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Processing of Poly(ethylene terephthalate) under Magnetic Fields

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Abstract

Heat treatment necessary for the magnetic orientation of poly(ethylene terephthalate) (PET) was examined by means of *in-situ* magnetic birefringence measurement. Amorphous film was heated above the melting point (259℃) up to the melting temperature (T_{max}) ranging from 270℃ to 300℃, followed by cooling down to the room temperature. Orientation was observed with T_{max} between 270℃ and 275℃. Differential scanning calorimetry indicated that some residual order surviving in this temperature range is responsible for the magnetic orientation. Magnetically aligned films exhibited birefringence of the order of 10^{-3}, suggesting a possible application to the fabrication of films demanded in optical use.

Key words
Magnetic alignment, Poly(ethylene terephthalate), Birefringence, Crystallization

1. INTRODUCTION

In an attempt to control polymer chain orientation, we have investigated the alignment of polymer chains by means of the heat-processing of crystalline polymers under magnetic fields. We reported that crystalline polymers, including poly (ethylene-2,6-naphthalate) [1, 2], isotactic polystyrene [3], poly(ethylene terephthalate) [4], and isotactic polypropylene [5], undergo magnetic alignment by solidification of the melt of these polymers in the magnetic field. Also, magnetic orientation was observed for paraffin under a similar condition [6]. It should be noted that all these polymers are not ferromagnetic but diamagnetic.

The conditions necessary for the magnetic alignment are summarized as follows: (1) material should have anisotropic diamagnetic susceptibility; (2) some ordered domain with a volume larger than a critical size should exist in order to overcome the thermal agitation; (3) low viscosity in order to have the anisotropic domain rotate in a reasonably short time period. Melts of crystalline polymers lack in anisotropic domains, that is, the condition (2) is not satisfied, and hence it was considered that they cannot undergo magnetic alignment. In a solid state, on the other hand, crystallites are embedded in a glassy amorphous matrix, and hence they cannot rotate under the action of magnetic torque because the viscosity of the surrounding matrix is too high. These considerations seem to suggest that magnetic alignment is not possible in crystalline polymer systems. This is in contrast to liquid-crystalline polymers, which satisfies all three conditions mentioned above and hence they can easily align in the magnetic field.

In our observation, magnetic orientation occurs during phase transition from melt phase to crystalline phase. It is intuitively acceptable to consider that the melt phase passes through some intermediate state before the completion of crystallization. In this intermediate state, the crystal embryos would start to form but the viscosity is not yet very high, satisfying the conditions (2) and (3). However, whether the orientation occurs or not strongly depends on the thermal history. Also detail of the heat treatment condition differs from polymer to polymer. The detail of this intermediate state is not fully elucidated at present time. This issue, termed as "what is happening in the induction period of crystallization, i.e. at very initial stage of crystallization", is currently under active discussion among polymer scientists.

This paper reports on a magnetic alignment of poly (ethylene terephthalate) (PET), focusing on the detail of the condition necessary for the magnetic alignment to occur. Since the orientation produces birefringence, we expect that this phenomenon could be applied to the fabrication of birefringence films demanded in optical use. Optical properties obtained by means of magnetic orientation are briefly reported.

2. EXPERIMENTAL

2.1 Materials

PET sample with Mw = 9600～10000 was supplied by Asahi Chemical Ind. Pellets of the sample were dried under vacuum and hot-pressed at 290℃ for 5 min and quenched in ice water to obtain a film with 50 μm thickness, then dried under vacuum for 24 h prior to the use. The film thus obtained was put in an Oxford superconducting magnet operating at 6 Tesla, and heat-treated according to the scheme shown in Fig. 1. The same treatment was also carried out outside the magnet. As indicated in Fig. 1, the film sample was melted at various maximum melting temperatures (T_{max}) between 270℃ and 300℃, which is above the melting

point 259℃, for 5 min and subjected to the cooling at 5 ℃ /min for crystallization down to the room temperature. Obtained samples were subjected to the optical measurements. The change during the heat treatment process was also studied by means of *in-situ* birefringence measurement.

2.2 Optical Measurements

Home-built optical apparatus [3] was used to carry out *in-situ* magnetic birefringence measurements under 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 is the impinging light intensity, θ, the angle of the magnetic field with respect to the analyzer, $\theta = 45$℃ in the present case, d, the sample thickness, Δn, birefringence, λ, wavelength of the He-Ne laser (632.8nm). The equation indicates that the transmitting light intensity changes sinusoidally when the change in Δn, associated with chain orientation, is large. Optical azimuthal scans were carried out using an Olympus BH-2 polarizing optical microscope system.

2.3 Differential Scanning Calorimetry

DSC measurements were carried out with a Seiko DSC200 system under nitrogen atmosphere. Sample film of ca. 5 mg was put in an aluminum pan and the temperature control same as shown in Fig. 1 was applied.

3. RESULTS AND DISCUSSION

Fig. 2 shows the results of *in-situ* optical measurements. If the cooling starts at 270℃ (Fig. 2a), we see a large difference between the measurements in and outside the magnet. A steep and large increase followed by a decrease in the case with the magnetic field is attributed to the orientation: this behavior is well explained in terms of equation (1). Around 232℃, the decrease in intensity turns out to be a sudden increase and then the intensity reaches a constant level. This sudden change might be due to the onset of crystal formation. This temperature corresponds to the onset of an exothermic peak in DSC measurement, which will be discussed later. At present, however, we cannot tell whether this increase is associated with the orientation of the crystallites. We could not rule out a possibility that the magnetic field affects the number and the size of crystallites, resulting in the increase in intensity around 232℃. A change in intensity is also observed around 232℃ in the case without magnetic field. In this case, the intensity decreases slightly in contrast to the case with magnetic field. In the case of the cooling starting at 280℃ (Fig. 2b), we only find a slight difference in a later stage of crystallization process. This difference might not be attributed to the orientation.

Fig. 3 shows the results of optical azimuthal

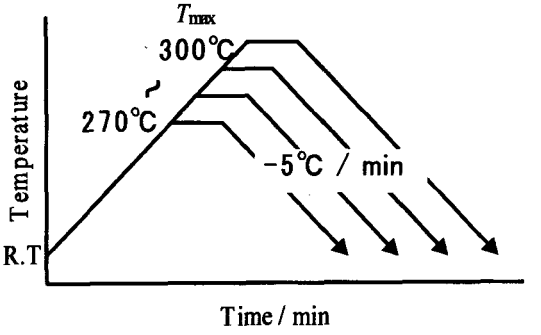

Fig. 1 Thermal history applied to examine the condition of magnetic alignment. A film sample is heated up to a maximum melting temperature (T_{max}) between 270℃ and 300℃, held at this temperature for 5 min, and then allowed to cool down to the room temperature.

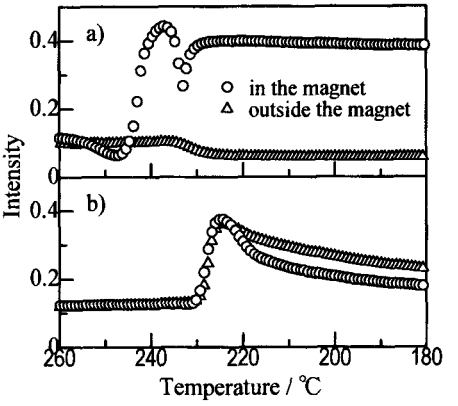

Fig. 2 Temporal change in transmitting light intensity measured under crossed polars during the cooling from the maximum temperatures T_{max} of (a) 270℃ and (b) 280℃.

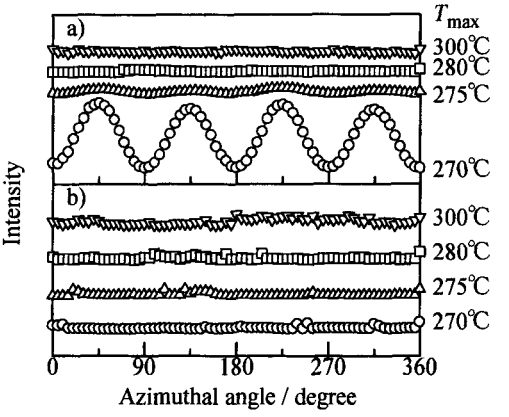

Fig. 3 Optical azimuthal scans for the samples obtained upon cooling from various starting temperatures (T_{max}) (a) in the magnet and (b) outside the magnet. The direction of the magnetic field corresponds to the zero azimuthal angle.

scans carried out for the samples obtained after completion of *in-situ* measurements with various starting temperatures (T_{max}) between 270℃ and 300℃. Depending on the Δn values which the individual samples possess, the transmitting light intensity changes according to the equation (1): no transmitting light is observed if $\Delta n = 0$, while a sinusoidal change ($\sin^2 2\theta$, with θ the azimuthal angle) is observed if $\Delta n \neq 0$. From Fig. 3a, it is found that the heat treatment in the magnet causes orientation when T_{max}=270℃. Also, T_{max}=275℃ seems to produce orientation. However, heating above 280℃ prevents the magnetic orientation. On the other hand, it is evident that no orientation is observed over the whole range of T_{max} examined if the samples are prepared without magnetic field (Fig. 3b).

Melting temperature dependence of the magnetic alignment discussed above strongly suggests the difference in melt structure. Some residual structure, possibly originating from the crystallites formed by cold crystallization during the heating of amorphous quenched sample, remains even above the melting point (259℃), and the degree and the amount of these remaining order might depend on the temperature. This phenomenon is partly related to so called "memory effect" often experienced when working on polymer melts [7, 8]. Magnetic alignment could provide a new means to analyzing the memory effect.

Though detail study has not been carried out yet for the melting temperature between 259℃ and 270℃, a preliminary result indicates that the alignment also occurs in this temperature range. Unlike the residual structure existing above 270℃, the crystallite itself might be responsible for the orientation because the endothermic peak due to melting of crystallites is not fully completed yet in this temperature range.

In order to see whether there is a difference in melt structure, the melt crystallization process was studied by means of differential scanning calorimetry (DSC). The quenched amorphous film used here was the same as that used for the *in-situ* optical measurement. The DSC measurement was carried out without magnetic field. Fig. 4 shows the DSC thermograms for the cooling process starting from various T_{max} indicated in the figure. The thermogram with T_{max}=270℃ exhibits a sharp exothermic peak starting around 232℃. This temperature coincides with that discussed previously with respect to the *in-situ* optical measurement. With increase in T_{max}, the onset of the peak shifts toward lower temperatures in association with the broadening of the peak. The sharpness and the higher onset temperature of the peak when started at T_{max}=270℃ suggests that some residual order exists which easily and promptly goes back to the crystal form. On the other hand, once the sample is heated up to 280℃, the crystallites formed during cold crystallization are melted completely to reach highly entangled isotropic melt. As a result, a lower temperature and a longer time are necessary for this melt to go back to crystal packing through disentanglement process. The DSC results are in good agreement with what is observed in the behavior of the magnetic alignment.

We finally show the results of the optical properties attained by the magnetic alignment. Here

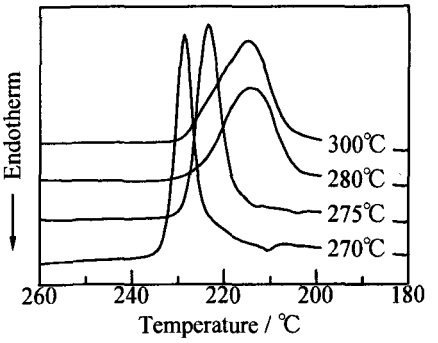

Fig. 4 DSC thermograms for the crystallization of the PET samples after melted at various temperatures (T_{max}).

Table I Optical properties of magnetically aligned PET.

T_{max} (℃)	T_c (℃)	t_c (min)	retardation (nm)	Δn
270	245	0	0	0
		10	0	0
		20	24.5	1.2×10^{-4}
		30	236	1.2×10^{-3}

T_{max}: melting temperature; T_c: crystallization temperature; t_c: crystallization time

the samples were not prepared by the thermal treatment displayed in Fig. 1, but were prepared by means of isothermal crystallization followed by quenching at various periods of crystallization time. Experimental detail will be reported elsewhere. With appropriate choice of crystallization time, we were able to obtain orientation of polymer chains before the extensive formation of crystallites. That enabled us to prepare film samples which exhibited transparency.

Table I shows the results of optical properties. The retardation reaches as large as 236 nm, corresponding to the birefringence Δn of 1.2×10^{-3}. Since the crystal formation was inevitable with longer heat treatment, the film sample with the largest Δn did not possess enough transparency. Optimization of the heat treatment condition is necessary to improve the transparency.

4. CONCLUSION

Magnetic orientation of PET occurs in a limited range of the melting temperature between 270℃ and 275 ℃. DSC measurements provided evidence supporting that some residual order remains in this temperature range, enabling magnetic orientation. Retardation results for the magnetically aligned films were presented, which suggests a possible application of this phenomenon to the fabrication of optical films with controlled distribution of birefringence.

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