature T_{max} .

including liquid crystalline and condic (conformational disordered) crystal phases, exists between the crystalline phase and isotropic melt phase. The local ordered structure that we have seen through magnetic orientation and with DSC measurements might correspond to this mesophase.

In our previous papers, we have reported that PEN^{2,3)} and iPS⁴⁾ undergo magnetic orientation during isothermal crystallization from melt. The start of the orientation is in the induction period where the X-ray diffraction cannot yet detect the crystal formation. This indicates that some ordered structure appears prior to the crystallization. Before our findings with magnetic orientation, it was reported that the ordered structure appears in the induction period of cold crystallization of PET.¹⁵⁾ In relation to the magnetic orientation, we examined a conformation change of PEN¹⁶⁾ and iPS¹⁷⁾ using *in-situ* infrared spectroscopy. In the case of PEN, the bands assigned to the amorphous *trans* conformation was found to increase prior to the increase in the band intensity due to the crystal *trans* conformation. In the case of iPS, we demonstrated that the conformation in the induction period is neither perfect crystal nor amorphous, but it is a partially disordered 3_1 helix. All these spectroscopic observations strongly indicate that some ordered structure appears prior to the crystal formation.

Figure 9 shows the X-ray azimuthal scans for various lat-

Fig. 9 X-ray azimuthal scans along the various lattice planes of iPP sample quenched from 200°C in the magnet. Azimuthal angles of 90° and 270° correspond to the direction of the magnetic field.

tice planes of the samples melted at 200°C followed by quenching. It is known that iPP forms the smectic phase by quenching of melt,¹⁸⁾ but iPP used in this study has a low molecular weight, resulting in some amounts of α -form crystals.¹⁹⁾ Though the analysis of the detailed crystal orientation is a subject of future study, Fig. 9 indicates that the *b*-axis aligns with the magnetic field, and the chain axis lies perpendicular to the magnetic field with an axial symmetry with respect to the magnetic field.

Now, let us consider the ordered structure responsible for the magnetic orientation. The diamagnetic susceptibility of the iPP chain is the most negative in the direction of the chain axis. Then, the chain axis aligns perpendicular to the magnetic field regardless if the ordered structure is (1) crystal, (2) conformational disordered crystal (condic crystal), or (3) liquid crystalline like phase with chain alignment which has axial symmetry with respect to the chain axis. If the ordered structure is like liquid crystalline (case (3)), the orientation of crystals formed from this ordered structure should exhibit a random distribution of orientation with respect to the chain axis. As a result, diffractions from the (*hk*0) planes are centered at 90° and 270°. This is the case for the magnetic orientation of paraffin,²⁰⁾ but it is not for Fig. 9. Incidentally, magnetic orientation of paraffin is also studied by another group.²¹⁾ On the other hand, if the ordered structure is of crystal (case (1)) or condic crystal (case (2)), the azimuthal profiles in Fig. 9 is explained satisfactorily. Since X-ray and infrared results do not show the evidence of crystals, we are led to conclude that the ordered structure responsible for the magnetic orientation is most likely the condic crystal phase.

In the previous papers, we reported the observation of magnetic orientation of PEN^{2,3)} and iPS⁴⁾ occurring in the induction period of the isothermal crystallization from melt. Also, PET⁵⁾ and iPP²²⁾ undergo magnetic orientation in the induction period. The point of the present study is that PET and iPP undergo magnetic orientation even in the molten state which is a more severe condition than in the induction period. Al-

though the same experiment has not been carried out for PEN and iPS, and hence a conclusive statement can not be drawn without future study, the possibility of the detection of the ordered structures in the melts of these polymers could be high in the light of the finding we reported in this paper.

At present, we have not reached a unified picture for the ordered structure responsible for magnetic orientation, but the current hypothesis is as follows. In the heating process, even a melt-quenched amorphous film crystallizes because of cold crystallization which occurs between the room temperature and the melting point. At the melting point, the crystallites formed start to melt, but the memory of crystal conformation is not completely lost in some temperature range above the melting point. The melt at this stage could be regarded as a mixture of condic crystal domains and isotropic melt. The condic crystals are difficult to detect by X-ray or optical means because their number is too small and/or their regularity is not high enough. However, the condic crystals can undergo magnetic orientation if they satisfy the criteria given in eq. (2). With an increase in temperature, the condic crystal changes to isotropic melt, and the orientation disappears accordingly. If the heating is turned off before the transition to the isotropic melt is completed and then the melt is subjected to the cooling or the isothermal crystallization, then the crystallization proceeds with the aligned condic crystal domains being the heterogeneous nuclei to cause crystal orientation. If the heating is turned off after the transition to the isotropic melt is completed, it will take a longer period of time for the formation of nuclei when the melt is cooled or isothermally crystallized. In this case, the formed nuclei might be scarce, small in size, and/or slow in growth so that they cannot align in the magnetic field. The above is a possible hypothesis which should be examined in future studies.

4. Conclusion

We have reported the magnetic orientation of iPP and PET in the molten state. The temperature range enabling alignment of iPP was between T_m (168°C) and 240°C, and that of PET between T_m (260°C) and 275°C. In these temperature ranges, the ordered domains of several tens to hundreds of nanometers in size were indicated. These domains were not stable but transient except in the vicinity of T_m . The phenomenon of magnetic orientation would provide a novel

means to analyze the size and shape, as well as the growth and annihilation of the ordered structures appearing in polymer melts. It will also be applied to the control of orientation of diamagnetic and paramagnetic materials, providing materials that have improved and novel properties.

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