

Magnetic orientation of poly(ethylene-2,6-naphthalate) during crystallization from melt

Hiroaki Sata, Tsunehisa Kimura*, Shintaro Ogawa and Eiko Ito

Department of Industrial Chemistry, Faculty of Engineering, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-03, Japan

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Magnetic orientation of poly(ethylene-2,6-naphthalate) [PEN], reported in the previous paper, was studied in detail. Birefringence, X-ray and infrared analyses were carried out on the samples quenched at different periods of the crystallization time during the crystallization at 255°C in the magnet (6T). These analyses showed that the orientation observed in the birefringence measurements starts during the induction period in which little crystallinity is observed with respect to the X-ray and infrared measurements. At a later stage of crystallization, the samples exhibited the orientation of crystallites with the *c*-axis parallel to the magnetic field. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

It is well known that liquid crystalline polymers align under magnetic fields^{1–6}, but non-liquid crystalline polymers are usually regarded as being indifferent to the magnetic fields because these polymers lack the ability to form liquid crystalline phases. However, we have shown that poly(ethylene-2,6-naphthalate) [PEN]^{7,8} and isotactic polystyrene⁹ align under the magnetic field during the crystallization from a melt. In analogy to the magnetic orientation of liquid crystalline polymers, we have assumed that some liquid-crystalline-like structures appearing in the course of the crystallization process are responsible for the magnetic orientation. This assumption of a liquid-crystalline-like structure seems to be supported by the observation¹⁰ that a nematic-like structure appears during the induction period of a cold crystallization of poly(ethylene terephthalate), although the crystallization they studied was from a glassy state.

A number of studies have been reported^{11–19} on PEN which has a chemical structure similar to that of poly(ethylene terephthalate) and exhibits excellent physical properties. The magnetic orientation could provide a new way of processing PEN and expand the range of uses of PEN in final products. The present study is a continuation of our previous work⁷ and has been carried out to clarify the structures susceptible to the magnetic field and the condition of magnetic orientation.

EXPERIMENTAL

Material and sample preparation

A PEN sample ($M_n = 8000$) supplied by Teijin was dried under vacuum at 100°C for 24 h. The sample was put between two pieces of aluminium foil and melted at 300°C for 10 min, and pressed at 80 kgf/cm² followed by quenching in ice-water. The pressed film thus obtained

was dried under vacuum for three days. The thickness of the film was about 40 μm and the melting point was 264°C. This film was used for the preparation of the samples heat-treated in and outside the magnet for various periods of crystallization time. The sample for the magnetic birefringence measurements was prepared by the same methods, except that a polyimide film was used instead of the aluminium foil.

Figure 1 shows a schematic diagram of the furnace used to prepare samples heat-treated in a superconducting magnet (6T). A piece of the pressed film (20 × 30 mm), cut from a larger film with the aluminium foil remaining on both sides, was screwed between two aluminium plates (sample cell) and heated in the heating cell under a nitrogen atmosphere. The film was melted at 300°C for 10 min, cooled at a rate of 5°C/min to a given crystallization temperature, and subjected to the crystallization. This process was completely carried out in the magnet. The start of the crystallization process was defined as the point where the temperature reached the given crystallization temperature. After a given period of crystallization time, the sample cell was removed from the heating cell quickly and quenched in ice-water. The film was taken out from the sample cell and the aluminium foil was removed by dissolving in dilute hydrochloric acid followed by washing with water. The film thus obtained was dried under vacuum for 24 h. Exactly the same procedure was followed for the preparation of heat-treated samples outside the magnet.

The correction of the chromel–alumel thermocouple was necessary for use in the magnet⁹: the temperature indicated by the thermocouple in the magnet is 3.8°C higher than the actual temperature in the temperature range used in this study. This is due to the effect of the magnetic field on the thermocouple. This value was determined by the melting point measurements of the tin and lead.

Wide angle X-ray measurements

Wide angle X-ray diffraction measurements were carried out by using a MAC Science MXP system operating at

* To whom correspondence should be addressed

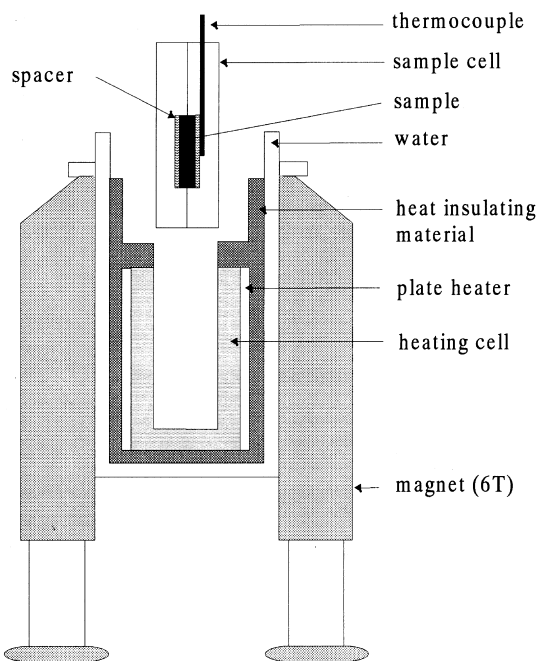


Figure 1 Schematic figure of the furnace used for the sample preparation in the superconducting magnet (6T)

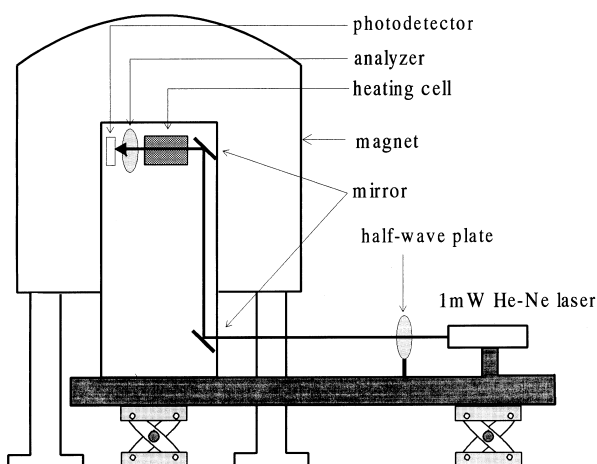


Figure 2 Block diagram of the apparatus for the measurement of the magnetic birefringence

40 kV and 300 mA to generate a Ni-filtered CuK_α X-ray beam. A fixed time method (5 s, 0.02°) was used to obtain equatorial diffractions, and a continuous method was used for the acquisition of azimuthal profiles.

Infrared measurements

A Nicolet Magna 750 was used for Fourier transform infrared (FT-IR) measurements with a resolution of 2 cm^{-1} and 128 scans.

Optical measurements

Birefringence measurements were carried out by using a home-built optical apparatus, as shown in Figure 2. Details on the apparatus have been reported elsewhere⁹. The direction of the magnetic field (6T) makes an angle of 45° to the analyser. By using a half-wave plate, the polarizing plane of the impinging He-Ne laser beam is set parallel or crossed with respect to the analyser. The same thermal history was applied as was employed for the sample

preparation in the furnace: the film was melted at 300°C for 10 min, cooled at a rate of $5^\circ\text{C}/\text{min}$ to a given crystallization temperature and subjected to the crystallization. The start of the crystallization was defined as the point where the temperature reached the given crystallization temperature, and the crystallization time measured from this point is referred to as the elapsed time. The same calibration for the thermocouple was applied for the measurements in the magnet. The reproducibility was about ± 5 min with respect to the peak position observed under the crossed polars.

Temperature calibration among measurements

The thermocouple is not monitoring the sample temperature itself, but it monitors the temperature in the vicinity of the sample. Hence, the actual sample temperature could differ from the temperature indicated by the thermocouple. Since we need to compare the data from the optical measurement with the spectroscopic data obtained for the sample prepared in the furnace, temperature calibration between the optical apparatus and the furnace was necessary. The calibration was made with respect to the hot stage/microscope system (an Olympus BH-2/a Mettler hot stage FP82HT). The *in situ* optical measurement was carried out on the pressed film by using the hot stage/microscope system, and the temporal change in the transmitting light intensity was monitored by a photo-monitor.

In Figure 3, the measurements with the optical apparatus are compared with those with the hot stage/microscope system, where the temperature for the optical apparatus is corrected by 5°C lower than the value indicated by the thermocouple. Both measurements were carried out under the parallel setting of the analyser, and the decrease in the transmitting light intensity is a reflection of the formation of ordered structures including crystallites. Similar decay rates in both measurements indicate that the correction of 5°C is appropriate. This value of correction is the same as was used in previous work⁹.

The transmitting light intensity for the sample, which was crystallized in the furnace followed by quenching at a given period of the crystallization time, was measured on the microscope with the photo-monitor. The intensity is

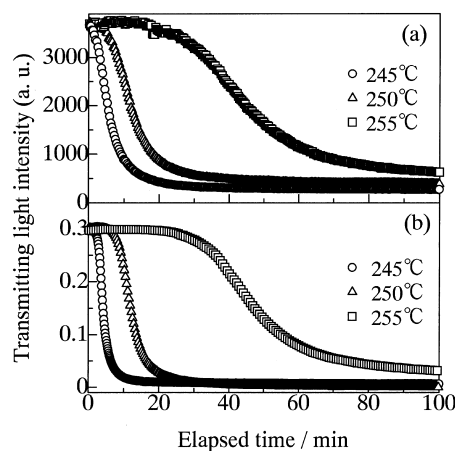


Figure 3 Comparison of the temporal change in the transmitting light intensity between the measurement on the hot stage (a) and the measurement on the optical apparatus (b) during the crystallization at various temperatures. The analyser is set parallel. The correction of -5°C is made on the temperatures in (b). Similarity in decay rates suggests that the correction of -5°C is appropriate

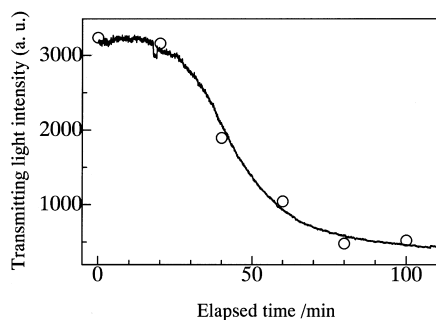


Figure 4 The temporal change in the transmitting light intensity obtained for the measurement on the hot stage at 255°C is compared with the measured transmitting light intensities obtained for the samples quenched at respective elapsed times in the furnace (open circles). The furnace temperatures are corrected by +2°C. Similarity in decay rates suggests that the correction of +2°C is appropriate

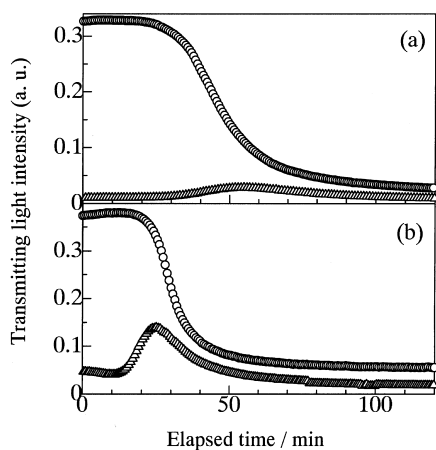


Figure 5 Change in transmitting light intensity during the crystallization at 255°C monitored outside the magnet (a) and in the magnet (b). The circle and triangle indicate the measurements with the parallel setting and under the crossed polars, respectively

normalized by the film thickness. In *Figure 4*, the intensity data are compared with the *in situ* measurement carried out on the hot stage/microscope system, where the temperature for the furnace is corrected by 2°C higher than the value indicated by the thermocouple. Similar decay rates in both measurements indicate that the correction of 2°C is appropriate.

Hereafter, the corrected temperatures are used: the temperatures indicated by the thermocouple are corrected by -5°C and +2°C for the optical apparatus and furnace, respectively. In addition, a further correction of -3.8°C is applied for the experiments in the magnet.

RESULTS AND DISCUSSION

Magnetic birefringence

Figure 5 shows the temporal changes of the transmitting light intensity measured under the crossed polars and the parallel setting during the crystallization at 255°C. The decrease in the intensity observed under the parallel setting is attributed to the scatter of the light caused by the formation of ordered structures including crystallites. The decrease may also occur due to the rise in orientation along the direction of the magnetic field, because in the parallel setting the impinging polarizing light and analyser are inclined by 45° against the magnetic field. On the other

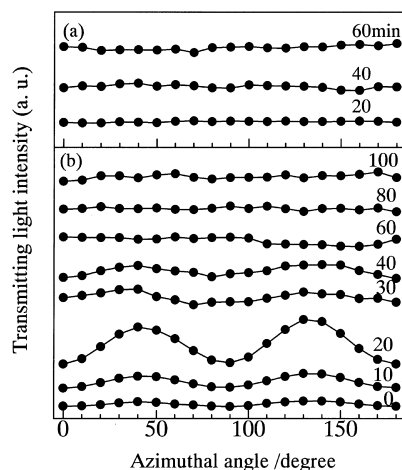


Figure 6 Optical azimuthal scans for the samples heat-treated at 255°C for various elapsed times indicated in the figure, (a) outside the magnet and (b) in the magnet. Measurements are under the crossed polars, and the zero azimuthal angle corresponds to the direction of the magnetic field

hand, the increase in the intensity observed under the crossed polars indicates the formation of the oriented structures whether they are oriented randomly or to a specific direction. This increase turns out to be a decrease because of the enhancement of the scattering due to the formation of crystallites. For the measurement outside the magnet, the intensity under the crossed polars starts to increase at about 30 min, while for the measurement in the magnet, the increase starts at about 15 min. In addition, a higher intensity is observed for the measurement in the magnet.

The high birefringence observed in the magnetic field suggests that the oriented structures are aligned macroscopically in the direction of the magnetic field. To confirm this, the samples quenched at several points of the elapsed time were prepared and subjected to the optical azimuthal scans. *Figure 6b* clearly demonstrates that the sample quenched at 20 min is highly oriented. Even the samples quenched at 0 and 10 min exhibit a slight orientation. For the samples quenched at longer elapsed times, the azimuthal scans are flat, but this does not mean that there is no orientation. This is due to the low intensity of transmitting light caused by the enhancement of the scattering light by crystallites. As will be discussed later, the orientations of crystallites are confirmed by X-rays for the samples quenched at prolonged elapsed times. No macroscopic orientations are observed for the samples heat-treated outside the magnet (*Figure 6a*).

FT-IR

Infrared spectra of the samples quenched at different elapsed times are shown in *Figure 7*. With an increase in the elapsed time, the intensity of the bands assignable to crystals increases for the samples prepared both in and outside the magnet. *Figure 8* shows the difference spectra in order to show clearly the increase in the crystal bands: the spectrum of the pressed sample was subtracted from the spectra quenched at the respective elapsed times so that the gauche band at 1450 cm⁻¹ disappears^{12,19}. The difference spectrum of the sample quenched at 80 min exhibits the crystal bands of the α -form (812, 839, 905, 932, 983, 1005, 2908, 2971 and 2990 cm⁻¹). The trace of bands appearing at 921 and 975 cm⁻¹ indicates the formation of the β -form¹⁹. The crystal bands at 812, 932 and 2990 cm⁻¹ are relatively

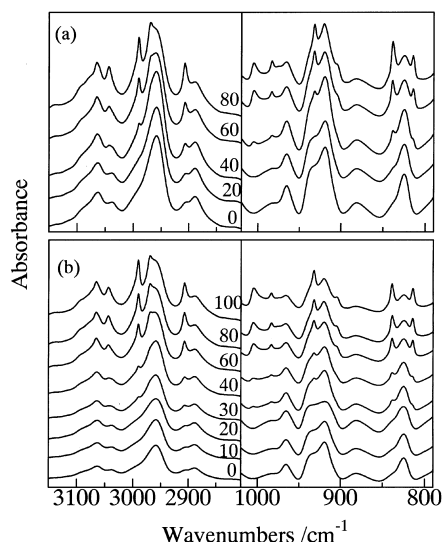


Figure 7 FT-IR spectra for the samples heat-treated at 255°C for various elapsed times (min) indicated in the figure, (a) outside the magnet and (b) in the magnet

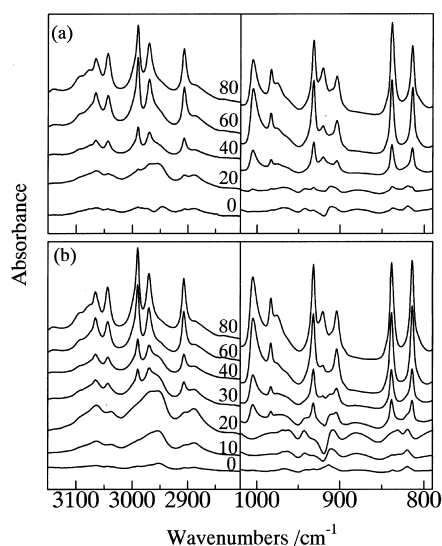


Figure 8 Difference spectra showing the change in conformation during the crystallization. The spectrum of the pressed sample was subtracted from the respective spectra in Figure 8, so that the gauche band at 1450 cm^{-1} disappears. (a) Outside the magnet and (b) in the magnet. Elapsed times (min) are indicated in the figure

stronger in the spectrum for the sample quenched in the magnet than that for the sample quenched outside the magnet. This is attributed to the orientation of crystals.

Since the crystal bands are not clearly observed for the samples quenched at 30 min or shorter, the initial period of crystallization up to 20 or 30 min could be regarded as the induction period. The X-ray data also supports this, as will be shown later. The samples quenched during the induction period (0, 10 and 20 min) exhibit some bands different from the crystal bands. These bands might reflect some conformation changes during the induction period, including the formation of the amorphous-*trans* conformation, as was suggested in our previous work¹⁹ on the *in situ* FT-IR measurement. However, the bands characteristic of the amorphous-*trans* conformation are not available in the present work, except the 2960 cm^{-1} band, because the sample is thick. The appearance of the band around

2960 cm^{-1} during the induction period seems to support the increase in the amorphous-*trans* conformation, but the data are insufficient to draw a definite conclusion.

As was shown in Figure 5, the onset of the increase in transmitting light under the crossed polars is located at around 15 min in the case of measurement in the magnet. The azimuthal scan shown in Figure 6 confirms that this increase is attributed to the orientation. The results of the infrared measurements suggest that the magnetic orientation starts during the induction period or at the end of the induction period in which no significant crystal growth has yet is started. This supports the assumption we made in our previous work⁷ on PEN as well as on isotactic polystyrene⁹ that some ordered structures²⁰ appearing during the induction period, most probably a liquid-crystalline-like structure similar to the structure occurring during the cold crystallization of poly(ethylene terephthalate)¹⁰, are responsible for the magnetic orientation.

X-ray

Figure 9 shows the X-ray diffraction patterns. The samples quenched at 60 min exhibit high crystallinity. Large peaks at $2\theta = 15.6, 23.3$ and 27.0° are attributed to the (010), (100) and ($\bar{1}10$) planes of the α -form¹¹, respectively, while small peaks at $2\theta = 16.4, 18.6$ and 25.5° are attributed to the ($\bar{1}\bar{1}1$), (020) and (242) planes of the β -form¹⁵,

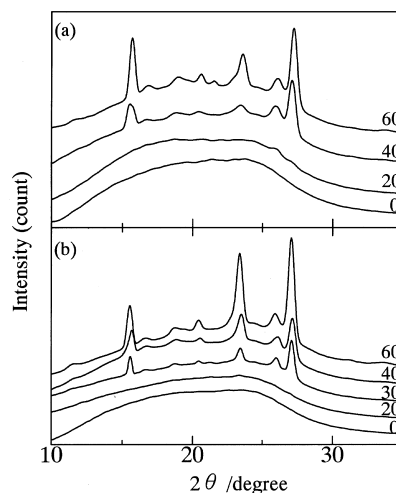


Figure 9 Wide angle X-ray diffraction of the samples heat-treated at 255°C outside (a) and inside (b) the magnet for various elapsed times (min) indicated in the figure

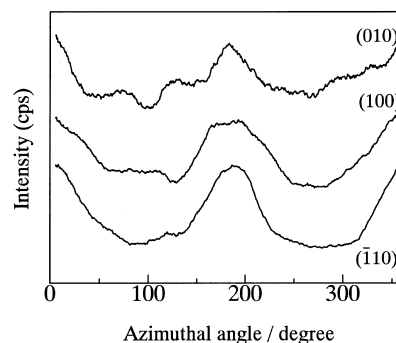


Figure 10 X-ray azimuthal scans along the (010), (100) and ($\bar{1}10$) planes of the samples heat-treated at 255°C for 80 min in the magnet. The zero azimuthal angle is normal to the direction of the magnetic field

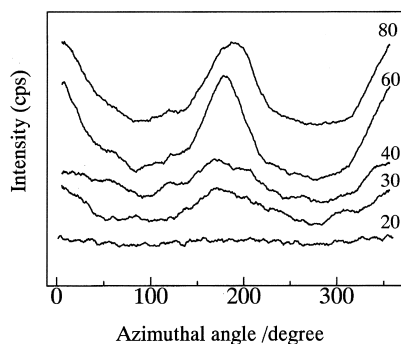


Figure 11 Change in X-ray azimuthal profile with respect to the heat-treatment time (min) in the magnet

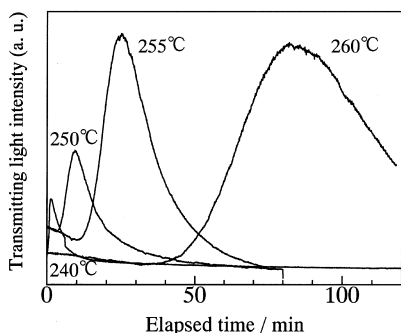


Figure 12 Temperature dependence of magnetic birefringence measured at different temperatures

respectively. Since no crystal peaks are observed up to 20 min, this period of the crystallization process is regarded as the induction period, which is in agreement with the infrared results.

The azimuthal scans for the (010), (100) and ($\bar{1}10$) planes of the α -form are displayed in *Figure 10*. The peaks around 0, π and 2π indicate that the c -axis is oriented along the magnetic field. *Figure 11* shows the development of the crystal orientation viewed as the change in the azimuthal scan of the (100) peak. The orientation is observed as early as 30 min. In the present experiment, it is not clear whether the orientation is a result of the orientation of the crystals or the oriented structures are crystallized in time resulting in the orientation patterns in the X-ray scan. The intensity of the peak increases with the elapsed time, but the half-width seems almost unchanged. This indicates that the degree of orientation of the crystallites is not enhanced in time, although the amount of the oriented crystallites is increased.

Temperature dependence

The optical measurements under the crossed polars in the magnet were carried out at various temperatures, and the results are shown in *Figure 12*. The onset of the increase in the transmitting light intensity shifts toward shorter elapsed times with the increase in the supercooling temperature ΔT . The magnetic orientation at 255°C suggests that the increase observed at other temperatures is associated with the orientation of some ordered structures. Since a critical volume of the ordered structures is necessary for the magnetic orientation to start, the onset time, t_{on} , reflects the time required for the ordered structures to reach a certain critical volume large enough to be susceptible to the magnetic field, and hence the inverse of t_{on} is related to the growth rate of the ordered structures.

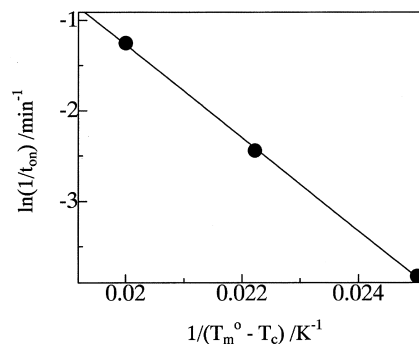


Figure 13 Onset time t_{on} plotted as a function of the inverse of the supercooling temperature

In *Figure 13*, the logarithm of t_{on}^{-1} is plotted against the inverse of the supercooling temperature $\Delta T = T_m^0 - T_c$, where T_c is the crystallization temperature and 300°C is used for the value of T_m^0 . A linear dependence on ΔT^{-1} is obtained. However, this does not necessarily mean that t_{on}^{-1} is an exponential function of ΔT^{-1} , because the number of data points is limited and other choices of the abscissa, e.g. $1/(T_c \Delta T)$ or $1/T_c$, also give a linear dependence. In any case, the temperature dependence of t_{on}^{-1} seems to suggest that a nucleation process²¹ is involved in the formation of the ordered structures susceptible to the magnetic field. Further studies are necessary, however, to clarify the mechanism, since little is known so far about the structure formation during the induction period, except the study on poly(ethylene terephthalate) during the cold crystallization¹⁰.

CONCLUSIONS

The magnetic orientation of PEN during the crystallization at 255°C was studied by means of the magnetic birefringence, X-ray and infrared measurements. The onset of the orientation was observed during the induction period in which little crystallinity was observed with respect to the X-ray and infrared measurements. This suggests that some ordered structures, most likely liquid-crystalline-like structures, are responsible for the magnetic orientation. The infrared measurements suggest that the conformation of these structures is different from the crystalline or amorphous conformations, but the quality of the spectra was not sufficient to draw a definite conclusion. A further study is needed. The orientation of crystallites was observed for the samples quenched after the end of the induction period. It is not clear whether the observed orientation of crystallites is ascribed to the fact that the crystallites randomly oriented when they were formed were aligned under the influence of the magnetic field, or if it is a result of the crystallization of the aligned structure already formed during the induction period. The crystallites observed at the later stage of crystallization exhibit the orientation with the c -axis parallel to the magnetic field.

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