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Structure development in the uniaxial-drawing process of poly(ethylene naphthalate)

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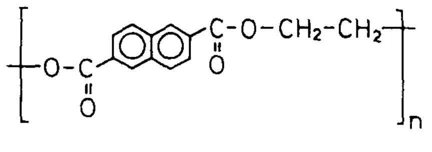
Amorphous films of poly(ethylene naphthalene-2,6-dicarboxylate) were drawn isothermally up to desired draw ratios at 130, 140, 150 and 160°C mainly to study structure formation during uniaxial drawing by wide-angle X-ray diffraction (WAXD). The results were analysed in comparison with stress–strain curves in order to find the draw ratio associated with the onset of crystallization at the above-mentioned temperatures. To obtain further detailed information, birefringence and density were measured for the films drawn at 150°C to elucidate the relationship between the degree of chain orientation and the crystallinity. A series of results was discussed in relation to previously reported interesting phenomena of the time-resolved two-dimensional WAXD patterns recorded using the imaging plate system (*Polymer* 1995, **36**, 291). Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(ethylene naphthalene-2,6-dicarboxylate); X-ray diffraction; stress–strain curve)

INTRODUCTION

Drawing or stretching induces alignment of polymer chains in the drawing direction and promotes its resultant crystallization. It plays an important role in leaving inherent excellent properties of the polymer in the final products and also in providing them with some additional characteristics in compliance with their use. Hence studies on structural changes of the polymer during drawing are not only of academic interest but also full of industrial significance because of the basic researches on structure control for producing better manufactured goods.

Poly(ethylene naphthalate) (PEN), namely poly(ethylene naphthalene-2,6-dicarboxylate):



is known as a high-performance polymer for wide use. PEN has a higher modulus and a higher melting temperature (>270°C) than poly(ethylene terephthalate) (PET) because it contains napthalene rings instead of all the benzene rings in PET. Accordingly, it has been utilized, for example, for electric appliances such as base films for longplay videotape of high quality[1]. Very recently the solid-state structure of PEN has been studied extensively[2–15] but the mechanism of structural formation still remains unsolved.

In our previous report[14], we investigated the structural formation/changes in the uniaxial-drawing process of an unoriented amorphous PEN film at various temperatures up to 160°C and in the heating process of the pre-deformed PEN film by using respectively the heating/drawing device and the high-temperature furnace[16] designed for the X-ray diffraction system equipped with imaging plates (IP). Using this system, we could record *in situ* a time-resolved series of two-dimensional X-ray diffraction/scattering patterns and afterwards analysed their intensity profiles[17–19]. When an unoriented amorphous film of PEN was stretched below its T_g (= 117°C), for example at 65°C, the draw ratio (DR) reached 4–5 via necking into an oriented amorphous film. In this drawing, most polymer chains of PEN were aligned in the stretching direction without any crystallization.

In the previous paper[14], a time-resolved series of wide-angle X-ray diffraction (WAXD) patterns was measured for molecular orientation by drawing uniaxially amorphous PEN films and the reported patterns are shown again as *Figure 1* in this paper. The drawing was done isothermally using the heating/drawing device at a constant rate of $5\,\mathrm{mm\,min^{-1}}$ at 150°C. It is seen that the broad amorphous-halo moved to the equator and became concentrated there in the WAXD pattern with increasing DR for $DR < 1.5$. At $DR \approx 1.5$, the three major crystalline reflections started to appear on the equator, being accompanied by streaks on the off-equatorial layer lines, and afterwards increased in intensity with increasing DR. Finally the film usually had a fibre structure. These results indicate that in the drawing process of an unoriented amorphous film of PEN at a high temperature, the film comes to have a fibre structure accompanied by lattice

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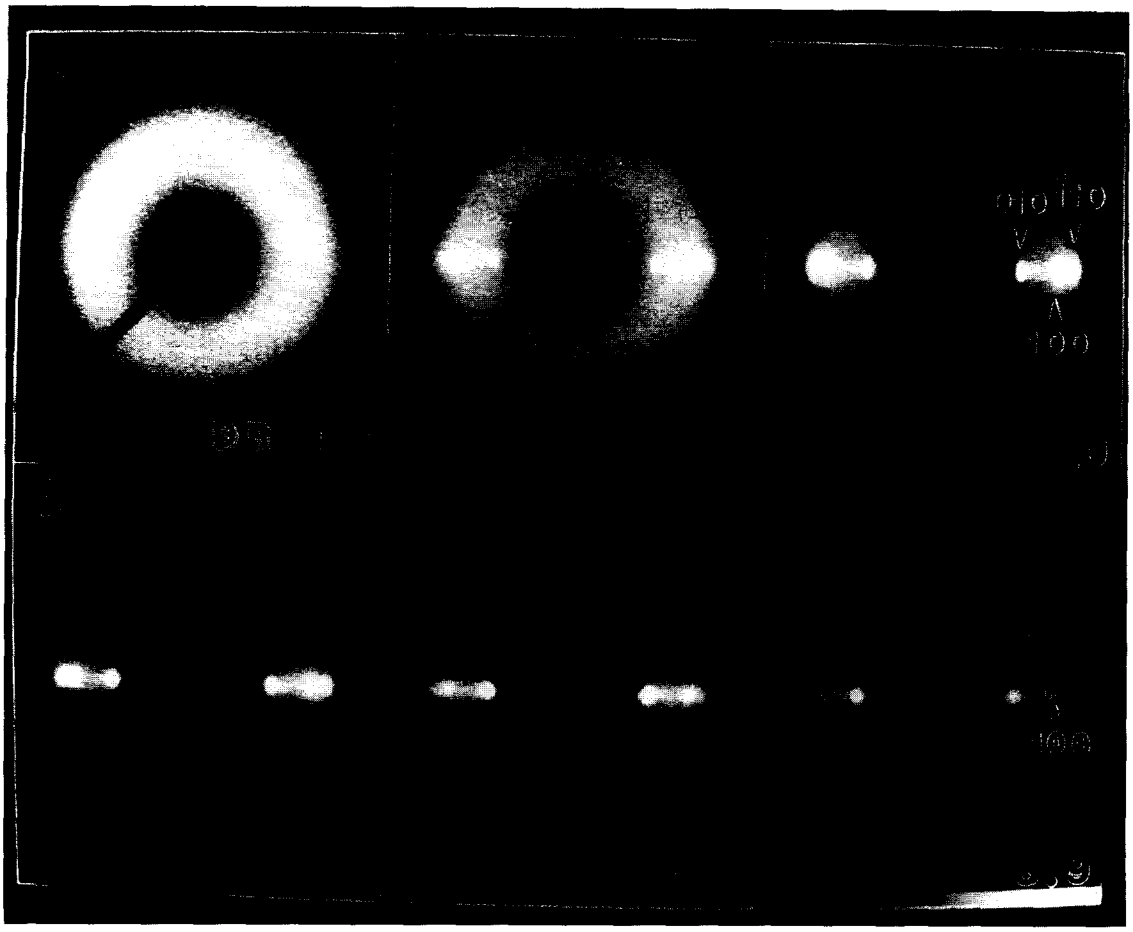

Figure 1 A time-resolved series of the WAXD patterns obtained using the X-ray IP systems from an unoriented amorphous film of PEN during drawing at a drawing rate of 5 mm min^{-1} and at 150°C[14]. These six patterns were displayed together on the CRT of a personal computer and the CRT screen was photographed. The figure written and the oblique dark rod observed in each pattern indicate a draw ratio (DR) and the beam stop, respectively. It should be noted that the DR values are not accurate except for DR = 1 and DR = 3.9 because the DR at the mid-time of each exposure in the run was calculated by proportional allotment[14]. All the definitive crystalline reflections on the equator in these patterns were well attributed to the α-form. The final pattern (f) shows the uniplanar axial texture because of disappearance of the $(\bar{1}10)_\alpha$ reflection

distortion due to the axial shift of polymer chains relative to one another along the chain axis[20]. Occasionally the reflection of the $(\bar{1}10)_\alpha$ plane disappeared indicating the uniplanar axial texture (see *Figure 1f*). In the above-mentioned experiment using the X-ray IP system, however, we could not determine the accurate DR values corresponding to the starting point of necking and to the onset of crystallization, since it was difficult in principle to assign the exact DR at each exposure in the run except for DR = 1 (initial, undrawn film) and the final DR[14,19].

In this report, therefore, WAXD photographs are taken for the PEN films which were drawn isothermally up to desired DRs using a tensile testing machine and then quenched. The analysis is done in comparison with the stress–strain (S–S) curves in order to elucidate the relationship between structural information and mechanical properties of the films, especially to find the DR corresponding to the starting point of structural formation associated with the onset of crystallization. Birefringence and density of the films will also be measured for evaluating a relationship between the degree of chain orientation and the crystallinity.

EXPERIMENTAL

Samples

Initially, amorphous and unoriented PEN films of approximately 0.5 mm thickness were supplied through Prof. M. Cakmak, University of Akron, by the Goodyear Polyester Division (intrinsic viscosity: IV = 0.7 dl g^{-1})[14].

Stress–strain (S–S) curves

A tensile testing machine (Autograph IM100; Shimazu-seisakusho Ltd.) equipped with a high-temperature chamber (LTS-2) was used. The rectangular test strips of 4 mm in width and 20 mm in length were uniaxially stretched at a drawing rate of 10 mm min^{-1} at various temperatures. In the present experiment the sizes and shapes of the test strips were determined on the basis of the following. Though in our previous report[14] the dumbbell-shaped test strip (total length: 60 mm) with the narrow mid-section of approximately 3 mm width and 20 mm length was stretched at a drawing rate of 5 mm min^{-1} in the time-resolved X-ray measurement using the IP system (see *Figure 1*), the region of accurate 3 mm width with parallel side-edges in the mid-section of the strip was 10 mm in length.

WAXD and small-angle X-ray scattering (SAXS) photographs

X-ray beams generated at 40 kV–70 mA using a rotating-anode X-ray generator (Rotaflex RU-3H, Rigaku-Denki, max.: 60 kV–100 mA) were monochromatized with a

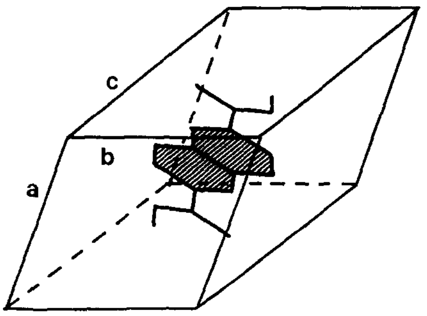

Figure 2 Crystal structure of the α-modification of PEN, which was illustrated according to the result of structure analysis made by Menčik[2]

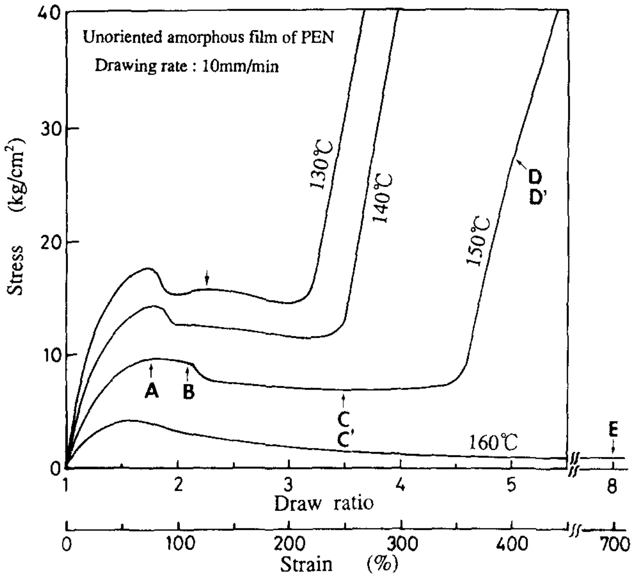

Figure 3 Stress–strain (S–S) curves of the unoriented amorphous PEN film when it was uniaxially stretched at a drawing rate of 10 mm min^{-1}. Here, 'stress' ≡ 'load'/'initial cross-sectional area'

graphite monochromator. The resulting Cu K_α X-ray beams were introduced onto the specimen through a pinhole collimator of 0.5 mm diameter for WAXD and through a double-pinhole collimator of 0.3 mm diameter for SAXS. The camera length of WAXD was 30 mm and that of SAXS was 300 mm. All the WAXD and SAXS patterns were recorded *in vacuo* onto the Kodak Diagnostic Films (DEF5) which were then developed with a developer equivalent to Ilford ID-62.

Birefrigence

The measurement using the D line of Na (wavelength: 589.3 nm) was undertaken with a polarizing microscope equipped with a Berek's compensator.

Density and crystallinity

The sample density was measured at 30°C using a density gradient column which contained *n*-heptane and carbon tetrachloride. To estimate crystallinity, the intrinsic crystal and amorphous densities of PEN must be defined. However, two crystal modifications have been reported: α-form and β-form[5,7]. The crystal structure of the α-form was already analysed as shown in *Figure 2*: triclinic, $a = 0.651$ nm, $b = 0.575$ nm, c (chain axis) $= 1.32$ nm, $\alpha = 81.33°$, $\beta = 144°$, $\gamma = 100°$[3]. Its unit cell contains one monomer unit of PEN, and the chains are parallel to the c-axis in the crystal. The theoretical crystal density of the α-form was accordingly computed at 1.407 g cm^{-3} (ref. 3). As for the β-form, its crystal structure is not yet analysed, but its lattice dimensions were reported[7]: triclinic, $a = 0.926$ nm, $b = 1.559$ nm, c (chain axis) $= 1.273$ nm, $\alpha = 121.6°$, $\beta = 95.57°$, $\gamma = 122.52°$. Four chains then pass through each cell and its theoretical density is 1.439 g cm^{-3}. This density value is rather larger than that for the α-form. In the present specimens, however, a weak reflection from the β-form was superposed upon the definitive reflections from the α-form on the equator of X-ray photographs (*Figures 4B–D*), indicating that the mass fraction of the β-form is much smaller than that of α-form. Accordingly, the density of the α-form, 1.407 g cm^{-3}, was employed as the intrinsic density of the crystal phase by neglecting the contribution from the β-form.

The density of amorphous phase was determined to be 1.327 g cm^{-3} (30°C) through the density measurement of initial amorphous films of PEN. This value is slightly greater than 1.325 g cm^{-3} which was already reported[10,11].

We calculated the crystallinity, $X_{\rm cr}$, using

$$1/d = X_{\rm cr}/d_{\rm c} + (1 - X_{\rm cr})/d_{\rm a} \qquad (1)$$

Here d means the observed density, $d_{\rm c} = 1.407$ g cm^{-3} and $d_{\rm a} = 1.327$ g cm^{-3}.

RESULTS AND DISCUSSION

Figure 3 shows the stress–strain (S–S) curves when such a film was uniaxially stretched at various temperatures of 130°C or above. The curves for 130–150°C show the unambiguous yield point. Beyond this point, the stress suddenly dropped and the curves then had a rather flat region. This phenomenon is caused by necking: necking was confirmed by direct observations of the stretching specimen with our own eyes. After necking, the stress increased drastically again with increasing DR.

In the stretching process at 130°C, the stress decreases considerably when necking takes place and it tends to increase again gradually up to the second yield point (indicated with the arrow in *Figure 3*). This is probably attributed to the improvement of chain orientation by necking. Beyond the second yield point, the stress decreases again probably due to relaxation. After necking, the stress increases drastically with increasing DR (>3). The S–S behaviours for stretching at 140°C and 150°C are basically similar to that for 130°C stretching, except for the disappearance of the second yielding. The S–S curves for 130, 140 and 150°C indicated that the lower the drawing temperature (1) the greater the stress at a given DR, (2) the more the degree of stress drop after the first yielding, (3) the smaller the DR corresponding to the stress drop after the yielding (apparent necking), and (4) the narrower the flat region in the S–S curve. The curve for 160°C, however, does not show any necking: the film was elongated uniformly under fairly low stress, and then broken at DR = 13–14 caused speculatively by partial melting during stretching. Thus in our experiment, 150°C was the highest temperature at which the unoriented amorphous film of PEN explicitly showed necking in the uniaxial-drawing process.

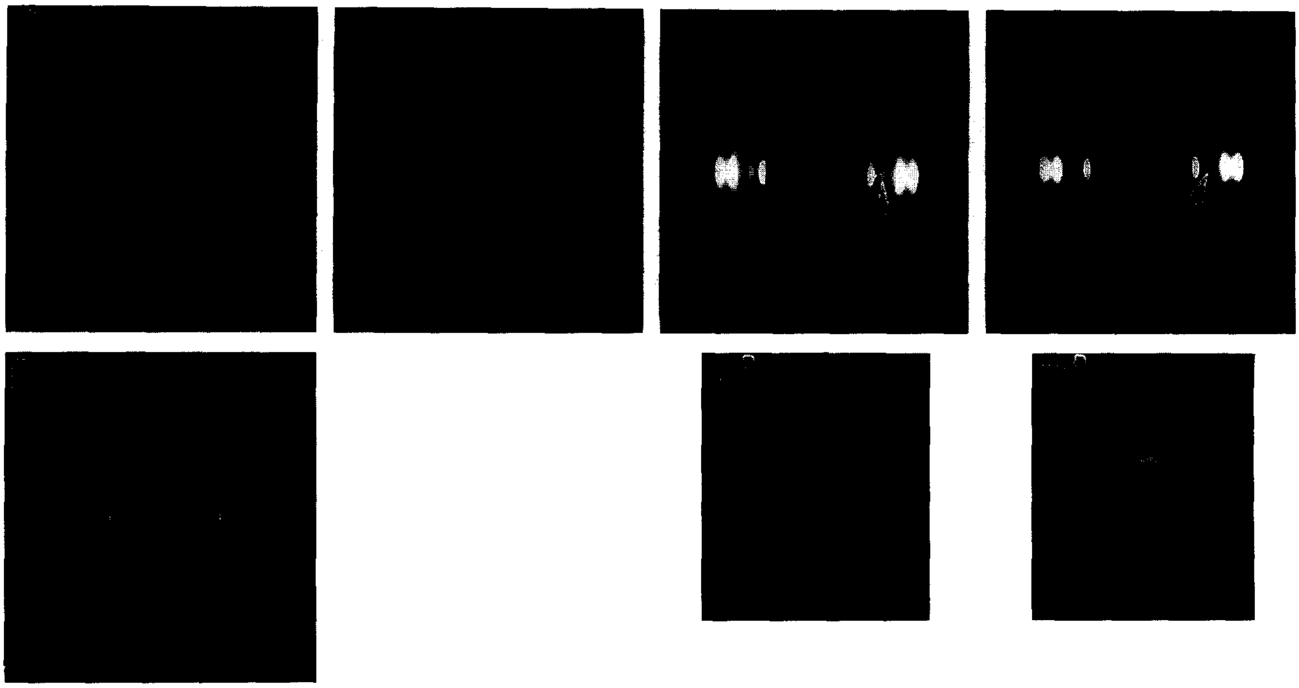

Figure 4 WAXD or SAXS photographs taken at various DRs indicated using the arrows and uppercase letters in *Figure 3*. Each photograph was obtained from the PEN film which had been drawn isothermally up to a given DR using a tensile testing machine and then quenched. The photograph marked with an uppercase letter in this figure corresponds to the DR indicated with the same letter in *Figure 3*. The prime (′) designates SAXS. The reflection indicated using the Greek letter β in (B), (C) and (D) is attributed to the (020) reflection of the β-form

Figure 4 shows the WAXD and/or SAXS photographs taken at various DRs, in which an uppercase letter in each photograph corresponds to the DR indicated with the same letter in *Figure 3*. In stretching at 150°C, the initial ring-like amorphous-halo (see *Figure 1a*) varied in intensity distribution and started to concentrate onto the equator at $\mathrm{DR} \approx 1.5$ (see *Figure 1b*). Even at the yield point ($\mathrm{DR} \approx 1.8$), the WAXD photograph of *Figure 4A* showed a very slightly oriented amorphous-state and does not have any crystalline reflections. This implies that in the drawing process at the high temperature, local stresses applied to chain segments were relaxed quickly because of active chain mobility, and accordingly the oriented crystallization was suppressed. Just before the onset of apparent necking (the point of stress drop after yielding), viz. at $\mathrm{DR} \approx 2.2$, however, the crystalline reflections, especially the (010) reflection of the α-form started to appear on the equator with being superposed upon a more oriented amorphous-halo (*Figure 4B*): this might be due to necking partly in a microscopic domain. As apparent necking took place beyond the yield point, the chain orientation in the stretching direction was more pronounced and the three major reflections of (010), (100) and $(\bar{1}10)$ of the α-form became clearer at $\mathrm{DR} = 3.5$ (*Figure 4C*). During necking, the oriented amorphous-halo lost its intensity and transformed into the crystalline reflections. The SAXS photograph (*Figure 4C′*) taken at the same DR (= 3.5), showed a two-point diagram made up of faint, broad maxima. Further stretching after necking gave a fibre pattern consisting of fairly spot-like crystalline reflections at $\mathrm{DR} = 5.0$, as illustrated in *Figure 4D*. Thus, the SAXS photograph (*Figure 4D′*) showed a well-defined two-point diagram which had the maxima corresponding to the long period of about 18 nm. Hirata *et al.*[12] reported that the crystallites of several tens of nm in width were grown in the direction perpendicular to the *machine direction* in the PEN film which had been stretched uniaxially at 140°C and thereafter annealed at constant length at 160°C under vacuum: they observed ultra-thin sections of the film by TEM. If a similar texture is made in the PEN film in our experiment, the long period of about 18 nm is assumed to come from a stacked lamellar structure though the film was as-stretched, viz. not annealed. Studies on this method of morphological observation of the film are now in progress.

Stretching at 160°C did not give better orientation of the chains in the stretched film even if the film was stretched up to $\mathrm{DR} = 8$, as illustrated in the WAXD photograph of *Figure 4E*.

It may be noted that the WAXD patterns (c)–(f) in *Figure 1* clearly show the streaks on the off-equatorial layer lines. In the corresponding WAXD photographs of *Figures 4C* and *D*, however, no streaks are recognized. This result suggests that the streaks in question, which come from the paracrystalline nature[20,21] caused by the axial shift of polymer chains with respect to one another in the direction of the chain axis, can be observed only during drawing but disappear when drawing is discontinued. This phenomenon is analogous to the appearance and disappearance of the monoclinic reflection in the uniaxial-drawing process of polyethylene[17,18,22,23]. Consequently, the paracrystalline state in the PEN film seems to consist of the chains that are almost parallel to one another in the drawing direction but not registered laterally enough in the crystallographical sense. That is to say, the oriented chains within the paracrystalline regions are in an unstable transient state, but they transform readily into a stable state by partial or total release of tensile stress before the film is quenched. The intensity distribution of equatorial reflections along the Debye–Scherrer rings due to crystallite orientation (see

Figure 4D) is rather broader than that in *Figures 1c–f*. This is certainly due to orientation relaxation of the crystallites after stretching.

Based on the above consideration, the following points might be concluded: before the yield point, molecular chains are aligned roughly in the drawing direction; during necking, the chains come to be aligned better in the drawing direction with being accompanied by the random axial shift of neighbouring chain stems relative to one another in this direction; and further drawing induces crystallization to overcome the axial shift under consideration and makes the PEN film have a fibre structure. In order to confirm this conclusion, the birefringence, which reflects the degree of chain orientation[13], was measured.

Figure 5 shows the birefringence (Δn) measured for the PEN films which had been drawn at 150°C up to the indicated DRs and then quenched. Comparison of this figure with the S–S curve for 150°C in *Figure 3* indicates that (1) before necking, Δn is rather small, (2) beyond the DR (of about 2) at which necking starts to occur, Δn increases rapidly with increasing DR, and (3) after necking, Δn increases slowly again with increasing DR. This result seems to indicate that Δn at the early stage of drawing is dependent not on the degree of orientation of amorphous chains but greatly upon the degree of crystallite orientation, because crystallization is promoted during necking, as described below. It should be emphasized here that the fairly small contribution of the chains in the amorphous phase to the birefrigence has already been reported in the case of high-speed melt-spinning of PET[24].

Figure 6 shows the plot of the density (d) and its resultant crystallinity (X_{cr}) against DR: the specimen film of PEN was made by uniaxial drawing at 150°C up to the indicated DRs and then quenched, and its amorphous density was assumed to be constant independently of drawing. For $DR < 2$, crystallinity increased very slightly with increasing DR. During necking, it increased gradually with increasing DR. Near the end of necking and just after necking, however, it rose fairly rapidly. Thereafter, for $DR >$ approx. 5, it increased slowly again in spite of a still fairly large increase in birefrigence, and at $DR \approx 7$, it reached about 30%, which was almost the highest equilibrium value of crystallinity in this experiment. Incidentally, however, the crystallinity of the films made by two-stage drawing is beyond 30% and reaches 50%[10].

As seen from *Figures 5* and *6*, during necking (approx. $2 < DR \leqslant$ approx. 4.5), the chains are gradually oriented into the stretching direction and accordingly the birefringence increases more rapidly than crystallinity. For $DR > 4.0$ ($DR = 4.0$ is before the end of necking), the crystallinity rises greatly, probably caused by crystallization of the chains oriented during necking. Beyond $DR \approx 6$, however, the birefringence increases fairly rapidly again in spite of a small crystallinity rise, probably due to additional chain orientation in the residual amorphous phase by further stretching.

Returning to *Figure 4*, an extra reflection appears between $(0\,1\,0)_\alpha$ and $(1\,0\,0)_\alpha$ on the equator, as indicated by the Greek letter β in *Figures 4B, C* and *D*. This reflection is attributable to the (020) of β-form. The reflection appeared in the WAXD photographs from the PEN film, which had been stretched up to $DR = 4$ or 5 at 150°C and then cooled down to room temperature at a constant length. The reflection in question increased in its intensity with increasing DR, but was weaker than the major equatorial reflections of the α-form at every DR. As demonstrated in *Figure 1*, the apparent reflection of the β-form was not recognized during drawing: i.e. all the definitive reflections on the equator in *Figure 1* were well indexed with the α-form[14]. Thus the β-form in the PEN film, which was drawn up to a given DR and then quenched, seems to appear by release of tensile stress before quenching or in the cooling process. In this connection, it should be added that, in our experiment, the better the orientation of crystallites in the drawn PEN films, the smaller the quantity of the β-form, as is well demonstrated in *Figure 7*.

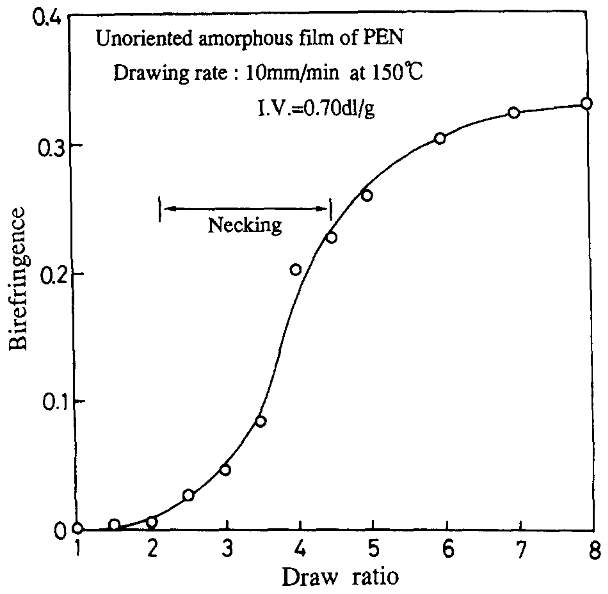

Figure 5 Relationship between birefringence and DR. Birefringence was measured for the PEN films which had been drawn at 150°C up to given DRs and then quenched

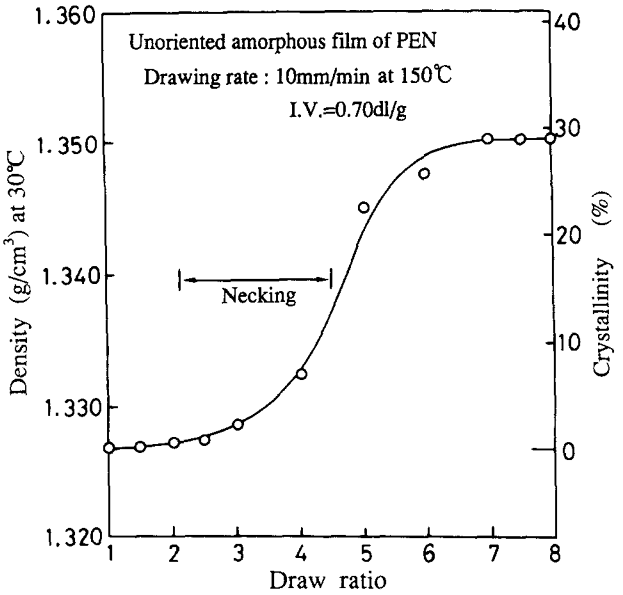

Figure 6 Relationship between density (and its resultant crystallinity) and DR. Density was measured for the PEN films which had been drawn at 150°C up to given DRs and then quenched. The crystallinity was computed from the density using equation (1)

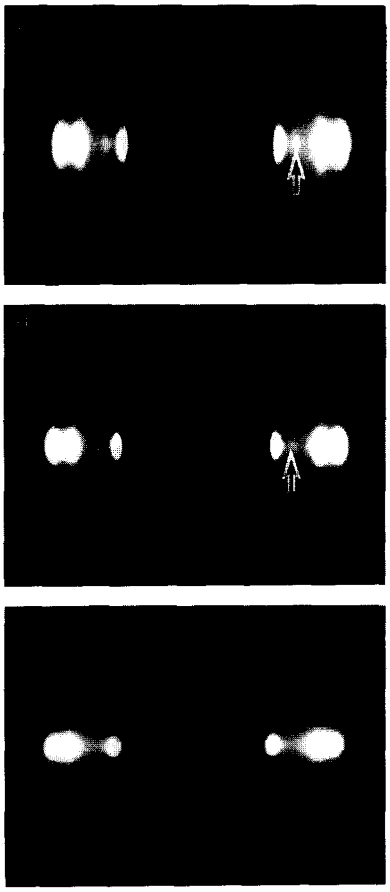

Figure 7 WAXD photographs taken from PEN films drawn at 150°C. The arrows in (a) and (b) indicate the (020) reflection of the β-form. The $(020)_\beta$ reflection loses its intensity as the crystallite orientation in the stretching direction is advanced from (a) to (c). (a) Drawn up to DR = 5 at a drawing rate of $10\,\mathrm{mm\,min^{-1}}$ using the tensile testing machine. (b) Drawn up to DR = 5 at a drawing rate of $6\,\mathrm{mm\,min^{-1}}$ using the improved heating/drawing device[16,26] for the IP system. (c) Drawn up to DR = 6 at a drawing rate of $6\,\mathrm{mm\,min^{-1}}$ using the same device as in (b)

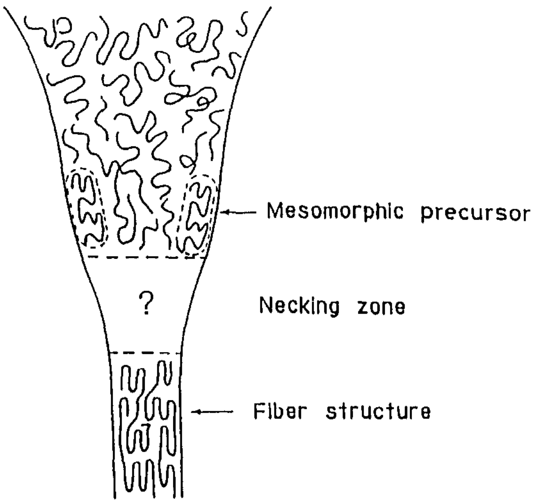

Figure 8 One of the models proposed for neck formation in the spin line during high-speed melt-spinning of PET[25]

Through a series of experimental results, a question can be raised as to why and how necking takes place. In the high-speed melt-spinning process of PET, the experimental result similar to that mentioned above was recognized: in the spin line, an abrupt necking-like decrease of diameter of the filaments occurred and then immediately crystallization took place[24,25]. *Figure 8* demonstrates one of the proposed models for neck formation in the high-speed melt-spinning process of PET[25]. It should be noticed, however, that the 'mesomorphic precursor' indicated in this figure means a momentary state which appears in the oriented melt before necking. On the other hand, during stretching of the unoriented amorphous film of PEN, we observed the paracrystalline state of interest during and after necking. We can now have no good idea about the mechanism of neck formation in PEN only from the experimental results in this report, though it seems to be similar to that in PET.We will try, from now on, to find the answer to the question of why/how necking takes place.

CONCLUDING REMARKS

Based on the S–S curve (*Figure 3*) and WAXD photographs (*Figure 4*) obtained at 150°C, a plausible mechanism of structural formation in the uniaxial-drawing process of an unoriented amorphous film of PEN was deduced as follows. In the elastic DR range of the film, namely for $1 \leqslant \mathrm{DR} < 1.5$, the chains are oriented roughly in the stretching direction, but the film is still amorphous. Beyond the yield point, necking takes place and consequently the chain orientation into the stretching direction is promoted. The chain-to-chain distance between oriented chains becomes approximately fixed and the film crystallizes. During necking, nevertheless, on the off-equatorial layer lines in the WAXD pattern obtained *in situ* using the X-ray IP system, the crystalline reflections are less-defined and alternatively the obvious streaks, which come from the paracrystalline nature due to the axial shift of the polymer chains mentioned above, are definitely recognized (see *Figure 1*). Further stretching after necking gives a well-defined fibre structure exhibiting rather spot-like crystalline reflections, as demonstrated in the WAXD photograph of *Figure 4D*. In the SAXS photograph for DR = 3.5, a faint two-point diagram was recognized (*Figure 4C′*). In the SAXS photograph for DR = 5, a clear two-point pattern was observed, which indicated the long period of approximately 18 nm spacing (*Figure 4D′*). Progress of chain orientation and of crystallization is induced by necking, and additional drawing after necking seems to play an important role in further crystallization.

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