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Magnetic orientation of poly(ethylene-2,6-naphthalate) (PEN) and isotactic polystyrene (iPS) has been reported. The orientation starts to occur during the induction period of isothermal melt crystallization process, i.e. during the initial stage of crystallization process where no crystal growth is yet observed with respect to the wide angle X-ray diffraction. In the case of PEN, the crystallites obtained at later stages of crystallization were aligned with its *c*-axis parallel to the magnetic field, while in the case of iPS, the crystallites obtained were aligned with its *c*-axis perpendicular to the magnetic field. X-ray, infrared, and magnetic birefringence measurements indicated that mesophases appearing during the induction period could be responsible for the magnetic orientation of these polymers.

Keywords: poly(ethylene-2,6-naphthalate); isotactic polystyrene; magnetic orientation; induction period

INTRODUCTION

Liquid crystalline polymers (LCPs) align under magnetic fields due to their anisotropic diamagnetism and their propensity to form liquid crystalline phases[1]. On the other hand, crystalline polymers including the polymers studied in this work, poly(ethylene-2,6-naphthalate) (PEN) and isotactic polystyrene (iPS), have been considered to be indifferent to magnetic fields because they lack in liquid crystalline natures which LCPs possess. However, we have reported[2, 3] that these two polymers align in the magnetic field (6T) during the isothermal melt crystallization.

Some crystalline polymers exhibit stable liquid crystalline phases and hence are called liquid crystalline polymers. On the other hand, majority of crystalline polymers are not classified as liquid crystalline polymers because they do not form liquid crystalline phases in a stable and clearly distinguished manner. However, mesophases[4,5], including liquid crystalline (LC) phase and condis crystal (CC) phase exist between the isotropic melt and the crystal though they may be unstable and/or transient. Also exist the corresponding glasses including LC glass and CC glass[4,5]. For example, recent studies on the cold crystallization of poly(ethylene terephthalate)[6] have revealed that a liquid-crystalline-like orientational order appears during the induction period of crystallization, prior to the appearance of crystals. Another example is isotactic polypropylene which is usually regarded as a crystalline polymer but forms a liquid crystal glass when quenched from a melt[7].

These observations seem to indicate that our finding of the magnetic orientation of PEN and iPS is explained in terms of their liquid crystallinity, or mesophases in general, which shows up probably during the induction period of the crystallization process. In this study, we report the condition of the magnetic orientation and the orientation structures of these polymers studied by the magnetic birefringence, the X-ray diffraction, and the FT-IR spectroscopy in relation to the liquid crystallinity.

EXPERIMENTAL

Pellets of PEN (M_n=8000) supplied by Teijin Co. Ltd. were dried and pressed at 300℃ for 10 min followed by a quench in ice water to obtain amorphous films. Pellets of PEN with other molecular weights (M_n=9500, 12500, 17000), supplied by Teijin Co. Ltd., were also used for the study of molecular weight dependence. Pellets of iPS (M_w=400000) purchased from Scientific Polymer Products, Inc. were pressed at 255℃ for 2 min followed by a quench in the air to obtain amorphous films. These amorphous films were subjected to the isothermal crystallization to measure the temporal change in magnetic birefringence. The films were also subjected to the heat treatment to prepare samples quenched at various periods of crystallization time.

The magnetic birefringence measurements were carried out in an Oxford superconducting magnet (6T) by using the apparatus, which is reported elsewhere[3]. The measurements without the magnetic field were also carried out by using this apparatus. The analyzer was fixed to make an angle of 45° with respect to the direction of the magnetic field. The polarizing plane of the impinging He-Ne laser light (632.8 nm) was set perpendicular (crossed polars) to the analyzer. Under the crossed polars, the transmitting light intensity detects the increase in the birefringence caused by the formation of anisotropic structures or the magnetic orientation of these structures. The temperature detected by the chromel-alumel thermocouple was corrected against a Mettler hot stage FP82HT system. The correction necessary due to the effect of the magnetic field was also made. The amorphous film sample was put between two cover glasses and set in the heating cell. Then, the sample was brought to the melt and kept for 5 min followed by a cooling down to the isothermal crystallization temperature. The start of the crystallization time was taken at the time where the temperature reached the isothermal crystallization temperature. The melt temperature was 300℃ for PEN and 255℃ for iPS, and the isothermal crystallization temperatures were 245 to 255℃ for PEN and 205 to 215℃ for iPS. The measurements were carried out both in the magnet

and outside the magnet.

PEN samples quenched at various periods of the crystallization time were prepared in a furnace designed to carry out the heat treatments in the magnet (6T) as well as outside the magnet[8]. The crystallization temperature was 255℃. Quenched iPS samples were prepared by introducing cold nitrogen gas to the heating cell unit in the apparatus used for the magnetic birefringence measurement[3]. The same thermal history was applied as was used for the magnetic birefringence measurements. The crystallization temperature was 210℃.

X-ray diffraction analyses were carried out by using a MAC Science MXP system. Fourier transform infrared measurements were carried out by using a Nicolet Magna 750. The *in-situ* FT-IR spectroscopy was carried out on the same spectrometer with the use of a Mettler hot stage FP82HT system.

Refractive index measurements were carried out by using a KOBRA-21ADH/DSP system (Oji Scientific Instruments Co.).

RESULTS AND DISCUSSION

Magnetic Birefringence

Figure 1 displays the change in transmitting light intensity measured under

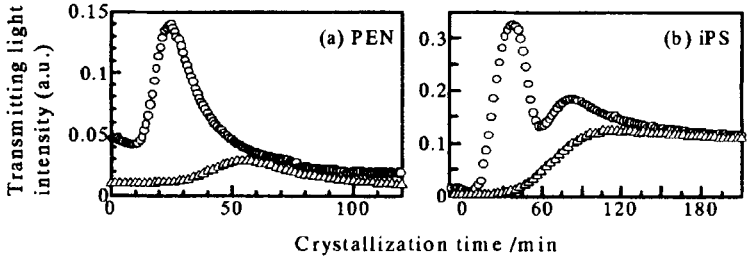

FIGURE 1 Change in transmitting light intensity during the crystallization of PEN at 255℃ (a) and of iPS at 210 ℃ (b) measured under the crossed polars. The circle and the triangle indicate the measurements inside and outside the magnet, respectively.

the crossed polars during the isothermal crystallization from a melt for both PEN (a) and iPS (b). In both cases of PEN and iPS, the changes in intensity with crystallization time measured in the magnetic field are different from those measured without the magnetic field. The increase in the intensity is attributed to the formation of some anisotropic structures. In the absence of magnetic field, the increase in the intensity is associated with the formation of crystals, which is evidenced by the X-ray measurement of the quenched samples as will be discussed later. The decrease of the transmitting light intensity observed in the later stage of the crystallization is due to the enhanced scattering of the impinging light by the crystallites developed.

Under 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. In the case of the iPS, the initial increase is followed by a decrease and an increase before ending up with a monotonous decrease at a later stage of the crystallization. The decrease at the later stage is attributed to the scattering by the crystallites as it is the case for the measurement outside the magnet. The reason for the initial sinusoidal behavior observed in iPS is not clear at present. However, a possible explanation would be given by the following equation describing the change in the transmitting light intensity measured under the crossed polars:

$$I^2 = I_0^2 \sin^2(2\theta)\sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \tag{1}$$

where θ is 45° in this study, thus giving the unity for the first factor; d is the sample thickness, λ is the wavelength of the impinging He-Ne laser light, and Δn is the birefringence. The second sine square factor including Δn explains the sinusoidal behavior when the increase in Δn is sufficiently large. In this view, the increase in Δn for PEN is not very large.

Magnetic Orientation

The birefringence behavior observed in the magnetic field indicates a large change in Δn probably associated with the magnetic orientation. In order to confirm this, we carried out the optical azimuthal measurements on the samples quenched at various periods of crystallization time. If the orientation exists, this measurement gives a sinusoidal curve according to the first sine square factor in Eq. (1). Figure 2 compares the azimuthal scans of the sample prepared with and without the magnetic field. It is clearly demonstrated that the samples prepared in the magnetic field exhibit the orientation in the direction of the magnetic field, while no orientation is observed for the samples prepared outside the magnetic field. The sinusoidal behavior is less enhanced for the samples with prolonged heat treatments, which is because of the low transmitting light intensity caused by scattering by crystallites.

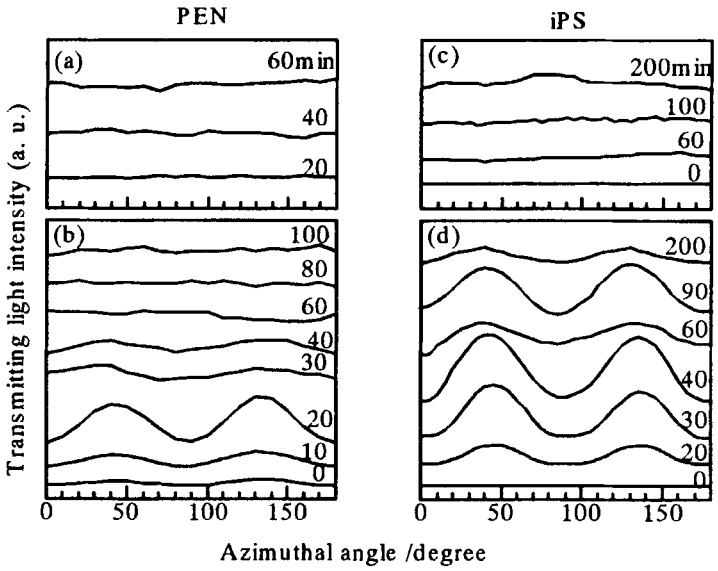

FIGURE 2 Optical azimuthal scans for PEN and iPS films quenched at various periods of crystallization time indicated in the figure. Crystallization temperature were 255 ℃ for PEN and 210 ℃ for iPS. (a) and (c) are for the samples prepared outside the magnet, and (b) and (d) are for these prepared in the magnet.

The quenched samples were also subjected to the X-ray diffraction measurements (Fig.3). The crystallization form of PEN obtained was of the α-modification[9]. The samples quenched in the vicinity of the onset of the magnetic orientation (10-20min) exhibit little diffraction peaks assignable to crystallites. This is the case for both PEN and iPS. Therefore, we might say that the magnetic orientation starts during the induction period. In the case of iPS, the onset of the crystal formation appears earlier (ca. 30 min) in the magnetic field than outside the magnetic field (ca. 60 min), indicating that the magnetic field accelerates the crystallization process. On the other hand, the acceleration is not evident in the case of PEN.

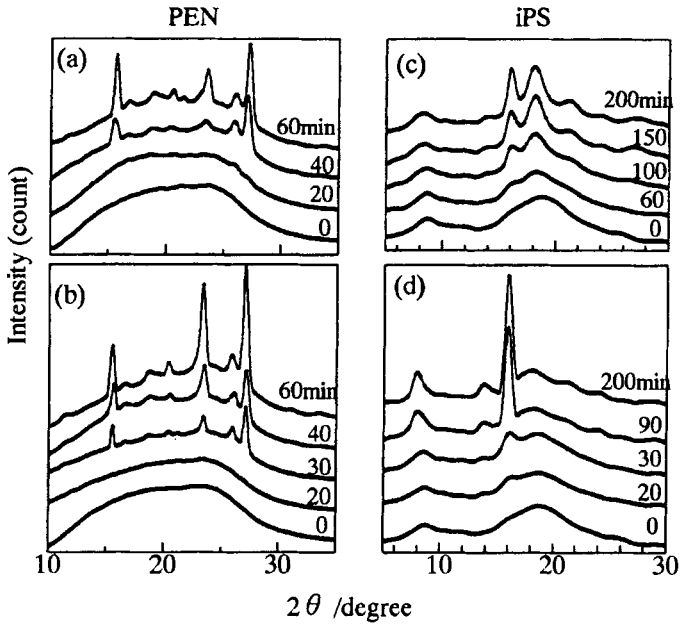

FIGURE 3 Wide angle X-ray diffraction for PEN and iPS films quenched at various periods of crystallization time indicated in the figure. Crystallization temperature were 255℃ for PEN and 210℃ for iPS. (a) and (c) are for the samples prepared outside the magnet, and (b) and (d) are for these prepared in the magnet.

Figure 4 shows the X-ray azimuthal scans carried out for the quenched samples. The orientation of crystallites is evident for the samples prepared in the magnetic field. No orientation of crystallites was observed for the PEN and iPS samples heat-treated outside the magnet. PEN aligns with its

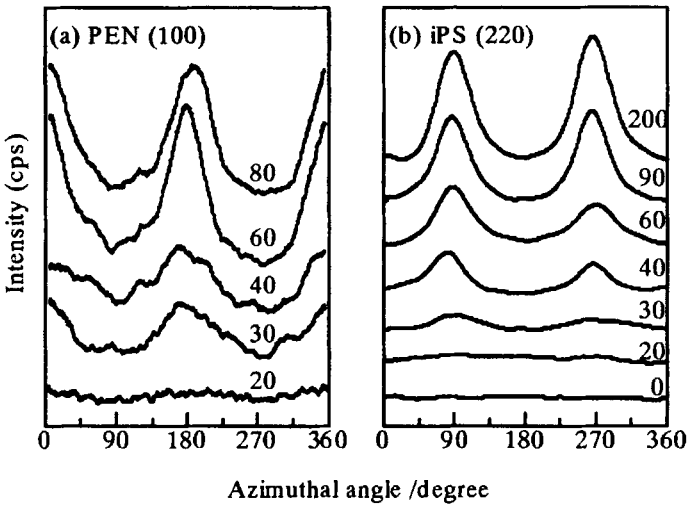

FIGURE 4 Change in X-ray azimuthal profile for PEN (a) and for iPS (b) with respect to the crystallization time (min) inside the magnet. The direction of the magnetic field is taken at 90°. Azimuthal profiles for (010) and (110) of PEN also exhibit the maxima at 0° and 180°. In addition, the edge view for (100) exhibits the maxima at 0° and 180°. All these observations indicate the orientation of the *c*-axis parallel to the direction of the magnetic field. Maxima at 90° and 270° observed for iPS indicates the orientation of the *c*-axis perpendicular to the direction of the magnetic field.

c-axis parallel to the magnetic field, while iPS aligns with its *c*-axis perpendicular to the magnetic field. The direction of orientation is reasonable in considering the crystal structures of these polymers. Both polymers contain aromatic rings which could be the main source of the magnetic anisotropy of these polymers. Because of the ring current induced by the magnetic field, the aromatic rings are energetically more

stable when they align with the ring plane parallel to the magnetic field than perpendicular to the magnetic field. The iPS chain forms 3_1 helix in the crystal and the benzene rings are pending approximately with its plane lying perpendicular to the axis of the helix. Hence the parallel alignment of the benzene ring is achieved by the orientation of the *c*-axis perpendicular to the magnetic field. In the case of PEN, the parallel orientation of the *c*-axis with respect to the magnetic field is consistent with the parallel alignment of the naphthalene rings. However, this orientation of the *c*-axis is not the only one that is consistent with the parallel alignment of the naphthalene rings. The detail of the anisotropic magnetic susceptibility of the naphthalene ring is necessary for the further discussion.

Molecular Weight Dependence

PEN samples with different molecular weights (M_n=9500, 12500, 17000) were also subjected to the heat-treatment in the magnet by using the furnace described before. The thermal history was the same as that applied to the sample with M_n=8000. Figure 5 shows the X-ray azimuthal scans along (100) plane. The orientation of the *c*-axis along the magnetic field is clearly observed. In the birefringence measurements, the samples with larger molecular weights do not exhibit a clear difference regarding the onset time of the increase in the transmitting light intensity between the measurements in the magnet and outside the magnet.

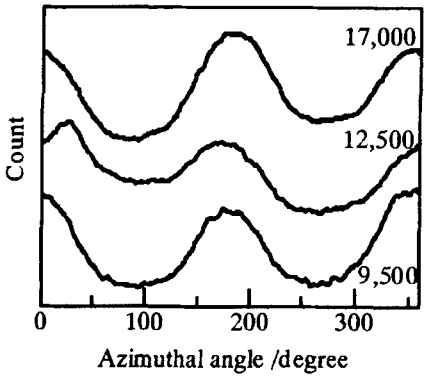

FIGURE 5 X-ray azimuthal scans along the (100) plane of magnetically oriented PEN with different molecular weight indicated in the figure.

Effect of Magnetic Field on the Formation Rate of Anisotropic Structure

In the birefringence measurements, we have seen that the time required for the onset of the transmitting light intensity (t_{on}) measured under the crossed polars is shorter in the magnet than outside the magnet. If we assume that a critical size or a critical order parameter value of an anisotropic domain is necessary for the onset of the transmitting light intensity, the value t_{on}^{-1} would be a measure of the growth rate of the anisotropic domain. Therefore, a shorter t_{on} in the magnetic field could indicate the acceleration of the formation of the anisotropic structure.

Figure 6 displays the temperature dependence of the logarithm of t_{on}^{-1}. The plot is made against $(T\Delta T)^{-1}$, where ΔT is the supercooling measured from the equilibrium melting temperature (243 and 300℃ for iPS and PEN, respectively) determined by means of Hoffman-Weeks plot. In the Figure 6, circles indicate the original data with the open ones for the measurement in the magnet and the filled ones for the measurement outside the magnet. Filled triangle symbols are for the plots in which the original data obtained in the magnetic field are shifted by adding 4 and 5℃ to the actual ΔT values for iPS and PEN, respectively.

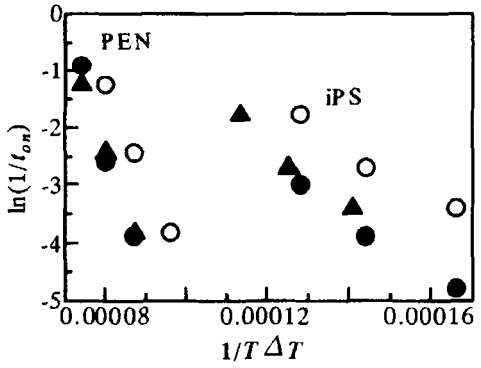

FIGURE 6 The inverse of time t_{on} required for the onset of the increase in transmitting light intensity is plotted against $1/T\Delta T$ with ΔT the supercooling.

The linearity of the plot indicates that t_{on}^{-1} is proportional to $\exp(-1/T\Delta T)$. Since the t_{on}^{-1} is a measure of the rate of formation of the anisotropic structure[10], this temperature dependence seem to suggest that some nucleation process is involved in the formation of the anisotropic structures.

The shifted data obtained for the measurements in the magnetic field approximately fall on the same line obtained for the measurements outside the magnet. Therefore, we might conclude that the magnetic field has an effect to increase the supercooling temperature, resulting in the acceleration of the formation process. Of course, other evidence is necessary to confirm this conclusion because t_{on} is just a rough measure for the formation of the anisotropic structures. In addition, as was mentioned in a preceding section, no acceleration is observed for the PEN samples with higher molecular weights, suggesting that the diffusion term is also important.

However, the following would be one possible explanation supporting this conclusion: The difference between the free energy densities of an anisotropic domain located inside and outside the magnetic field **H** is given[1] as

$$\Delta F_{M,ani} = F_{M,aniso} - F_{aniso} = -\frac{1}{2}\chi_{\perp}H^2 - \frac{1}{2}\chi_a(\mathbf{n}\cdot\mathbf{H})^2, \qquad (2)$$

where $F_{M,\,aniso}$ and F_{aniso} are the free energy densities inside and outside the magnetic field, respectively, $\chi_{\perp}$ is the magnetic susceptibility perpendicular to the direction of the director **n** representing the direction of the anisotropic axis, and χ_a is the anisotropic susceptibility ($=\chi_{//} - \chi_{\perp}$, with $\chi_{//}$ being the magnetic susceptibility parallel to **n**). The sign of $\chi_{//}$ and $\chi_{\perp}$ is negative and that of χ_a is positive. The first term is independent of the orientation, just increasing the free energy because $\chi_{\perp}$ is negative. The second term, on the other hand, is dependent on the angle between **n** and **H** and it reduces the free energy because χ_a is positive. The amount of the reduction is largest when the director is parallel to the magnetic field. This means that an anisotropic domain aligning in the direction of the magnetic field is energetically stable by the amount of the second term in comparison to the domain aligning perpendicular to the magnetic field. On the other hand, the difference between the free energy densities of an isotropic domain located inside and outside the magnetic field is given as

$$\Delta F_{M,iso} = F_{M,iso} - F_{iso} = -\frac{1}{2}\chi H^2, \tag{3}$$

where $F_{M,iso}$ and F_{iso} are the free energy densities inside and outside the magnetic field, respectively, and $\chi = (\chi_{//} + 2\chi_{\perp}) / 3$. We therefore obtain that

$$\Delta F_M = F_{M,aniso} - F_{M,iso} = \Delta F + \chi_a H^2(1 - 3\cos^2\theta)/6, \tag{4}$$

where $\Delta F = F_{aniso} - F_{iso}$ and θ is the angle between **n** and **H**. Since ΔF_M represents the difference in free energy densities between the anisotropic and isotropic phases located in the magnetic field, this quantity could be proportional to $-\Delta T$. Since ΔF is negative, the parallel alignment (θ =0) gives most negative ΔF_M value resulting largest ΔT.

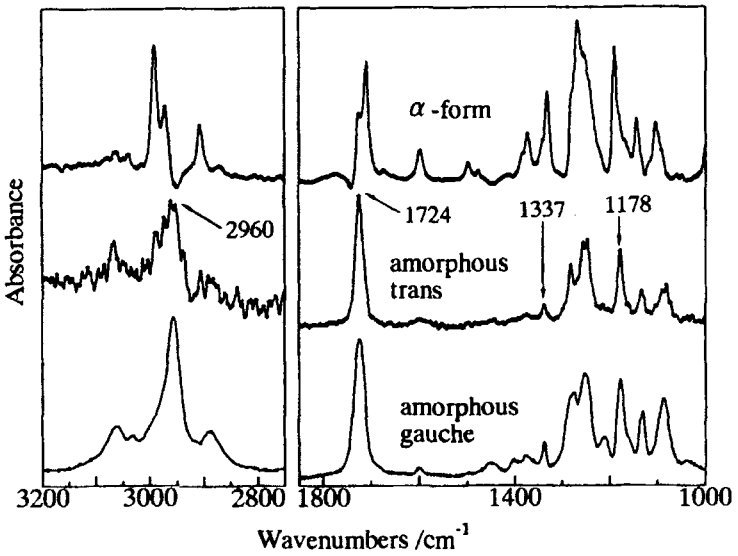

FIGURE 7 Difference spectra obtained for the α-form (top), the amorphous-*trans* conformation (middle), and the *gauche* conformation (bottom) obtained for the PEN sample melted at 300℃ and crystallized at 245℃. The amorphous-*trans* conformation is characterized by the bands at 1178, 1337, 1724, and 2960cm^{-1}.

On Anisotropic Structures Responsible for the Magnetic Orientation

In-situ FT-IR measurements were carried out without the magnetic field to investigate the anisotropic structures responsible for the magnetic orientation[11]. Figure 7 shows the infrared spectra obtained during the early stage of the isothermal crystallization of PEN at 245℃, deconvoluted into three components, that is, the α- crystalline phase, the intermediate phase, and amorphous gauche phase. The spectrum of the intermediate phase is obtained by the subtraction of the spectra of the α-crystalline and amorphous gauche phases from the whole spectrum obtained during the early stage of the crystallization. The detail is described elsewhere[11]. The spectrum of the intermediate phase is clearly distinguished from the spectrum of the crystal.

Figure 8 shows the infrared spectra obtained during the isothermal crystallization of iPS at 200℃[12]. Here, the spectrum corresponding to the

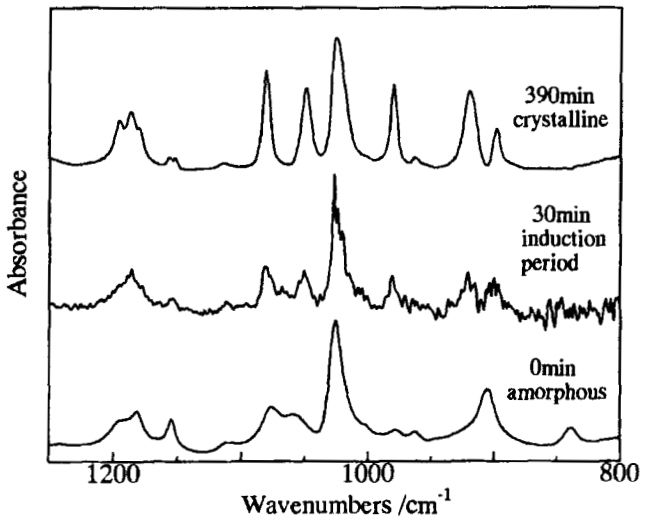

FIGURE 8 Infrared spectra of iPS obtained during the isothermal crystallization at 200℃. The spectra are normalized at 1024 cm^{-1} band. Spectra for 30 and 390 min are the difference spectra where the amorphous component is subtracted from the original spectra.

amorphous phase is subtracted, and hence the difference spectrum is the contribution from the crystalline and intermediate phases. The spectrum thus obtained during the induction period is slightly different from that obtained for highly crystallized sample and also different from that obtained for the amorphous sample. The feature characterizing the spectrum of the induction period, in comparison to the crystal spectrum, is that the band at 981 cm^{-1} attributed to the crystalline conformation is relatively weak, and the bands at 899, 920, 1050, and 1081 cm^{-1} attributed to the 3_1 helix conformation are also weak. The spectral profile is also different from that for the amorphous phase in that no helical and crystal related bands are observed in the amorphous phase.

In both cases of PEN and iPS, the intermediate phase is identified during the induction period, and the infrared spectra suggest that in this phase the polymer chains are in more regular conformations than those in the amorphous phase, but the regularity is not so high as in the crystal phase. These observations indicate some ordered structures which could respond to the magnetic field.

Optical Anisotropy

Figure 9 shows the refractive indices of the iPS films heat-treated at 210℃ in the magnet (6T) plotted against the crystallization time. Here the *x*-, *y*-, and *z*-directions indicate the directions of the magnetic field, the width (perpendicular to the magnetic field), and the thickness, respectively. The figure shows that the refractive index (n_x) is the largest and those in the other two directions (n_y and n_z) are almost of the same magnitude. This suggests that the helical

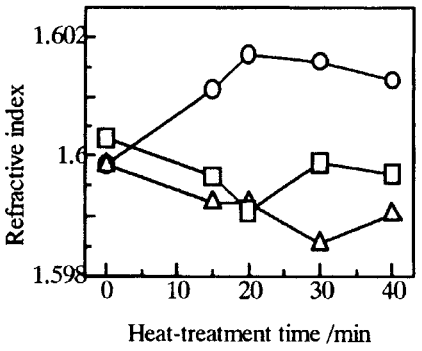

FIGURE 9 Refractive indices n_x (○), n_y (△), and n_z (□) in the direction of the magnetic field, the width, and the thickness, respectively. The average is set as n=1.6.

axes are distributed uniformly on the plane normal to the magnetic field. The films prepared during the crystallization time shorter than 20 min do not exhibit crystallites, and they are almost transparent. This indicates the possibility of applying the magnetic orientation to the fabrication of products demanded for the optical use.

Acknowledgments

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