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A study on the structural changes during uniaxial drawing and/or heating of poly(ethylene naphthalene-2,6-dicarboxylate) films

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The structural changes in the uniaxial drawing process of an unoriented amorphous film of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) and in the heating process of an oriented amorphous film of PEN were studied using X-ray diffraction apparatus equipped with imaging plates. This apparatus allows us to record a time-resolved series of two-dimensional patterns of wide-angle X-ray diffraction in rapid succession, and, therefore, we can follow the structural changes during uniaxial deformation and/or thermal treatment processes. The results are as follows: (1) When an unoriented amorphous PEN film was stretched below T_g (=117°C), it could be elongated up to a draw ratio (*DR*) of 4–5 via neck formation and became an oriented amorphous film. (2) In the heating process of the oriented amorphous film (*DR* = 3.6, 65°C), crystalline reflections started to appear near 120°C, accompanied by streaks on the off-equatorial layer lines. The existence of these streaks on such layer lines indicates a lattice distortion due to the axial shift of neighbouring chains along the chain axis with respect to one another. Finally the film exhibited a fibre structure (transverse isotropy). (3) When an unoriented amorphous PEN film was drawn at 150°C, the film exhibited a fibre structure accompanied by a lattice distortion that is similar to that mentioned above, and thereafter frequently showed so-called double orientation (uniplanar axial orientation: $(\bar{1}10)[001]$) in which naphthalene rings in the main chain are preferentially aligned parallel to the film surface despite the fact that the film was deformed in the mode of uniaxial free-width drawing.

(Keywords: poly(ethylene 2,6-naphthalate); oriented crystallization; X-ray diffraction)

INTRODUCTION

When a crystallizable synthetic polymer is melt-processed to form a product such as fibres, it is important to control the degree of chain orientation and also the crystallinity. This is done in order to make the best use of the polymer's inherent properties and then to give a certain advantage to the product over its competitors[1,2]. The effects of chain orientation and/or crystallinity on the final product are, for example, investigated in the following two ways: (1) crystallization from the oriented melt, e.g. by applying deformation fields (shear, elongation, etc.), or crystallization from an oriented amorphous solid by heating (both are called 'oriented crystallization'); (2) crystallization of an unoriented amorphous solid at a given constant temperature by drawing. These two, of course, may proceed concurrently in real melt processes. Further drawing of a specimen that was crystallized beforehand may improve its quality if the drawing brings higher chain orientation and accordingly higher tenacity[3]. The study on the structural formation and/or change in the above-mentioned two ways of crystallization can reveal the optimum processing strategies to maximize the desired properties.

Structural studies on poly(ethylene terephthalate) (PET) in the drawing process have been reported by many investigators[4], and we have studied the structural changes in amorphous PET fibres and on oriented crystallization of PET[5,6]. We have also investigated the structural change accompanying phase transition in the drawing process of high-molecular-weight polyethylene (PE) using a wide-angle X-ray diffraction (WAXD) TV system equipped with an image orthicon camera[7]. Recently, the drawing process of ultrahigh-molecular-weight PE was studied using the new WAXD apparatus equipped with imaging plates (IP)[8,9]. Using this apparatus, we can record a time-resolved series of two-dimensional WAXD patterns and afterwards analyse their intensity profiles.

Poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) possesses naphthalene rings in its main chain in place of all the benzene rings of PET (see *Figure 1a*). Accordingly, PEN has a higher modulus and a higher melting temperature than PET[10–12]: the melting point of PEN

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is measured at about 270°C by d.s.c. (for example *Figure 6*)[13–15]. Thus, PEN is expected to be one of the materials with practical uses, e.g. for automobile parts[16] and electric appliances[17]. Except for a few structural studies[13–15,18–20], however, the solid-state structure of PEN has not been studied extensively. In this report, we investigate, using the WAXD apparatus equipped with IP, the change of chain orientation in an unoriented amorphous PEN film in the drawing process, namely the structural change during drawing and the mechanism of oriented crystallization of PEN.

EXPERIMENTAL

Sample preparation

Initially amorphous and unoriented films of PEN were supplied by Goodyear Polyester Division (intrinsic viscosity = 0.7 dl g^{-1}): the films were about 0.5 mm thick. From these films, dumbbell-shaped strips of 60 mm in total length were cut out and then were marked with fine graduations in ink for later estimation of local draw ratio. The narrow mid-section of the dumbbell-shaped test strip was 3 mm in width and 20 mm in length.

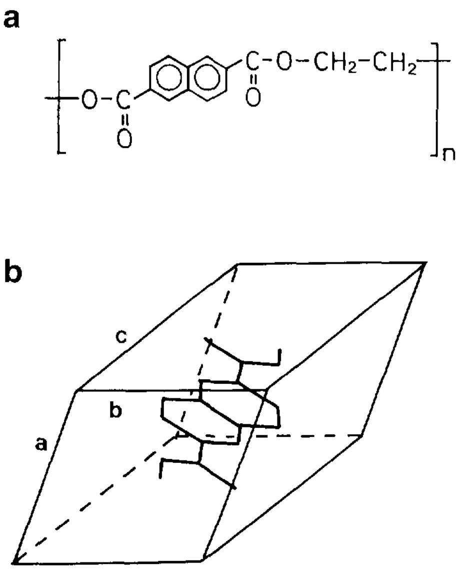

Figure 1 (a) Molecular formula of PEN. (b) Crystal structure of the α modification of PEN, on the basis of the result of structural analysis by Mencik[18]

Wide-angle X-ray diffraction

WAXD was carried out using a rotating-anode X-ray generator (Rigaku-Denki, RU-300) operated at 40 kV and 240 mA. Cu K_α X-ray beams monochromatized with a graphite monochromator were shone onto the specimen through a pinhole collimator of 0.5 mm in diameter. As an X-ray detector, the IP system (MAC Science, DIP-220) was utilized. *Figure 2* shows the IP system with a hexagonal drum[8]: each of the six lateral faces of the drum has an IP film, which is able to record two-dimensional patterns by shifting the drum along its axle. Of course, the drum can rotate around the axle. By computer-controlled rotation/shift of the drum, a large number of patterns can be recorded onto the six IP films attached on the drum in sequence: in the experiments reported in this paper, the exposure time for recording one pattern onto one IP film was kept constant at 2 min. The digitized intensity data, which are read out from the IP films, are stored on magneto-optical (MO) disks through a personal computer. Later, the data are loaded again from the MO disks into a computer and are displayed on a CRT as two-dimensional pictures. Picture processing including data analysis is performed if necessary.

Compared with highly sensitive X-ray photoemulsions, which need, say, 10 min or more exposure time in this experiment, the IP recording is very short (2 min), and the dynamic range of IP is very wide: it covers X-ray intensities of a dynamic range of 10^5 (ref. 8). Accordingly, the IP is expected to be increasingly more popular in measuring the two-dimensional distribution of X-ray intensities when the distribution consists of strong discrete diffraction maxima and weak diffuse scatterings.

A high-temperature furnace for oriented crystallization and a drawing device were newly designed for X-ray measurement using IP. Though the details of the furnace and the device will be reported elsewhere[21], a brief description of them is given here.

In the drawing device, the specimen temperature is controlled by blowing thermostated hot air vertically into the specimen chamber in which the specimen is designed to be drawn in the horizontal direction in order to attain a uniform distribution of temperature over the whole

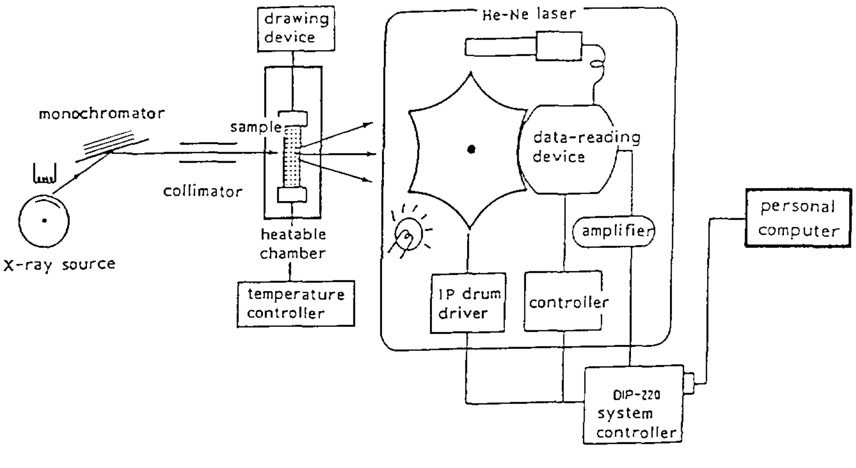

Figure 2 Schematic representation of our X-ray diffraction system equipped with imaging plates (IP)

specimen. The specimen temperature, viz. the temperature of the air in the chamber, is monitored with a chromel–alumel (C–A) thermocouple placed in the vicinity of the specimen area, which is illuminated with the X-ray beams. The precision of temperature regulation is, for example, ±1°C at a specimen temperature of 150°C. In this report, the draw ratio (*DR*) at a given time, viz. at the mid-time of each exposure (2 min), was defined as follows: After finishing a drawing run, the drawn specimen was cooled down to room temperature and then taken out of the drawing device. From the elongated graduation marks in the specimen area illuminated with the X-ray beams, the 'final' *DR* was estimated. Then, based on the drawing rate and the total drawing time for that run, the *DR* at the mid-time of each exposure in the run was calculated by proportional allotment. Thus it should be noted that the *DR* values shown below are not accurate, except for $DR = 1$ (initial, undrawn film) and the final *DR*.

In the furnace, the specimen temperature, viz. the temperature of specimen holder, is monitored with a C–A thermocouple. It needs about 30 s to reach >90% of an expected equilibrium temperature for heat treatment, say of 150°C. The precision of temperature regulation in the furnace is much better than that in the drawing device. The value of specimen temperature or that of elapsed time of heat treatment at the mid-time of each exposure in the heating process was written in the text and figures presented below.

Differential scanning calorimetry

D.s.c. measurement was carried out using a DSC-8230B (Rigaku-Denki) at a constant heating rate of $10^\circ\mathrm{C\,min^{-1}}$ for a specimen of about 10 mg under a dry nitrogen atmosphere.

RESULTS AND DISCUSSION

When an unoriented amorphous film of PEN is drawn below T_g (=117°C; see *Figure 6*), it can be elongated up to a draw ratio (*DR*) of 4–5 via neck formation and this stretching results in an oriented amorphous film. *Figure 3* shows the change in WAXD pattern when an unoriented amorphous film of PEN was drawn at 65°C and at a drawing rate of $5\,\mathrm{mm\,min^{-1}}$. For smaller *DR* than about 1.5 (viz. $DR < 1.5$), the amorphous halo became concentrated gradually onto the equator with increasing *DR*. For *DR* above about 1.5 (viz. $DR > 1.5$), necking took place and the amorphous halo was well concentrated on the equator. The WAXD pattern at $DR = 3.7$ (see *Figure 3f*) indicates that the drawn film is still amorphous, but fairly oriented.

Figure 4 shows the equatorial intensity profiles of the WAXD patterns of *Figure 3*: as mentioned above, these patterns were obtained from an initially unoriented amorphous film of PEN when it was drawn to a series of *DR* up to 3.7 at 65°C and at the drawing rate of $5\,\mathrm{mm\,min^{-1}}$. In the unoriented film ($DR = 1$), the profile of each of the halo maxima in *Figure 4* has a nearly symmetrical shape about $2\theta \simeq 20^\circ$ at which the top of the maxima is located (2θ is scattering angle, θ is Bragg angle). For $DR > 1.5$, i.e. after neck formation, the profile becomes increasingly asymmetrical with increasing *DR*: the higher-scattering-angle side of the asymmetrical maxima is steeper than their lower-angle side.

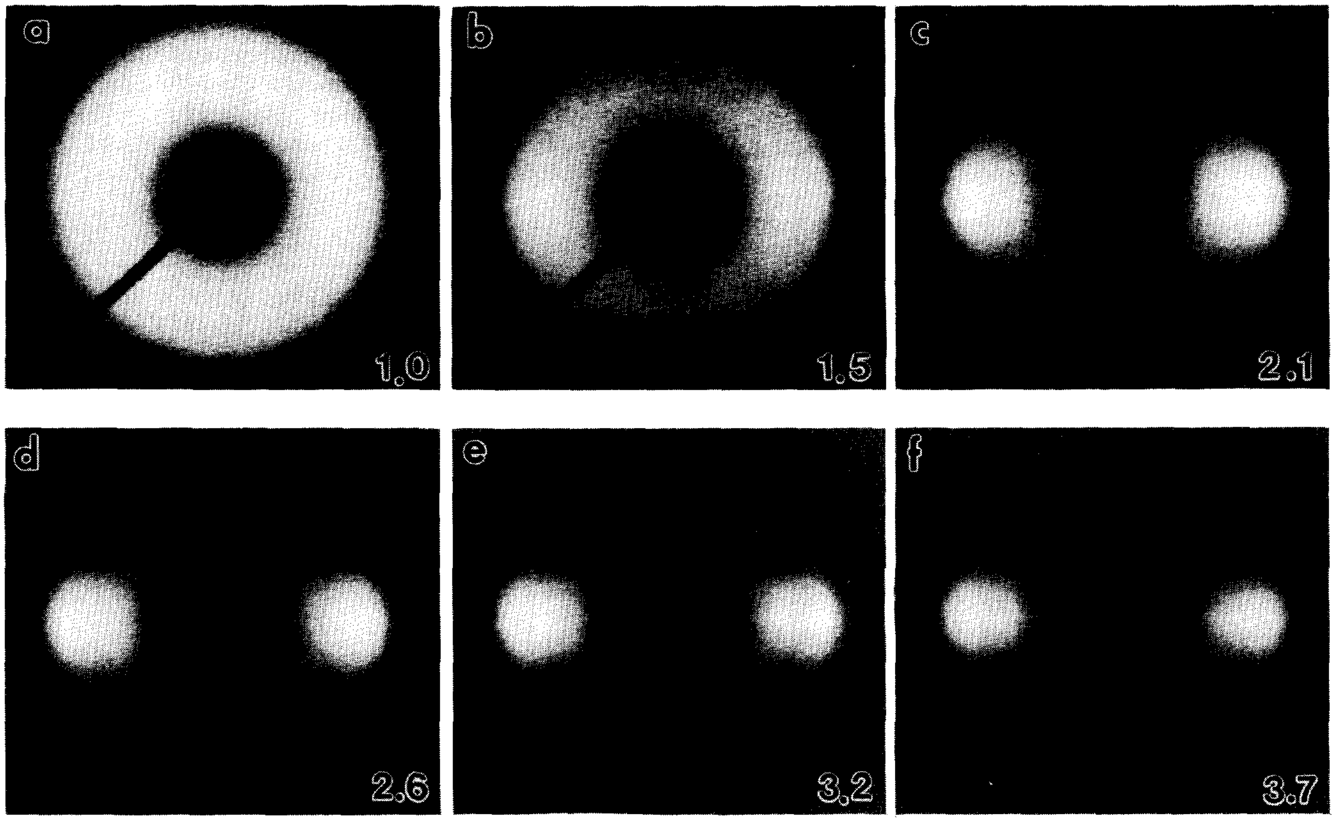

Figure 3 Change in the WAXD pattern from an unoriented amorphous film of PEN during drawing at a drawing rate of $5\,\mathrm{mm\,min^{-1}}$ and at 65°C. Also shown are the draw ratio (*DR*) and the beam stop (the oblique dark rod)

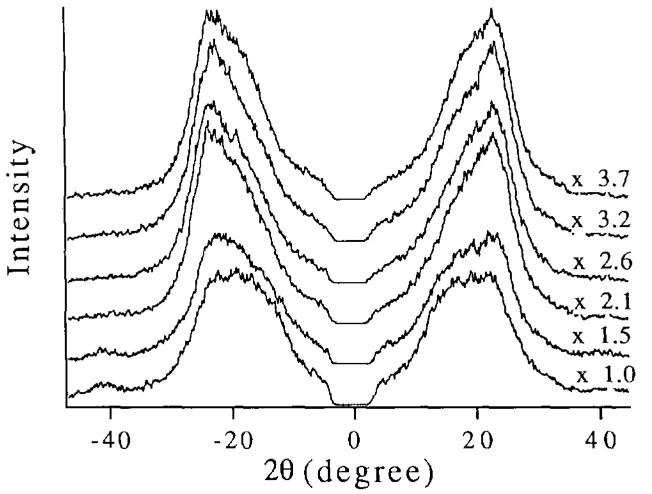

Figure 4 Intensity profiles on the equator of the WAXD patterns of *Figure 3*. Also shown on the right-hand side of each profile is the draw ratio (*DR*)

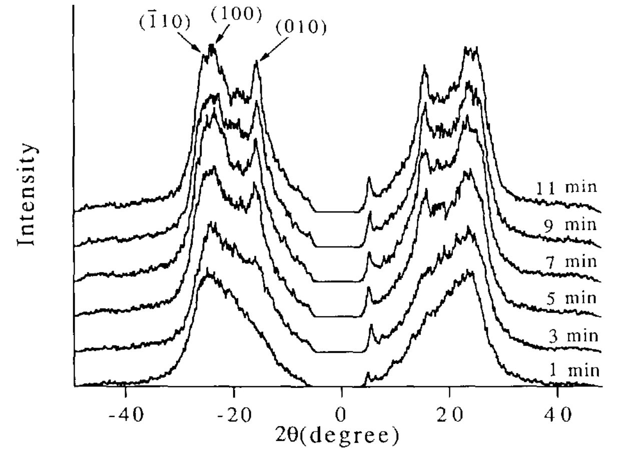

Figure 5 Change in the equatorial intensity profile of the WAXD pattern from the oriented amorphous film of PEN during isothermal crystallization at 118°C: the film had been made beforehand by drawing an unoriented amorphous film at 65°C to $DR = 3.6$. Also shown on the right-hand side of each profile is the elapsed time of heat treatment

This asymmetrical profile indicates that the polymer chains are not randomly oriented but ordered to some extent. As described on *Figure 3*, even at $DR = 3.7$ the profile does not indicate the presence of any crystalline reflections.

When the oriented amorphous film, which had been made by drawing an unoriented amorphous film up to $DR = 3.6$ at 65°C, was heat-treated at a temperature below T_g (= 117°C), for example at 115°C, then practically no crystalline reflections were observed in the WAXD patterns. On the other hand, as shown in *Figure 5*, which is the equatorial profiles of WAXD intensity from the initially oriented amorphous film when it was heat-treated at 118°C, the profiles changed gradually with time. Treatment time of 3 min gives a slight change in the profile, and then at elapsed time of 5 min, crystalline reflections of (010), (100) and ($\bar{1}$10) have started to appear, which are those from the α modification[15]. The crystal structure of this modification was already analysed by Mencik[18]: triclinic, $a = 0.651$ nm, $b = 0.575$ nm, chain axis $c = 1.32$ nm, $\alpha = 81.33°$, $\beta = 144°$, $\gamma = 100°$. As illustrated in *Figure 1b*, the unit cell contains one monomer unit of PEN and its naphthalene ring is set nearly parallel to the ($\bar{1}$10) plane in this modification. Zachmann *et al.* have found another crystal modification[14,15], namely the β form[15,22,23]. In our report, however, all the crystalline reflections observed in WAXD experiments were well attributed to the α modification.

As demonstrated in *Figure 5*, after 11 min of heat treatment, the crystalline reflections have become fairly strong, but additional treatment did not cause such remarkable increase in reflection intensity. In the case of heat treatment above 120°C, well defined crystalline reflections were observed. It is thus concluded that highly oriented amorphous films of PEN are able to crystallize above T_g. This conclusion is also confirmed by d.s.c. as demonstrated in the following experiment.

Figure 6 shows the d.s.c. thermograms of the original unoriented amorphous film of PEN and of the oriented amorphous film that was drawn to $DR = 3.6$ at 65°C. In the unoriented amorphous film, crystallization starts to take place at 190°C, which is much higher than T_g. In the oriented amorphous film, however, crystallization begins to occur just above T_g, for example even at 120°C. Preferential orientation of polymer chains by uniaxial drawing results in the decrease of conformational entropy of the chain. It is thus naturally understood that crystallization readily takes place in the oriented amorphous specimens where most of the polymer chains ought to be aligned parallel to one another owing to drawing.

Figure 7 shows the change in the equatorial intensity profiles of the WAXD pattern from the pre-oriented amorphous PEN film ($DR = 3.6$ at 65°C) in the heating process at a heating rate of 3°C min^{-1}. At 120°C, crystalline reflections of (010), (100) and ($\bar{1}$10) are clearly visible. These reflections become sharper and increase in their intensities with increasing temperature up to around the melting point, namely about 270°C. This result suggests that the crystallite size increases with an increase in temperature. In the intensity profile of the WAXD

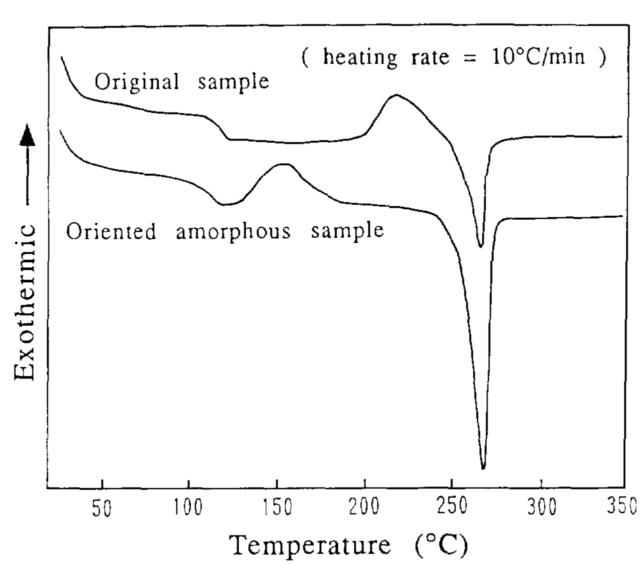

Figure 6 D.s.c. thermograms of the original sample (an unoriented amorphous film of PEN) and of the oriented amorphous one that was made by drawing the unoriented amorphous film at 65°C to $DR = 3.6$

pattern obtained at 255°C, the (010) reflection is much stronger than the others: this result is an indication of 'double orientation' (uniplanar axial texture). It is also noted that the width at half-maximum of the (010) reflection is smaller than those of the others. *Figure 8* is a series of WAXD patterns corresponding to the profiles in *Figure 7*. This figure (*Figure 8*) clearly shows that the crystalline reflections on the equator become sharper with increasing temperature. These reflections are accompanied by streak-like scattering on the off-equatorial layer lines up to 160°C. These streaks indicate the existence of paracrystalline nature, which is caused by the axial shift of polymer chains with respect to one another in the direction of the chain axis and thereby reducing the transverse registry. All the streaks become stronger in intensity with an increase of temperature, and finally they turn to spot-like reflections above 180°C. The whole pattern (*Figure 8f*) of the final film indicates fairly high crystallinity, and it also appears to show so-called fibre orientation (transverse isotropy) of crystallites, though the result of *Figure 7* suggests the presence of slight uniplanar axial texture as mentioned above.

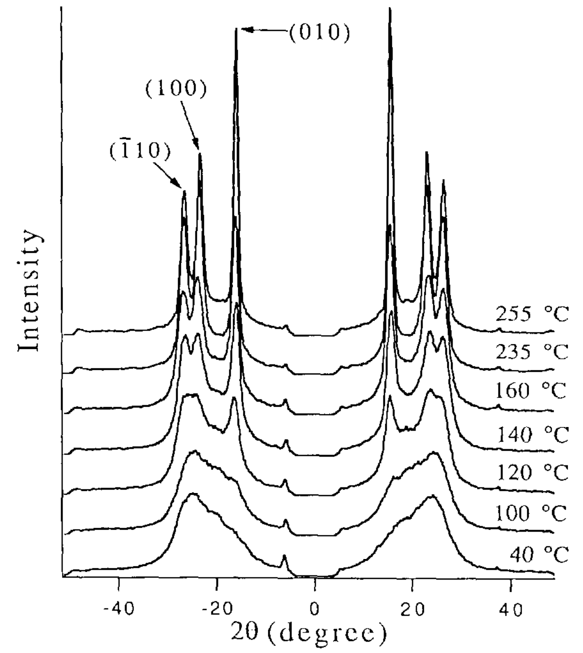

Figure 7 Change in the equatorial intensity profiles of the WAXD pattern from the oriented amorphous film of PEN in the heating process at a heating rate of 3°C min^{-1}: the film had been made beforehand by drawing an unoriented amorphous film at 65°C to $DR = 3.6$. Also shown on the right-hand side of each profile is the specimen temperature

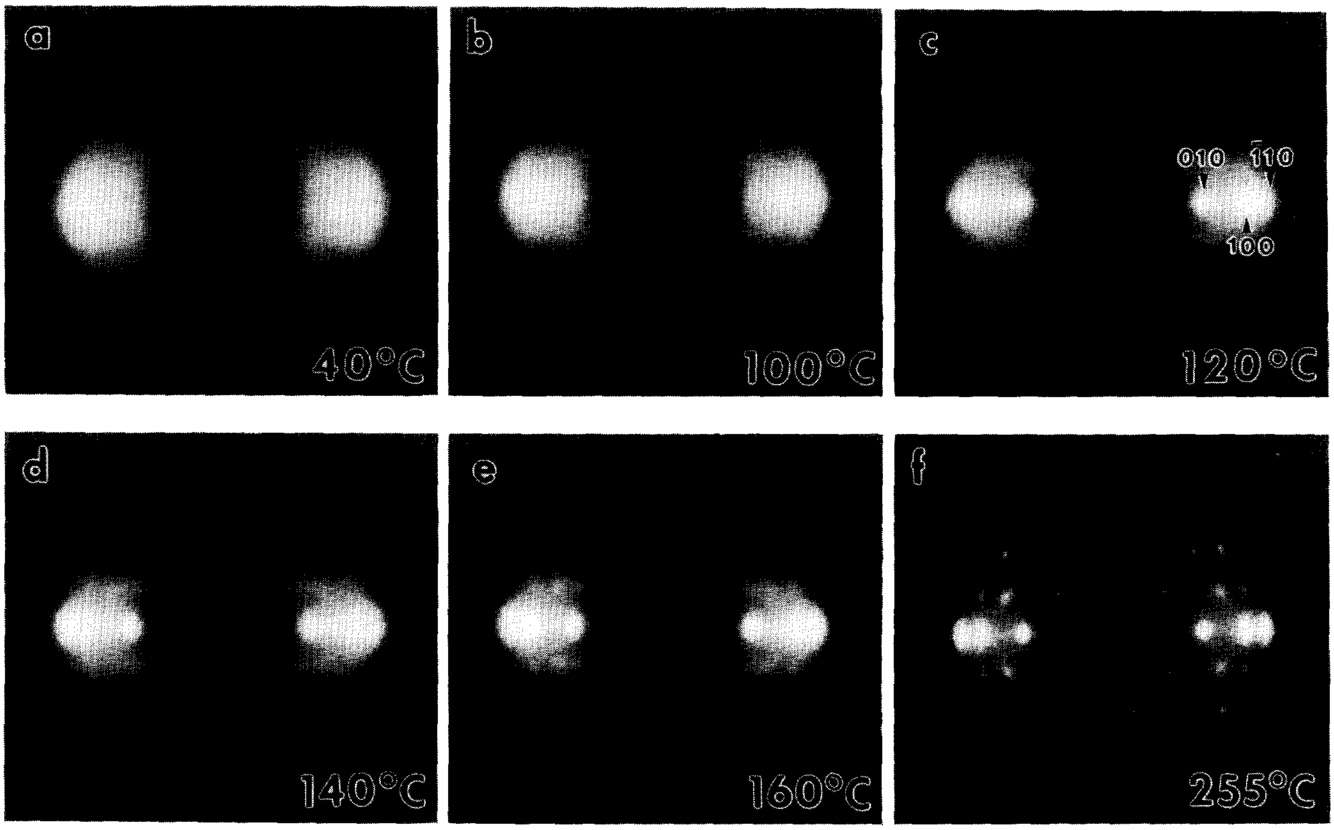

Figure 8 WAXD patterns corresponding to *Figure 7*. Also shown are the specimen temperature and the beam stop (the oblique dark rod)

Figure 9 shows a series of WAXD patterns from an unoriented amorphous film of PEN when it was drawn at 150°C and at a constant rate of drawing of 5 mm min^{-1}. The broad amorphous halo moves to and becomes concentrated on the equator with increasing *DR* for $DR < 1.5$. The crystalline reflections start to appear on the equator at $DR = 1.5$, and then their intensities increase with increasing *DR*. The reflections are accompanied by streaks on the off-equatorial layer lines. The streaks indicate the existence of paracrystalline nature discussed on *Figure 8* in the previous paragraph. The intensities of the streaks are greater than those observed in the heating process of the oriented amorphous film (see *Figure 8*). *Figure 10* shows the equatorial intensity profiles of the WAXD patterns of *Figure 9*. At $DR \simeq 1.5$, the (010) reflection appears abruptly. Then at $DR \simeq 2$, the (010), (100) and $(\bar{1}10)$ reflections become still stronger and are

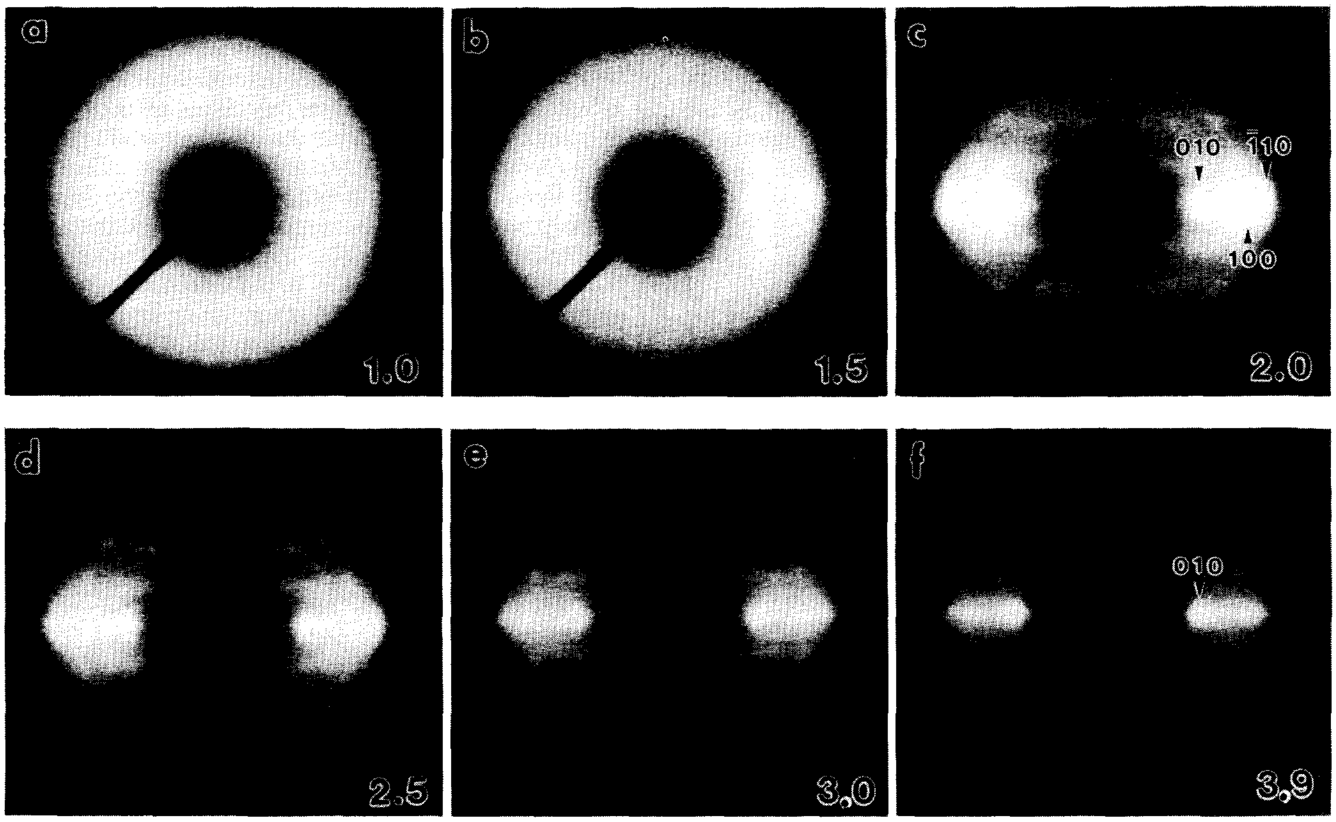

Figure 9 Change in the WAXD pattern from an unoriented amorphous film of PEN during drawing at a drawing rate of 5 mm min^{-1} and at 150°C. Also shown are the draw ratio (*DR*) and the beam stop (the oblique dark rod)

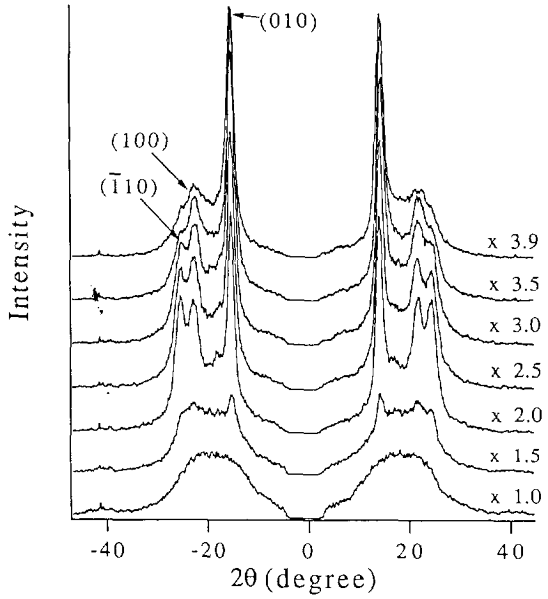

Figure 10 Intensity profiles on the equator of the WAXD patterns of *Figure 9*. Also shown on the right-hand side of each profile is the draw ratio (*DR*)

separated more clearly from one another after neck formation[24]. For $DR > 2$, the (010) reflection becomes strong and sharp with increasing *DR*. In addition, in the case of *Figure 10*, the $(\bar{1}10)$ reflection decreases in its intensity with increasing *DR* for $DR \geqslant 3.0$, and finally at $DR = 3.9$, the reflection has almost disappeared but the weak and broad (100) one still remains. It is, therefore, concluded that, in the drawing process of an unoriented amorphous film of PEN at a high temperature, the film has fibre structure accompanied by lattice distortion due to the axial shift of polymer chains relative to one another along the chain axis. Frequently the film finally shows uniplanar axial texture with the $(\bar{1}10)$ lattice planes parallel to the film surface while the *c* axes orient along the stretching direction ($(\bar{1}10)[001]$ texture), as demonstrated in *Figures 9* and *10* as a typical example: this was confirmed from the fact that, on the equator in the 'edge-view' WAXD photograph of the drawn film, the sharp $(\bar{1}10)$ reflection appeared with much greater intensity than the others[24]. Since the naphthalene rings are approximately parallel to the $(\bar{1}10)$ lattice plane in the α-form crystal of PEN as shown in *Figure 1b*, the uniplanar axial texture in question means that the naphthalene rings are oriented nearly parallel to the film surface.

CONCLUDING REMARKS

Structural differences between crystallization of an oriented amorphous film by heating and that of an unoriented amorphous film by drawing at a high temperature are as follows:

The film crystallized by heating shows the fibre structure (transverse isotropy).

In the case of crystallization by drawing, the film often shows 'double orientation' (uniplanar axial orientation, $(\bar{1}10)[001]$) via fibre orientation. That is to say, the naphthalene rings become parallel to one another and to the film surface while the chain axis orients along the stretching direction.

Usually, rolling[25] or uniaxial constant-width drawing[26] induces uniplanar axial orientation. For example, when a PET film was rolled to $DR = 4.5$ at 70–80°C and then annealed for 1 h at 170°C, the film showed uniplanar axial orientation, as judged by comparing the intensity of the (010) reflection with that of (100) in through-view and edge-view WAXD of the film[25]. In the PEN film, however, high-temperature uniaxial drawing solely could cause 'double orientation'. This result can be appreciated as follows: In PEN, a naphthalene ring consisting of two benzene rings ought to be more planar than a benzene ring in PET, and consequently by uniaxial drawing at a high temperature, the naphthalene rings are readily aligned parallel to one another when the polymer chains are oriented in the drawing direction. In addition, PEN films during drawing often lose their thickness more rapidly than their width in the present study: for example, a drawn film that showed typical 'double orientation' has about two-thirds the width and about half the thickness of the initial undrawn film. The rapid decrease in thickness probably induced a kind of compression effect similar to the rolling onto the specimen films (actually the rolled PEN films clearly showed the uniplanar axial texture)[24]. Accordingly, the naphthalene rings in PEN are apt to orient themselves parallel to the film surface during uniaxial free-width drawing, i.e. PEN films frequently show 'double orientation' (uniplanar axial orientation) even in the process of uniaxial free-width drawing, as in the case of uniaxial constant-width drawing of PET[26].

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