Magnetic orientation of poly(ethylene-2,6-naphthalate)

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A new finding is reported of the magnetic orientation of poly(ethylene-2,6-naphthalate) (PEN) near its melting point, evidenced by X-ray analyses and magnetic birefringence measurements. Since PEN does not exhibit features characteristic of liquid-crystalline polymers under a polarization microscope, the magnetic orientation was unexpected. The orientation is probably due to some ordered structure susceptible to a magnetic field, but the detail of the structure is not fully understood at present. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

With the recent development of high magnetic fields, it has become an interesting subject to study the effects of a magnetic field on polymeric materials. Liquid-crystalline polymers are known to be able to interact with magnetic fields[1-4], while non-liquid-crystalline polymers in the molten state have been assumed to be indifferent to magnetic fields. This comes from the analogy with small molecules[5]. Organic molecules, usually having diamagnetic anisotropy, experience a torque when an external magnetic field is applied. In the case of an isotropic phase, the torque on a single molecule is so small compared to thermal agitation that it cannot rotate the molecule. On the other hand, in the case of a nematic phase, the torque on each molecule can work cooperatively and cause the nematic domain to rotate.

In this preliminary report, we show some evidence of the magnetic orientation of poly(ethylene-2,6-naphthalate) (PEN) near its melting point. This polymer does not exhibit any texture patterns typical of liquid-crystalline polymers under a polarization microscope, and hence the magnetic orientation was unexpected. Possible reasons for the magnetic orientation of PEN are discussed in terms of some ordered structure probably present in the molten PEN.

EXPERIMENTAL

Materials

PEN samples used in this study were supplied by Teijin Co. Ltd with nominal molecular weights of 8000, 13 000, 17 000, 19 000 and 21 000. Pellets were dried under vacuum at 90°C for 24 h, pressed at 290°C for 5 min and quenched in ice–water to obtain quenched film samples.

Heat treatment in a magnetic field

The quenched films were heat-treated in a furnace[6] designed for heating samples in a superconducting magnet (6 T). The films were heated at a heating rate of about 20°C min^{-1} and kept for various residence times from 30 min to 180 min at temperatures between 240 ± 5°C and 260 ± 5°C, followed by slow cooling (hereafter referred to as 'heating process'). For the sample of molecular weight 8000, another process of heat treatment was also applied: the films were molten at 285 ± 5°C for 5 min prior to the heat treatment at 235 ± 5°C for 60 min, then cooled slowly (hereafter referred to as 'cooling process'). In every experiment, the whole process was carried out in the magnet.

X-ray photography

X-ray photographs were taken using a Ni-filtered Cu Kα X-ray beam from a rotating anode X-ray generator (MAC Science MXP) operating at 40 kV and 250 mA. The camera distance was about 35 mm and the exposure time was 3 min.

### Differential scanning calorimetry

D.s.c. was carried out using a Seiko DSC200 equipped with a thermal analysis system SSC5200H under a dry nitrogen atmosphere. A quenched sample was heated at a heating rate of 2 or 20°C min^{-1}, as well as cooled at a cooling rate of 2°C or cooled quickly by exposing the pan to the air, after being held at 290°C for 10 min.

Magnetic birefringence

In *Figure 1* is shown the block diagram of the apparatus used for the optical measurement of the orientation process of polymers in the superconducting magnet (6 T in strength, and vertical magnetic field). By using two mirrors fixed inside an aluminium cylinder (a diameter of 80 mm), a polarized He–Ne laser (1 mW, $\lambda = 633$ nm) beam is led to the top of the cylinder. The

laser source is arranged such that the polarization plane at the top of the cylinder makes an angle of 45° to the magnetic field. After further reflection by two mirrors, the light is led to an analyser whose angle can be adjusted such that the intensity of transmitting light is minimum (perpendicular) or maximum (parallel). The laser, the aluminium cylinder, the analyser and the detector are fixed tightly on an aluminium frame, which is jacked up in order to insert the cylinder part into the bore of the superconducting magnet. A separable attachment is set on the top of the cylinder to provide a thermally insulated space in which a cylindrical sample heating cell is fixed in alignment with the laser beam. A piece of sample film (ca. 50 μm) placed between two round coverglasses (diameter of 10 mm) with a polyimide film as a spacer is screwed into the cell. The plane of the coverglasses is parallel to the magnetic field and perpendicular to the laser beam. A thermocouple is set near the heating cell, but calibration is not carried out.
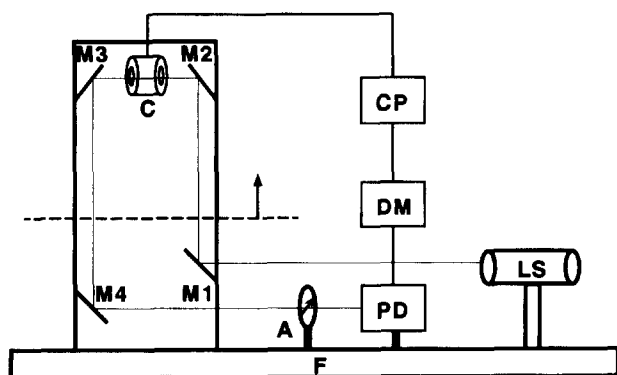
Figure 1 Block diagram of the apparatus for measurements of magnetic birefringence in a superconducting magnet: LS, laser light source; M1 to M4, mirrors; A, analyser; PD, photodetector; DM, digital multimeter; CP, computer; C, sample cell; F, aluminium frame. The upper part of the cylinder shown by the arrow is to be inserted into the magnet
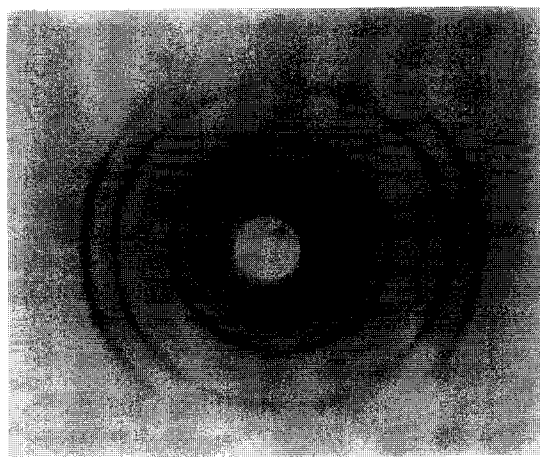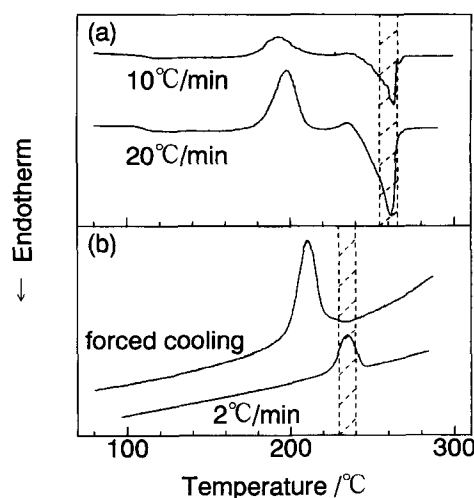
RESULTS AND DISCUSSION

Among the samples with different molecular weights, the one with the lowest molecular weight (8000) exhibited magnetic orientation under some heat-treatment conditions. In *Figure 2* is shown the X-ray photograph of the PEN sample prepared through the 'heating process', in which the sample was heat-treated at 260 ± 5°C (near the melting point) in the magnet for 60 min. Two broad arcs on the equator, corresponding to (1 0 0) and ($\bar{1}$ 1 0) of the α modification of PEN[7], are clearly observed, indicating the orientation of crystallites. Broad arcs on the ring corresponding to (0 1 0) seem to imply a complicated orientation distribution[8], which is different from the orientation observed in mechanically stretched PEN samples[9,10]. No sign of orientation was observed when the same experiment was carried out outside the magnet. The orientation was also observed for the sample obtained through the 'cooling process' in which the sample was pre-heated at 285 ± 5°C before the heat treatment at 235 ± 5°C for 60 min. A similar X-ray photograph was obtained for this sample.

Figure 3a shows the d.s.c. curves of the quenched PEN film. The exothermic peak corresponding to the cold crystallization process shifts towards higher temperatures with the increase in heating rate, which the endothermic peak corresponding to the melting point stays around 261°C irrespective of the heating rate. The hatched area indicates the heat-treatment temperature for which the magnet orientation was observed in the 'heating process'. *Figure 3b* shows the d.s.c. curves of the cooling process in which the quenched PEN film was molten at 290°C for 10 min before cooling. The exothermic peak corresponding to the crystallization process shifts to lower temperatures when the cooling rate is increased. The two cooling rates used, 2°C min^{-1} and the forced cooling, seem to give the lower and upper limits of the actual cooling rate, respectively, between which the PEN sample was cooled in the magnet from 285 ± 5°C to 235 ± 5°C to obtain the oriented sample ('cooling process'). Hence, the exothermic peak in the actual 'cooling process' may fall somewhere between the

Figure 2 X-ray photograph of the sample heat-treated (260 ± 5°C for 60 min) in the magnet (6 T). This is for the sample obtained with the 'heating process'; the same photograph is obtained for the sample obtained with the 'cooling process' (235 ± 5°C for 60 min). Magnetic field is in the vertical direction

Figure 3 D.s.c. curves for the quenched PEN film (a) on heating and (b) on cooling. Heating and cooling rates are shown in the figure. Hatched areas indicate the temperatures necessary to bring about magnetic orientation

two exothermic peaks shown in the figure. Therefore, the hatched area indicating the heat-treatment temperature necessary for the magnetic orientation might be located in a temperature region slightly higher than the crystallization temperature.
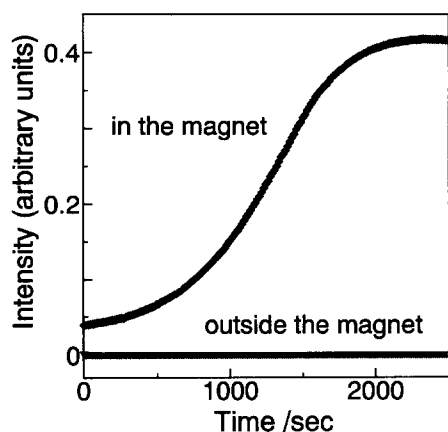
In the d.s.c. measurement, we have seen that the heat-treatment temperature necessary to obtain magnetic orientation is around the melting point in the case of the 'heating process' and slightly above the crystallization temperature in the case of the 'cooling process', indicating that the material is in a molten or nearly molten state when heat-treated in the magnet. However, it does not necessarily mean that the magnetic orientation proceeds in a molten or nearly molten state: the orientation may develop at lower temperatures during crystallization on cooling.

The optical measurement was carried out to clarify further the condition of magnetic orientation. The intensity of the transmitted light monitored under the perpendicular setting of the analyser is expressed as:
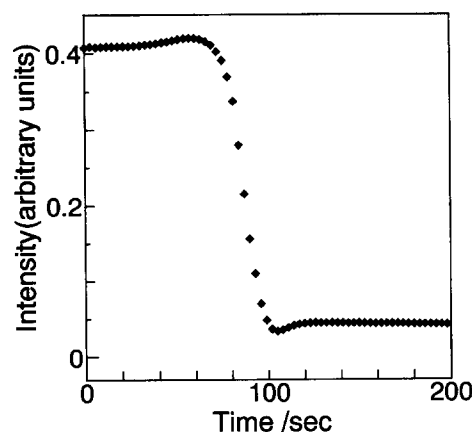
$$I^2 = I_0^2 \, \sin^2(2\theta) \, \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \quad (1)$$

where θ is the angle between the magnetic field and the polarized plane of impinging light (45° in our measurement), d is the sample thickness, λ is the wavelength and Δn is the difference of refractive indices. With our apparatus no appreciable increase in I^2 was observed for simple organic liquids such as nitrobenzene, probably because the magnitude of Δn of these materials is too small. The magnetic birefringence (Cotton–Mouton effect) observed for PEN is far larger compared to those for simple organic liquids.

Since the thermocouple did not monitor exactly the sample temperature in the present apparatus because the space is limited for the thermocouple to be set very close to the sample, the molten or nearly molten state was estimated by the intensity of the transmitted light under the parallel setting of the analyser. First, the heater voltage was set so as to obtain high transmission, which

Figure 5 Change in transmitted light intensity upon heating of aligned structure attained in the experiment shown in *Figure 4*. The analyser set-up is perpendicular. The initial temperature was the same as in *Figure 4* and the final temperature was presumably about 10°C higher than the initial temperature. The exact heating rate was not available

indicates a molten state; then the heater was turned off to observe an abrupt decrease in transmission. The abrupt decrease is assigned to the onset of crystallization, because light is scattered significantly on crystallization. The range of the heater voltage realizing molten or nearly molten states was thus determined. In molten or nearly molten states, the transmitted light was nearly zero under the perpendicular setting of the analyser.

In *Figure 4*, the time evolution of the transmitted light monitored under the perpendicular setting of the analyser is shown for a fixed value of the heater voltage. First, the sample was pre-heated at a higher heater voltage and then the voltage was brought to a fixed value slightly lower than the pre-heating value. It was confirmed by the observation of the high transmission at the parallel setting of the analyser that a molten or nearly molten state was achieved. The measurement was first carried out outside the magnet. As seen in the figure, the transmission intensity monitored under the perpendicular setting of the analyser is nearly zero and does not change, which indicates that no orientation develops. Then, the optical system was inserted into the magnet. An increase in transmission some periods after the insertion is displayed in the same figure. This observation indicates that the magnetic orientation occurs in a molten or nearly molten state. Upon increase in temperature by a slight increase in the heater voltage, the magnetic orientation already attained disappears, as shown in *Figure 5*. Also, the orientation seems to break upon cooling, though this is not fully confirmed because of the interference by a concomitant process of crystallization.

We now consider the reason for the magnetic orientation of PEN. A possible rationalization would be, in analogy to liquid crystals or liquid-crystalline polymers, that some ordered structure susceptible to a magnetic field exists in the molten or nearly molten state. Ordered structures in molten PEN have been suggested by Buchner et al.[11]. They reported in their study on the crystallization of PEN that PEN crystallizes in the α modification irrespective of crystallization temperatures if it is pre-heated at 320°C, while it crystallizes in the β modification at crystallization temperatures higher than

Figure 4 Change in transmitted light intensity at a constant temperature observed under the perpendicular setting of the analyser measured outside the magnet first, then in the magnet subsequently. Both are displayed on the same abscissa. The sample was pre-heated before being brought to the constant temperature. The exact temperature was unknown (see text), but the high transparency under the parallel setting of the analyser assures that the sample is almost molten at this temperature

200°C if the pre-heating temperature is 280°C. To explain this, they assumed crystal embryos which are stable in the melt and act as nuclei when the melt is cooled down to the melting point, and they attributed the crystallization in different modifications to the difference in size distributions of α and β embryos at the different pre-heating temperatures. The embryos in the molten state of PEN might reflect some aspects of the ordered structure causing the magnetic orientation, but they are not exactly the same because the ordered structure in our experiment seems stable in a narrow range of temperature. Incidentally, we should not exclude the possibility that the residual crystallites that may possibly exist at the heat-treatment temperature may respond to the magnetic field.

Recently, Imai et al.[12-14] have reported the orientation fluctuations of poly(ethylene terephthalate) (PET) taking place during the induction period of crystallization above T_g. Based on the theory of the concentration fluctuation of stiff polymers[15-17], they described the formation of these orientation fluctuations in terms of transformation from the isotropic to the nematic phase. They estimated the critical concentration ν^* and the concentration ν of PET at the annealing temperature, and showed that the criterion for the instability of the isotropic phase, $\nu > \nu^*$, is achieved in the induction period of the PET. Though it was in the induction period of cold crystallization that they found the formation of the liquid-crystalline-like orientation order prior to the crystallization, a similar phenomenon could take place in melt crystallization[18,19]. In fact, small-angle and wide-angle X-ray scattering studies have been reported on the melt crystallization of poly(vinylidene fluoride)[20] as well as of poly(ether ether ketone) and nylon-6,6[21], where it is suggested that long-range density fluctuations occur prior to short-range ordering (crystallization), although no definitive conclusion has yet been drawn. It is therefore probable that the ordered structure in the molten or nearly molten state assumed in our experiment on PEN might be related to a liquid-crystalline-like state.

Finally, we discuss the effect of molecular weight on the magnetic orientation. The relaxation time τ of the magnetic orientation of an ordered domain under the influence of a magnetic field could be determined by the ratio of two factors: that is, magnetic torque that makes the domain rotate, and a force resisting against domain rotation due to the viscosity η:

$$\tau = \frac{\eta}{\mu_0 \chi_a H^2} \tag{2}$$

where $\chi_a = \chi_\parallel - \chi_\perp$ is the diamagnetic anisotropy, μ_0 is the magnetic permeability of vacuum and H is the strength of the magnetic field. If we take η as the melt viscosity at low shear rate, τ might be larger for samples with higher molecular weights because of a strong molecular-weight dependence of η. This might explain why no appreciable magnetic orientation was observed in the X-ray photographs for samples with higher

molecular weights. Of course, the molecular weight could affect the relaxation time differently through the static and kinetic properties of the ordered structures.

CONCLUSION

We have shown by using X-ray analyses and magnetic birefringence measurements that PEN develops orientation in molten or nearly molten states under a magnetic field. The condition of the orientation is limited to a narrow range of heat-treatment times and temperatures. We believe that some orientation order, possibly crystal embryos, residual crystallites, nematic phase, or a combination of these, is responsible for the magnetic orientation, but the detail of the ordered structure is not fully identified yet. Finally, we notice that the orientation order assumed here could suggest the possibility of an electric-field-induced orientation of this material. A study on this is in progress.

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