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Morphology of a wholly aromatic thermoplastic, poly(ether nitrile)

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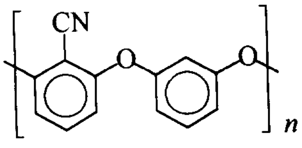
The morphology of solution-cast, solution-grown and melt grown crystals of poly(ether nitrile) (PEN) was studied using mainly transmission electron microscopy. Fibrous, lamellar crystals (F crystals) develop during casting from solution followed by heat treatment, and via crystallization from solution and the melt. Electron diffraction studies indicate that PEN crystals grow rapidly along the a^* axis, along which the cyano groups are aligned. It can be suggested that an interaction between cyano groups and phenyl rings along the a^* axis should favour nucleation on the (2 0 0) growth front. F crystals coalesce to form wide lamellar crystals (L crystals) during heat treatment at temperatures above 250°C. PEN formed spherulites with positive birefringence from solution and the melt: the radial growth direction of the spherulites corresponds to the a^* axis. In view of the orientation of the cyano groups in the unit cell, it can be suggested that the refractive index along the radial direction is larger than that in the tangential direction. Stacked lamellar structures are formed from the melt under shear; the a^* axis is parallel to the transverse direction and the b axis is parallel to the thickness direction. It seems reasonable to assume that preferential nucleation at the bc plane occurs on the substrate during oriented crystallization.

(Keywords: aromatic polymer; poly(ether nitrile); morphology; electron microscopy)

INTRODUCTION

Recently, wholly aromatic polymers such as poly(aryl ether ketone)s (PAEKs), poly(aryl ether sulfide), poly(ether sulfone)s and thermoplastic polyimides have become important as high-performance thermoplastic polymer materials. The structures and properties of these polymers have been studied by many workers, most of them focusing on some PAEKs[1–8].

Poly(ether nitrile)s (PENs) belong to a new class of high-performance semicrystalline thermoplastic polymers that exhibit high melting temperature, excellent mechanical properties and high chemical resistance. These polymers are prepared from dichlorobenzonitrile (DCBN) and some aromatic diols such as resorcinol, hydroquinone and biphenol, in polar solvents using a base as catalyst. The present investigation deals with PEN obtained from DCBN and resorcinol. The chemical repeat unit of this PEN is as follows:



In recent years, the synthesis, mechanical properties, practical applications and crystal structure of PEN have been reported by some workers[9–11]. In this paper, the morphology of solution-cast, solution-grown and melt-grown PEN crystals was studied using mainly a transmission electron microscope (TEM). It has been found that an elongated, lamellar crystal with folded chains is the structural unit of the supermolecular structure of PEN; the preferred direction of rapid growth is the a axis of the unit cell, along which the CN groups are aligned. Attempts have been made to elucidate the origin of the morphological characteristics of PEN on the basis of its crystal structure. This paper is part of a series of studies on the morphology of high-performance, wholly aromatic thermoplastic polymers[12–14].

EXPERIMENTAL

Material

PEN was kindly supplied by Idemitsu Kosan Co. Ltd. The viscosity of PEN was measured at a concentration of $0.2\,\mathrm{g\,dl^{-1}}$ in p-chlorophenol (CP) solution at 60°C using an Ubbelohde viscometer. PEN with a viscosity number (η_{sp}/c) of 0.87 was used throughout this work.

Sample preparation

Thin films of PEN suitable for TEM studies were prepared according to the procedure of Thomas[15]. A 0.1% solution of PEN in CP was cast onto polyphosphoric acid (PPA) at 160°C, at which the solvent was evaporated. After the PPA was cooled to room temperature, thin films were transferred onto a carbon-coated copper grid, washed with water, dried, heat-treated, and shadowed with Au/Pd alloy in a vacuum evaporator.

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PEN was dissolved in CP at 160°C, to which a certain amount of propylene glycol (PPG) was added. Slow cooling of 0.05% solution of PEN in CP/PPG (60/40(vol.)) made it possible to obtain spherulitic structures or aggregates of lamellar crystals. The solution-grown crystals were placed on a carbon-coated copper grid and shadowed with Au/Pd alloy.

The as-received PEN powders were placed on a glass slide, melted at 380°C, and then crystallized isothermally at 320°C. Crystallization was also carried out under shear stress applied by sliding a glass plate over the slide on which the molten PEN layer was placed; the shear-induced crystallization was also carried out at 320°C. The extraction replication technique was employed for the observation of this thin PEN film. A cellulose nitrate film was cast on the surface of the thin PEN film and peeled off the glass plate together with the thin PEN film. After carbon was deposited on the PEN film side, the film was placed on an electron microscope grid, and the cellulose nitrate was dissolved away in amyl acetate.

Measurements

TEM studies were carried out with a Nihon-Denshi 2000FXII transmission electron microscope. Selected-area e.d. patterns (s.a.-e.d.), micro-e.d. patterns, bright-field and dark-field images were obtained. Polarizing microscopy was done with an Olympus polarizing microscope equipped with a camera, Olympus OM-2N. A first-order red tint plate was used to determine the birefringence sign of the spherulitic structures under crossed polars. Differential scanning calorimetry (d.s.c.) was performed using a Seiko DSC-200. The sample was heated at a rate of 10°C min^{-1}. The temperature range of the scans was from 20°C to 380°C.

RESULTS AND DISCUSSIONS

Thermal behaviour of PEN

The thermal behaviour of the melt-quenched PEN was studied using d.s.c. As *Figure 1* indicates, the thermogram for the heating of PEN exhibits three thermal events, a glass transition at 139.4°C, a crystallization exotherm at 211.8°C, and a melting endotherm at 337.1°C. The casting temperature and heat-treatment temperatures of the as-cast PEN films were assessed by reference to the thermogram in *Figure 1*. The glass transition temperature of PEN is lower than that of a wholly aromatic thermoplastic polyimide, poly[(3,3′-dioxyphenyl)diphenylene pryomellitimide] (N-TPI)[12], by 100°C. This result is attributable to the two benzene rings linked at the *meta* position by two ether bonds that have a relatively shallow rotational conformational energy barrier.

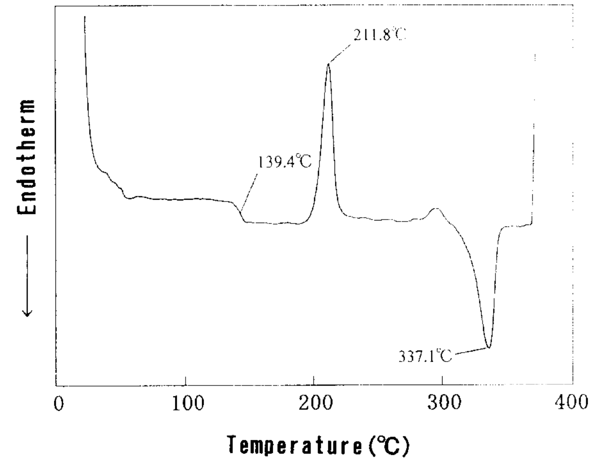


Figure 1 D.s.c. thermogram of PEN prepared from the melt by quenching

Morphology of PEN

Thin films cast from solution onto hot polyphosphoric acid. The effect of heat treatment on the morphology of solution-cast thin films of PEN was investigated. The as-cast thin films of PEN and those heat-treated at $T = 200-320°C$ for 1 h will hereafter be abbreviated as PEN(AS) and PEN(T), respectively.

Figures 2a, 2b and *2c* show the TEM micrograph, the corresponding s.a.-e.d. pattern of PEN(AS), and the schematic representation of $(hk0)$ reciprocal lattice pattern. Some disc-like structures of 2–3 μm diameter with indefinite shape are visible in the TEM micrograph (*Figure 2a*). Perhaps these disc-like structures originate from the droplets of PEN solution formed on hot PPA during casting. Similar disc-like structures are formed in a thin film of N-TPI cast from CP solution onto PPA[12,14].

The supermolecular structures of PEN(AS) are characterized by narrow striations extending on either side of a central line; the dotted line in the disc-like structure in *Figure 2a* indicates the central line. The

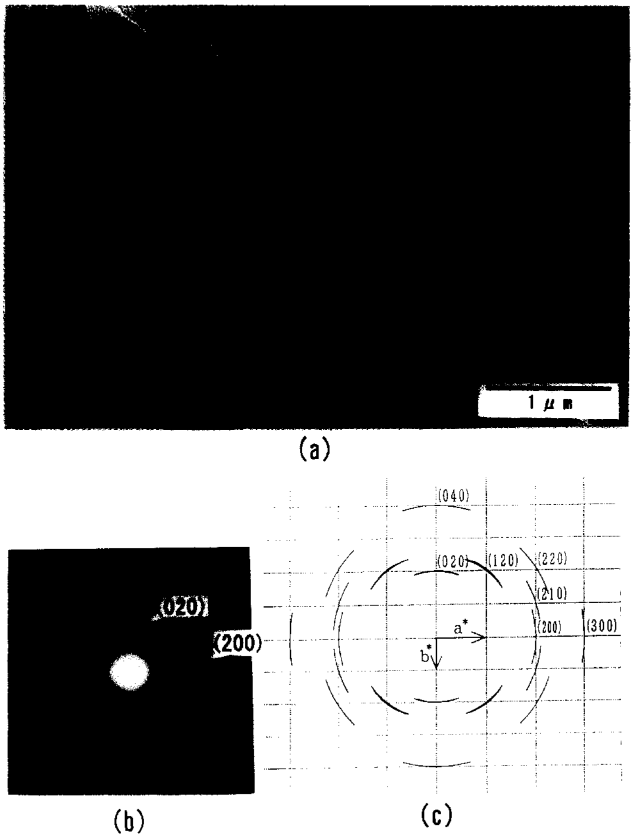


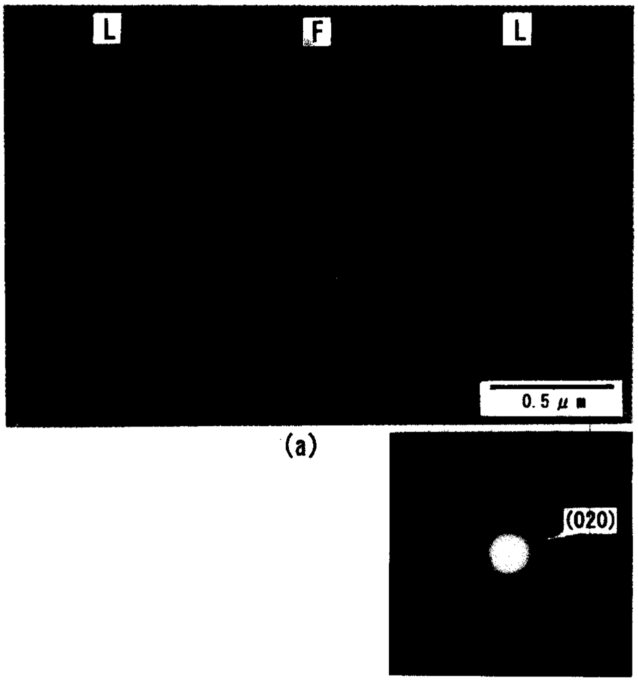
Figure 2 Electron micrograph (a) and the corresponding electron diffraction pattern (b) of as-cast thin film of PEN. The $(hk0)$ reciprocal lattice pattern is shown in (c)

width of these striations is rather constant at approximately 20 nm. These striations are suggested to be immature, fibrous crystals of PEN.

The accompanying s.a.-e.d. pattern obtained from a central region of 2.7 μm diameter is in accord with the scheme of a $(h\,k\,0)$ reciprocal lattice pattern (*Figure 2c*), indicating that the longitudinal, transverse and thickness directions of the striations correspond to the a^*, b and c axes, respectively. The arcing of the $(h\,k\,0)$ reflections in the s.a.-e.d. pattern is attributable to the disorientation of the striations.

Well developed fibrous, lamellar crystals (F crystals) are observed in the TEM micrograph of PEN(200); this TEM micrograph is not shown here. It seems reasonable to assume that these F-crystals originate from the original immature fibrous crystals. On the other hand, as *Figure 3a* shows, both the F crystals and the wide lamellar crystals (L crystals) coexist in the thin film of PEN(250). The micro-e.d. pattern obtained from a region (F) of ca. 0.7 μm diameter indicates that the orientation of the crystallographic axes of the unit cell in these F crystals is essentially the same as that in the original, immature fibrous crystals; two sets of $(h\ k\ 0)$ patterns are superimposed in this micro-e.d. pattern (*Figure 3b*).

Figure 4a shows the TEM micrograph of PEN(300), showing F crystals and L crystals. The micro-e.d. pattern inserted in *Figure 4a* was obtained from the central region (labelled F + L), where the L and F crystals coexist. The micro-e.d. pattern indicates that both of these crystals have common crystallographic axes. It seems reasonable to assume, therefore, that the F crystals coalesce to form wide L crystals. *Figure 4b* is another TEM micrograph and the corresponding micro-e.d. pattern, showing only the well developed L crystals that give a clear e.d. pattern with $(h\ k\ 0)$ spots. It is interesting to note that the L crystals in *Figures 4a* and *4b* also originate from the original, immature fibrous crystals (*Figure 2*): significant restructuring occurs during the heat treatment at 300°C.



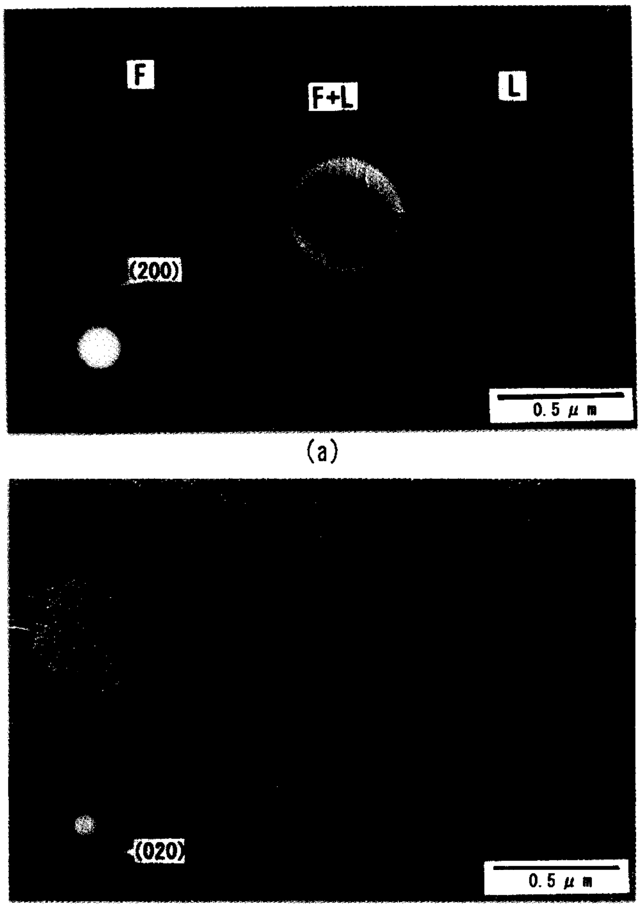
(a)

(b)

Figure 3 Electron micrograph (a) and the corresponding electron diffraction pattern (b) of PEN thin film heat treated at 250°C. Narrow, fibrillar crystals (F crystals) and wide, lamellar crystals (L crystals) are observed in the regions denoted by F and L, respectively

Solution-grown crystals. PEN has been crystallized from CP/PPG solution in the form of spherulitic structures, as well as aggregates of elongated lamellar crystals. The spherulitic structures are characterized by coarse and open fibrillar structures. An application of polarizing optical microscopy has revealed that the spherulites are optically positive: the refractive index along the radial direction is larger than that in the tangential direction.

Figure 5a shows the TEM micrograph of the solution-grown PEN crystals, showing the fibrous, lamellar crystals. It can be suggested that the fibrous, lamellar crystal observed in *Figure 5a* is a structure element of the texture of PEN. *Figure 5b* shows another TEM micrograph and the corresponding s.a.-e.d. pattern of solution-grown PEN crystals, showing aggregates of fibrous, lamellar crystals. The s.a.-e.d. pattern inserted in *Figure 5b* shows that the longitudinal and transverse directions of these crystals correspond to the a^* and b axes, respectively: the c axis lies perpendicular to the lamellar surface of the crystal. This result indicates that



(a)

(b)

Figure 4 Electron micrographs and the corresponding electron diffraction patterns of PEN thin films heat treated at 300°C. The electron diffraction pattern in (a) was obtained from the region F + L, where F crystals and L crystals coexist. Only the well developed L crystals are observed in (b) these fibrous, lamellar crystals are essentially identical to the F crystals.

Quiescent crystallization from the melt. PEN was crystallized at 320°C from the melt on a glass plate. The typical appearance of the PEN spherulites is shown in a polarizing optical micrograph (*Figure 6*). The well developed spherulitic structures cover most of the field of view; these spherulites are optically positive. It seems likely that the elongated lamellar crystals constitute the melt-grown spherulite as is the case with the solution-grown spherulite.

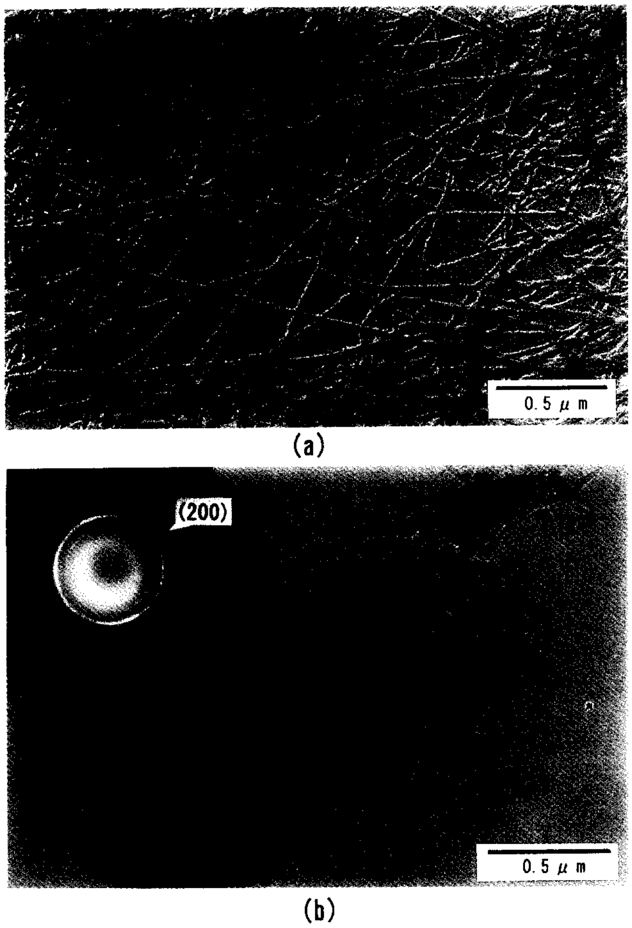


Figure 5 Electron micrographs and electron diffraction patterns of solution-grown PEN crystals. Isolated F crystals and aggregates of F crystals are observed in (a) and (b), respectively

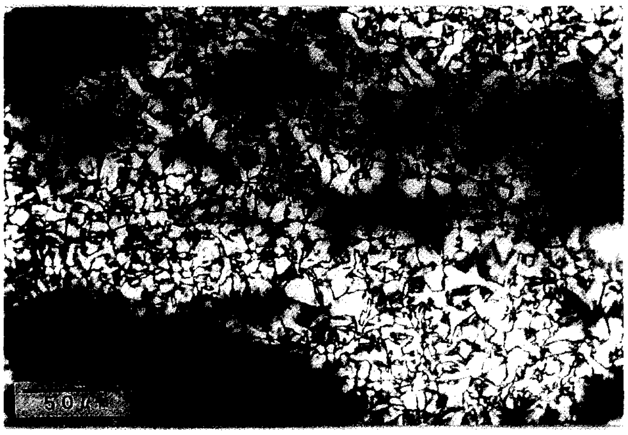


Figure 6 Polarizing optical micrograph of melt-grown spherulites of PEN

Oriented crystallization from the melt. The morphology of thin films of PEN crystallized under shear in contact with a glass slide was also studied: a thin layer of molten PEN on a glass microscope slide was rapidly sheared and crystallized at 320°C.

Figure 7 is a TEM micrograph and the corresponding s.a.-e.d. pattern of PEN crystals formed under shear, showing the stacked lamellar structure. Their morphological features are very similar to those of melt-extruded flexible polymers, suggesting that oriented crystallization occurs. The (h k 0) reflections are concentrated on the equator of the s.a-e.d. pattern, indicating that the c axis is aligned along the shear direction. Strong (2 0 0) reflections are present on the equator, whereas (0 2 0) reflections are very weak. These results indicate that the a^* axis is parallel to the long rib of the stacked lamellar crystals, while the b axis is parallel to the thickness direction.

SUMMARY AND CONCLUSIONS

The results described in the above sections may be summarized as follows.

(1) Immature, fibrous crystals developed in the as-cast PEN film are transformed into wide, lamellar crystals (L crystals) via fibrous, lamellar crystals (F crystals) during heat treatment at temperatures above 250°C. *Figure 8* shows the schematic representation of the F crystal; the a^* axis of the unit cell is parallel to the growing direction of the F crystals. It can be suggested that F crystals coalesce to form L crystals at higher temperatures.

(2) PEN crystallized from the melt or from CP/PPG solution in the form of spherulites with positive birefringence. The radial growth direction of the PEN spherulites corresponds to the a^* axis (*Figure 9a*).

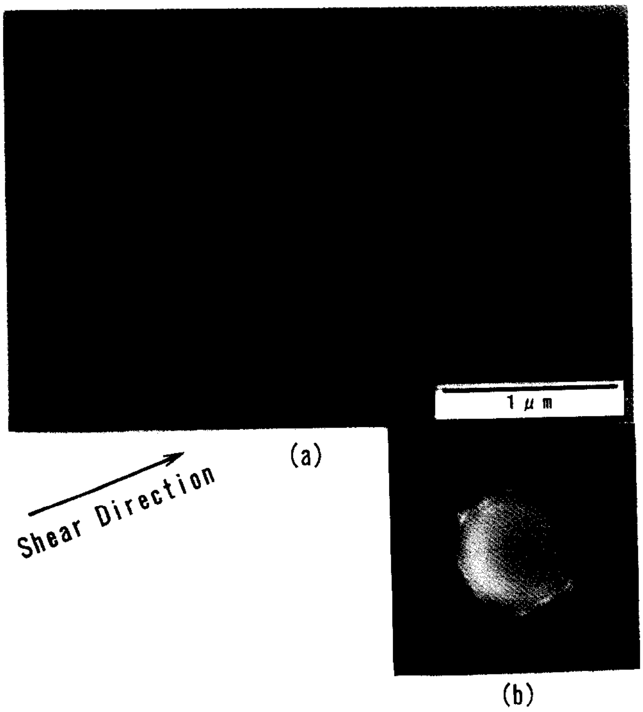


Figure 7 Electron micrograph (a) and the corresponding electron diffraction pattern (b) of PEN thin film crystallized under shear

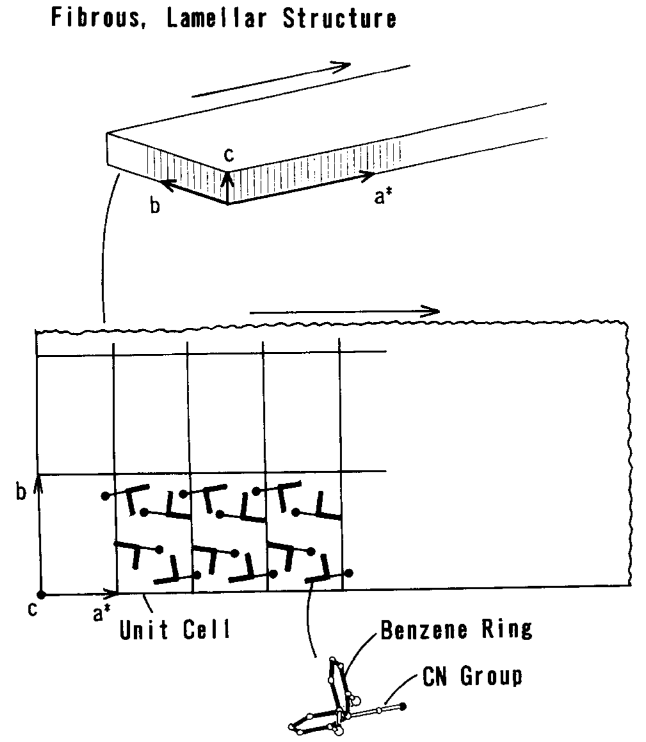


Figure 8 Schematic representation of the molecular arrangement in the unit cell and the F crystal of PEN

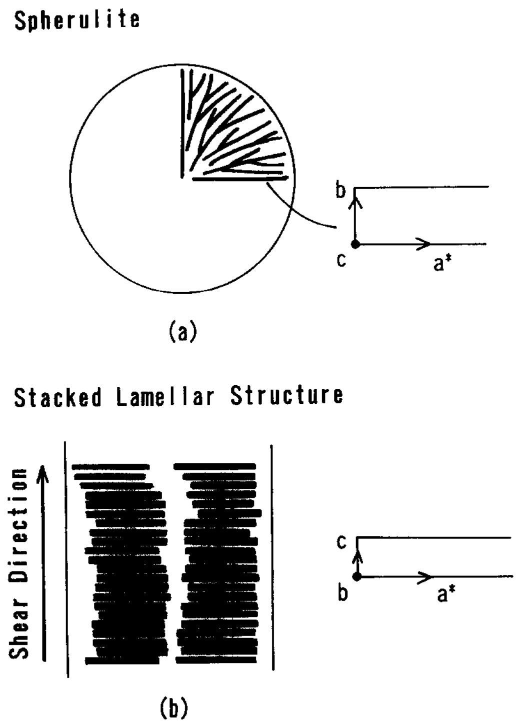


Figure 9 Schematic representation of the texture of spherulite (a) and stacked lamellar structure (b) of PEN

(3) Stacked lamellar structures are formed from the melt under shear; the a^* axis is parallel to the transverse direction and the b axis is parallel to the thickness direction (*Figure 9b*).

Attempts have been made to elucidate the origins of the morphological characteristics of PEN crystals, which are formed under various conditions, on the basis of its crystal structure. A monoclinic unit cell was proposed for PEN crystal by Ichikawa *et al.*[11]. Unit-cell dimensions are:$a = 0.832$ nm, $b = 1.307$ nm, c(fibre axis) $= 0.903$ nm, $\beta = 99.0°$ (ref. 11). Four PEN chains are contained in one unit cell. The manner in which these PEN chains are arranged within the unit cell is depicted schematically in *Figure 8*. According to this unit cell, two phenyl rings in a monomer unit are aligned almost parallel to the a and b axes in an alternating manner, while all cyano groups are aligned in the a direction of the unit cell.

As *Figure 8* shows, the F crystals of PEN are highly elongated along the a^* axis, suggesting that the existence of the preferential nucleation plane, (2 0 0), should favour growth along this direction. The morphological features of the F crystals of PEN are analogous to those of solution-grown poly(ether ether ketone) (PEEK) crystals. Lovinger *et al.* found that PEEK spherulites consist of very narrow, elongated lamellar branches that grow with the b axis in the radial direction[2]. They suggested that the backbones (phenyl rings) of PEEK all aligned in the b direction should favour growth along this direction and also contribute to the restricted widths and fragmentation of PEEK crystals. However, this is not the case for the PEN crystals, since two phenyl rings in a monomer unit are at right angles to each other[11].

We found fibrous, lamellar crystals with extended chains growing in the b direction during an earlier study of poly(p-phenylene terephthalamide) crystallized from sulfuric acid solution[16]. Similar crystals are formed when aliphatic nylons are crystallized from solution. A reasonable explanation for these results lies in the strong intermolecular hydrogen bonds along the long axis of the fibrous crystals. It seems reasonable to assume, therefore, that the strong interaction between cyano groups and phenyl groups along the a axis should favour nucleation on the (2 0 0) growth front, though the interaction between PEN molecules is not completely clear.

PEN forms spherulites with positive birefringence from solution and the melt. In these spherulites, the c axis lies vertical to the spherulite plane and the a^* axis is parallel to the radial direction. In view of the orientation of the cyano groups in the unit cell of PEN, it can be suggested that the refractive index along the a^* axis is larger than that along the b axis. Therefore, the above molecular orientation produces a positive birefringence in the PEN spherulite.

Lamellar crystals are stacked with their c axis parallel to the shear direction, their a^* axis parallel to the transverse direction, and their b axis parallel to the thickness direction. A plausible explanation would appear to involve oriented crystallization accompanied by preferential nucleation at the bc plane on the substrate. Such preferred orientation of PEN molecules during oriented crystallization on a substrate is also observed in PEEK[6] and poly(p-phenylene terephthalamide)[16] during oriented crystallization from the melt and the liquid-crystalline solution.

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