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Production of oriented polyacrylonitrile films by flow-induced chain extension and crystallization from solution

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Polyacrylonitrile $[-CH_2-CH(CN)-]_n$ is not considered to be a thermoplastic polymer. Fibres may be wet spun from solution, but oriented films are, in particular, difficult to produce by a coagulation process. In previous work, it was shown that when liquid propylene carbonate (PC) is blended with polyacrylonitrile (PAN) powder, the polymer can be processed like a thermoplastic. Thus, it was possible to make plasticized gel films by compression moulding. In the present work, it is shown that the gel films may be "remelted" and drawn, to give uniaxially or biaxially oriented PAN films. The process involves flow-induced chain extension and crystallization from solvent, and differs from other methods of producing PAN film or fibre which involve coagulation. The solvent can be removed from the film after drawing, to give oriented films with good mechanical properties. Infrared dichroism studies on uniaxially oriented films containing residual solvent suggested that the carbonyl group of the PC molecule was paired with the nitrile group of the PAN by dipolar interaction. X-ray diffraction experiments showed differences between PAN reactor powder, unoriented plasticized gel film and drawn films; these appear to be related to the presence of solvent.

1. Introduction

Polyacrylonitrile fibre has been made commercially for more than 40 years. It finds applications in textiles and as a precursor for carbon fibres. As the polymer cannot be melt spun, fibres are made by wet spinning and coagulation. The solvents most commonly used in industrial fibre spinning are dimethyl sulphoxide (DMSO), dimethyl formamide (DMF) and dimethyl acetamide as well as the inorganic solvents, NaSCN (aq) and $ZnCl_2$ (aq). However, films cannot be made as easily by extruding a solution of the polymer in these solvents, through a slot die and into a coagulation bath.

Polyacrylonitrile (PAN) does not crystallize from the above-mentioned solvents. However, in 1962, Holland *et al.* showed that single crystals of PAN could be grown from very dilute propylene carbonate solutions [1]. More recently, it was shown that 20% PAN–PC solutions formed thermoreversible gels on cooling to room temperature [2]. Gelation occurred due to the formation of crystallites when the concentrated solutions were cooled [2]. Further, it was shown that propylene carbonate-blended PAN powders with even higher polymer concentrations (30%–70%) behaved like a thermoplastic polymer and so could be compression-moulded to give plasticized sheets, which were mechanically stiffer than the gels [3].

In this study, it was found that the unoriented PAN sheets made by compression moulding PC-blended PAN powder [3], may be "remelted" and drawn to produce uniaxially or biaxially oriented films. The mechanical properties and the orientation in the drawn PAN films were studied. Before describing the production of oriented PAN films using propylene carbonate, other methods of producing PAN films are briefly reviewed.

1.1. Review of past work on PAN films

Good-quality PAN films have been difficult to produce in the past. Casting a polymer solution (using a solvent such as DMSO) and coagulating in a non-solvent leads to unoriented, weak and brittle films, which are difficult to draw afterwards. Although the coagulation method is satisfactory for producing fibres, it is unsuitable for films because the coagulated film is voided and becomes a glassy material which breaks easily if dried. Hence, post drawing of the coagulated film after drying is not possible. Further, for an extrudate with a thick cross-section, homogeneous coagulation is difficult to achieve. Homogeneous drawing of a partially coagulated material is also difficult because of the differing mechanical responses of the solidified outer skin and the liquid solution in the interior.

Another method of film formation is by casting from a solution followed by drying of the solvent. This gives a clear, unvoided film which can be drawn.

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This paper is dedicated to Professor Kurt Schoffner on the occasion of his 60th birthday.

Dobretsov *et al.* [4] reported making films by casting a very dilute solution of high molecular weight PAN in DMF and evaporating the solvent. After uniaxial drawing of the dried film, moduli of 31 GPa and strengths of 1.2 GPa were obtained [4]. These are very high values for PAN. However, it is difficult to make the casting and drying process continuous as there are no (readily available) volatile solvents for PAN. For such a process to work on a continuous extrusion line, the film has to solidify at least partially on-line, through a composition-induced phase change (i.e. by solvent evaporation), so that it has the mechanical integrity to be wound up on a take-up system.

There is also some work reported in the patent literature on the subject of PAN films. In 1978, Hungerford patented a process [5] whereby a hot solution of PAN homopolymer in DMSO was extruded on to a rotating drum which had a low energy surface. The drum was needed to support the extrudate, as it did not solidify spontaneously. Next, the supported extrudate was contacted with water to remove and partially exchange the DMSO with water and thereby generate the film. Hungerford termed this an "aqua-gel" film and stated that it contained as much as 50% water. The self-supporting aqua–gel film was biaxially stretched at 50–80 °C. Transparent films with good mechanical and gas barrier properties were reported [6–9].

It is known that pure water becomes a solvent for PAN at temperatures above about 170 °C [10]. In 1983, Hungerford patented another technique for making films by water-plasticized melt extrusion [11]. The PAN–water "melt" was extruded at 200 °C and cast on to a chill roller maintained at 25 °C in a pressurized environment (300–400 kPa) to prevent the water flashing off.

In another approach using water plasticization, Zwick patented a process for producing biaxially oriented PAN by film blowing [12]. The PAN–water melt was extruded through an annular die and the film was expanded with pressurized steam. The extrusion temperature used was 175 °C and the solidification zone was maintained at 118 °C in a steam environment [12].

Thus, water can be used as a solvent, but only at temperatures above its boiling point at atmospheric pressure. The main difficulty with water-plasticized melt extrusion, therefore, is that the system needs to be pressurized. Further, after extrusion, there has to be controlled de-pressurization to avoid a porous extrudate being formed. Although water would be a cheap, non-polluting solvent, these factors make it a difficult system to operate.

1.2. PAN films from propylene carbonate plasticization

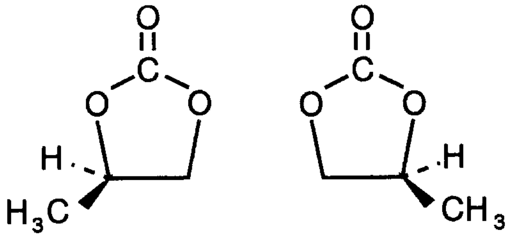
It is the purpose of this work to demonstrate a method of making uniaxially and biaxially oriented PAN films by flow-induced chain extension and crystallization, instead of by coagulation or solvent evaporation. The primary film was generated here by solidification on cooling, so that a voided structure was not obtained. Next, this film was hot-drawn in the presence of the propylene carbonate solvent. The PC was removed only after the orientation was achieved.

2. Experimental procedure

2.1. Polymer and solvent used

A commercial homopolymer PAN (Polysciences Inc., UK), was used. The inherent viscosity measured in DMF at 25 °C gave a value of 1.50 dL g^{-1}. Tacticity determination by ^{13}C nuclear magnetic resonance spectroscopy revealed that the polymer was atactic. The polymer was a white powder and will be referred to as "reactor powder" in the rest of the work.

Propylene carbonate (PC, Aldrich) is a polar organic solvent with a boiling point of 240 °C, a freezing point of -55 °C and a density of 1.18 g cm^{-3}. The molecular structure shown below indicates that the molecule has a chiral centre. The commercial solvent is a ($\pm$) racemic mixture of the two isomers.



2.2. Method of blending the PC with the polymer powder

Liquid PC was gradually added to finely divided polymer powder in a mortar, and ground with a pestle at room temperature. The PAN : PC ratio is quoted as a weight/weight percentage. Thus, a 30 : 70 PAN : PC blend means 3 g PAN and 7 g PC. Two PAN : PC compositions (30 : 70 and 40 : 60) were used in this study.

2.3. Method of primary film production

The PC-blended powder described above can be "melted" (i.e. dissolved) by application of heat and pressure; cooling afterwards gave a compression-moulded film [3]. In this work we shall refer to this moulded film, which was used for the drawing experiments, as the "primary film" or as the "plasticized gel-film".

A 20 cm x 20 cm piece of primary film was made by moulding 2 g of PC-blended polymer between two steel caul plates in a hot press at 190 °C, under a low pressure for 5 min. The primary films were cooled under pressure to 60 °C before removing from the press.

In the previous work, moulded films were made from 30 : 70, 40 : 60, 50 : 50, 60 : 40 and 70 : 30 PAN : PC blends and the cause of the gelation or solidification of PAN–PC solutions on cooling was investigated [3]. However, in this report, the drawing of primary films was restricted to primary films made from 30 : 70 and 40 : 60 PAN : PC blends, although films with higher PAN contents could also be drawn.

The moulded 30:70 and 40:60 primary films were wet and rubbery at room temperature. They were wrapped in aluminium foil for storage when not in use. This minimized PC evaporation. Primary film thicknesses were typically 100 μm; the exact thickness depended on the pressure used and could be varied.

2.4. Method of film drawing

The 40:60 PAN:PC blend was employed for making uniaxially drawn films while the 30:70 PAN:PC blend was used for biaxially drawn films.

Primary films were drawn on a hot bar whose temperature was regulated with a Eurotherm temperature-controller (Fig. 1). Generally, the optimum drawing temperatures for both polymer compositions were in the range 100–130 °C. Films were either uniaxially or biaxially drawn when in contact with the hot bar. To produce uniaxially drawn films, primary films were cut into strips 5 cm long, and 1 cm wide. Ink dots spaced 1 cm apart were imprinted on them for measuring draw factors. Films were clamped at either end and then were drawn manually over the hot bar at an elongation rate of about 1 cm s^{-1}, to the maximum draw factors possible. The film could be drawn either along the length of the hot bar (direction B, Fig. 1) or across the width of the bar (direction A, Fig. 1). In fact, the latter was used, so that the method is similar to zone drawing [13]. In such a case, the necked section of the film is moved out of the heated zone quickly and it cools rapidly under tension.

Biaxially drawn films could be produced either by sequential or simultaneous drawing. For sequential drawing, 5 cm × 5 cm square pieces were cut from the primary film and a 1 cm square grid was ink printed on it in the centre. Uniaxial drawing was first carried out in a direction parallel to two of the sides of the primary film (machine direction, MD), to a limited draw factor of about ×2–3. This film was removed from the clamps and reclamped perpendicularly for transverse drawing (TD). During TD, there was some shrinkage in the original draw direction due to the removal of the clamps. To reduce this effect, films were drawn across the edge of the hot bar (C in Fig. 1), so that most of the film surface was not in contact with the heat. This induced only localized heating and drawing in the film, so that shrinkage in the original MD was minimized. The film was again unclamped and reclamped for further draw in the original MD direction. Finally, the procedure was repeated once again in the transverse direction. Thus, biaxially drawn films with maximum draw factors of 5 × 5 were made in four, sequential drawing steps. Finally, 2 cm strips were trimmed away from the four borders of the drawn film to leave a piece of film with quite uniform biaxial orientation.

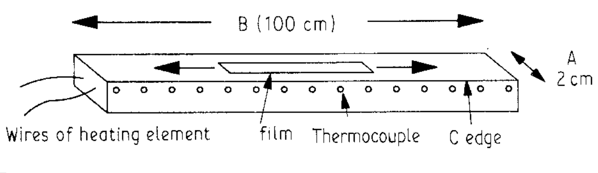


Figure 1 Hot bar used for drawing films. A is the width-wise and B is the length-wise direction of the bar. The film may be drawn either along A or B, but the figure indicates the film being drawn along A. For biaxial drawing, the primary film was drawn along the edge, C, so as to localize the heating to a narrow zone.

Simultaneous biaxial drawing was performed over the hot bar using 5 cm × 5 cm square pieces of the primary film. This required clamping at all sides of the square piece and two pairs of hands to pull simultaneously in two mutually perpendicular directions. However, this was done only to check the feasibility of simultaneous biaxial drawing. The films used for property tests were made by sequential drawing.

2.5. The dissolution temperature of the PAN–PC blends

As mentioned, the primary film was remelted, and drawing took place effectively in the "melting" (i.e. dissolution) zone of the particular PAN–PC composition. In order to show that this was the case, the melting curves of the moulded primary films were determined by differential scanning calorimetry (DSC).

The melting curves were recorded for both compositions using a Mettler DSC 30, which was fitted with a metal sensor and controlled by a TC 11 processor. Data storage and analysis were performed on an IBM microcomputer using Mettler TA 72 Graphware software.

The first melting run was ignored in case of poor thermal contact between the samples and the DSC pan; the samples were cooled and remelted, and the second run was recorded. The heating rate was 10 $°\text{C min}^{-1}$.

2.6. Propylene carbonate extraction

The PC remaining in the films after drawing was extracted by forced convection in a fan oven. The films were clamped to prevent shrinkage and placed in the oven at 100 °C for 10 min. The residual PC content was estimated by weighing the film at the various stages of the process (moulding, drawing and drying) and the total PC loss was found.

2.7. Mechanical testing

Tensile testing was carried out on biaxially drawn and dried films, to assess their mechanical properties. An Instron Series IV tensile testing machine was used to measure the Young modulus, E, ultimate tensile strength (UTS), and elongation to fracture, $\varepsilon(\%)$, of the films. All testing was carried out at room temperature (~20 °C). The crosshead speed was maintained at 5 mm min^{-1}. Measurements were made only in the two principal draw directions, and as the two values were very similar, they were averaged and only a single value is quoted for each film.

2.8. Morphology of drawn films

The drawn films could be either transparent or "pearlized" (opaque). The pearlized texture in the drawn films was found to depend on the microstructure. Hence, a Hitatchi S-4000 field-emission scanning electron microscope was used to study the microstructure.

2.9. Infrared dichroism and orientation in uniaxially drawn films

The orientation in uniaxially drawn films made from the 40:60 PAN:PC blend was studied using infrared dichroism. The infrared (IR) dichroic ratio was established using polarized IR spectroscopy. The instrument used was a Nicolet 740 FTIR spectrometer, equipped with a Spectra Tech wire grid polarizer. The measurements were made on a ×10 drawn film with a residual PC content, after drying, of approximately 5%.

The IR spectrum of a uniaxially drawn PAN film contained two convenient absorption bands for dichroism measurements. These were the band at 2244 cm^{-1} due to the $C \equiv N$ vibration of the PAN and the band at 1790 cm^{-1} due to the $C = O$ vibration of the residual propylene carbonate in the film, which also showed dichroism.

For dichroic ratio measurements, the IR spectrum was first recorded with the polarization direction perpendicular to the draw direction y, so that the vibration direction was confined to the xz plane while the direction of wave propagation was in the thickness direction of the film, z. Fig. 2 shows the coordinate directions. The IR spectrum was next recorded at the same position in the PAN film with the polarization direction now parallel to the draw direction y. The oscillation of the electric field vector was now confined to the yz plane with the propagation direction still z.

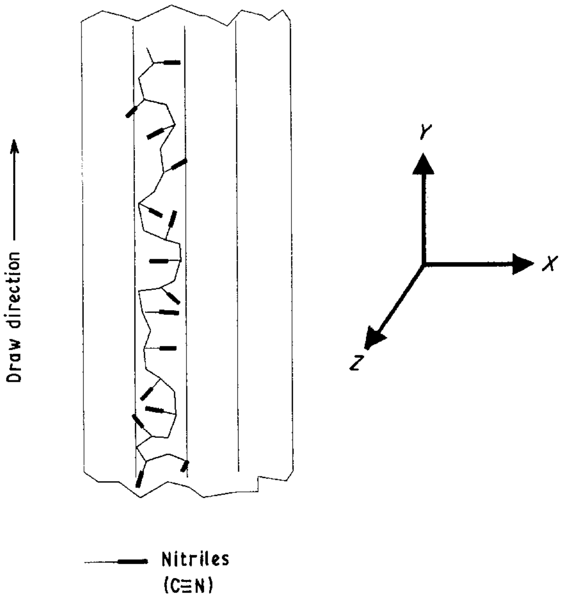


Figure 2 Schematic diagram of a uniaxially drawn film showing disposition of the nitriles and the co-ordinate directions. The chain adopts a rod-like conformation [20, 21], due to the intramolecular repulsions of the $C \equiv N$ groups.

2.10. X-ray diffraction

Wide-angle X-ray diffraction studies were conducted on three types of sample: (i) PAN reactor powder, (ii) primary film made by moulding 40:60 PAN:PC blends, and (iii) uniaxially drawn films made from (ii) with a draw factor of ×10. The drawn film had a residual PC content of about 20% (i.e. the film was not post-dried after drawing).

CuK_α radiation with nickel filter was generated using a Philips PW 1730 generator. The operating voltage and current were 40 kV and 40 mA. The diffractograms were obtained using a Philips 1050/81 diffractometer. A crystal-monochromated collection system was used to collect the diffracted data. The radial scans on the samples were carried out in the region $2\theta = 4°\text{–}40°$. The data were collected at 0.02° intervals with counting for 1 s at each step. Peak positions were determined by the APD 1700 (Version 4) software controlling the system.

For the uniaxially drawn film (iii), diffractometer traces were obtained from: (a) an equatorial scan, and (b) a meridional scan.

3. Results and discussion

The method of preparing and drawing PAN–PC gel films is discussed first. The properties of the drawn films are considered next, followed by the results from the IR dichroism and X-ray studies.

3.1. Method of blending PC with PAN powder

The first step in producing the plasticized gel film was to mix the liquid PC with the dry PAN powder. As it is not self-evident how a homogeneous distribution of a small volume of liquid with a large volume of powder may be achieved, the procedure developed in the previous work will be briefly discussed, but a more extensive explanation is given in [3].

The 30:70 PAN:PC blend formed a paste-like material [3]. However, blends with PAN contents greater than about 30% formed damp but free-flowing powders. Fig. 3b shows a 40:60 PAN:PC powder, which was free flowing, despite containing 60% by weight of liquid. The explanation for this was given previously: PAN powder from the polymerization reactor was very porous, with a pore volume fraction of about 70%, and hence it was able to take up and store a large amount of liquid PC by capillary action [3].

3.2. Primary film production

Fig. 3 shows the various stages in the conversion of the PAN powder to a thermoplastic, plasticized gel film. Applying heat and pressure to PC-blended PAN powder caused the polymer to "melt". The cause of the gelation or "solidification" of concentrated PAN–PC solutions on cooling, has been explained in recent papers [2, 3] as arising from the partial crystallization of the polymer. The gels [2] and moulded sheets [3] were thermoreversible and could be "remelted" by

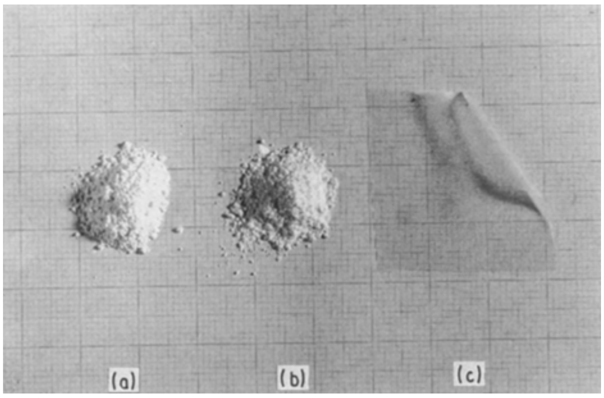


Figure 3 Stages in the conversion of PAN powder to a thermoplastic, plasticized gel film. (a) PAN reactor polymer is a free-flowing powder, which is not normally considered a thermoplastic material. (b) Propylene carbonate-blended polymer is still a free-flowing powder, despite containing 60% by weight of liquid. (c) Moulded PAN–PC gel film, made from the powder in the centre, is a flexible, rubbery material which can be hot drawn.

heating, which is a result of the crystallites redissolving when heated.

3.3. Uniaxial and biaxial drawing of primary films

Generally, the rubbery primary film (shown in Fig. 3) was not drawable to any significant degree at room temperature. However, drawing could be carried out in a semi-molten state. (Note that if the solvent was removed from the primary film by extraction with acetone, it became brittle and undrawable. Thus, it was essential to draw the primary film with the PC still present.)

The manual drawing technique shown in Fig. 1 was preferred to drawing in an Instron hot cabinet because, in fact, it approximates a continuous drawing process where the film is exposed to heat only for a short period. Although laboratory batch-drawing studies on polymers such as polyethylene are often conducted in a hot cabinet, here it would have been problematic, as the long times required for a large heated cabinet to reach thermal equilibrium would have resulted in plasticizer evaporation.

Ultimate draw factors depended on the homogeneity of the primary film, initial film thickness, polymer concentration, drawing temperature and drawing rate. The maximum uniaxial draw factors were typically × 10–15. The uniaxially drawn films generally splintered if overdrawn.

Pieces 15 cm × 15 cm of biaxially oriented film could be made by manual (sequential) biaxial drawing. Homogeneity of composition in the primary film was particularly important in biaxial drawing as premature tearing during drawing occurred otherwise. The maximum draw factors obtained were 5 × 5. The possibility of simultaneous biaxial drawing was also demonstrated. For a continuous process such as film blowing, simultaneous biaxial extensibility would be necessary. Thicknesses of biaxially drawn films could be varied from 2–50 μm; the final thickness depended on the starting thickness of the primary film and the draw factor.

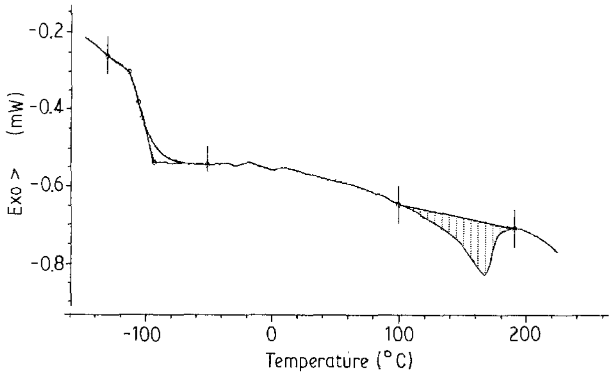


Figure 4 DSC "melting" curve of 30:70 PAN:PC gel film. Heating rate 10 °C min^{-1}, ΔH = 9.1 J g^{-1}, peak 166.8 °C. Glass transition onset − 114.4 °C, end point − 95.1 °C.

The optimum temperature zone for drawing was 110–130 °C, for both 30:70 and 40:60 PAN:PC primary films, although higher temperatures could be used. Drawing below this temperature required a higher stress and it led to fracture at low draw ratios. The DSC experiments indicated that the melting zone for the two compositions was 115–180 °C. Fig. 4 shows, by way of example, the DSC trace of the "melting" of a 30:70 PAN:PC primary film; the trace of the 40:60 PAN:PC film was similar and hence is not shown separately. It can be seen that the primary film was drawn at a temperature where the randomly oriented crystallites present in it just start to "melt".

It is well known that crystallizable polymers such as polyethylene can crystallize under appropriate conditions in the form of shish-kebab fibres when a solution of the polymer is subjected to elongational flow [14]. The same phenomenon can occur in the melts of crystallizable flexible-chain polymers which have been subjected to elongational flow. It has been reported that polyethylene melts subjected to extensional flow (during extrusion or during melt drawing) can crystallize under appropriate conditions, with an interlocking shish-kebab morphology which confers good mechanical properties [15, 16].

It is because PAN crystallizes from PC that it was possible to draw in the semi-molten state with a large amount of solvent present. We think that the drawing process here involves flow-induced chain extension and crystallization. This phenomenon has been explained by Peterlin [17]. As soon as the liquid phase contains extended chains, the phase transition from the liquid to the crystal is modified because the enthalpy and entropy of the oriented liquid differs from the values they have in the fully relaxed liquid. The entropy reduction in the strained liquid increases the melting (or dissolution) temperature, and hence at any temperature, the effective supercooling. The simultaneous reduction in heat content acts in the opposite direction, but its influence is smaller than the entropy change. The rate of nucleation and crystal growth is enormously enhanced as this depends on the square of the supercooling. It is noted that this process to produce oriented PAN films and fibres is not restricted to PC, but to any solvent or solvent mixtures from which the polymer will crystallize during flow [18].

Ferguson *et al.* [19] have shown that liquid–liquid phase separation can occur with even non-crystallizable polymers due to elongational flow, such as that which occurs during spin-line drawing of a filament from a concentrated solution. This leads to a concentrated solution phase separating out from a more dilute solution phase, causing gelation of the filament. However, after cessation of flow in this case, the concentrated phase redissolves spontaneously.

In the case of drawn PAN–PC films, much of the orientation is retained indefinitely if the sample is kept below the dissolution temperature, even without complete removal of the PC. For instance, the uniaxially oriented films were permanently birefringent, even with the presence of 20%–30% residual solvent in the film.

It is worth contrasting the behaviour of PAN solutions in the usual solvents such as DMSO, or NaSCN (aq). If such a solution is subjected to elongational flow, the chains can be extended and oriented temporarily, but generally the orientation cannot be retained because the polymer will not crystallize from these solvents at any temperature. On cessation of flow, or when the polymer emerges from the elongational flowfield, the orientation relaxes. Generally, such solutions have to be coagulated to generate the fibre or film.

The main difference between the coagulation process and the PAN–PC process is that in the former, phase change occurs due to a change in composition whereas in the latter, the phase change occurs due to a thermal change. Coagulation thus involves a mass transfer whereas the thermal solidification process involves a heat transfer. As mass-transfer rates are slower, it is difficult to produce thick films by coagulation, whereas flow-induced chain extension and crystallization would be a better method for producing oriented films.

3.4. Propylene carbonate removal after drawing

Although a high degree of orientation is retained in the films even with the PC present, there is some relaxation of the orientation with time, to some equilibrium condition, as the PC is a plasticizer which facilitates chain motion at room temperature in the amorphous regions. With uniaxially drawn films, this was manifested by a slight slackening of the film immediately after drawing. In biaxially drawn films, it manifested itself by the wrinkling of the film with time. Thus, for the best mechanical properties and dimensional stability, the PC should be removed after drawing.

About 5% PC was lost during the moulding of the primary film and a further 40% was lost during biaxial drawing. PC exudes to the surface of the film during drawing (this is visible) and evaporates. The remaining PC was removed from the drawn films using convection oven heating. Thin, biaxially drawn films could be dried to a 5% PC level by heating at a moderate 100 °C for 10 min. The dried films were dimensionally stable and did not shrink or warp with time thereafter. Pearlized films were easier to dry than transparent ones, presumably because the porous morphology of the former (described in the next section) facilitates solvent evaporation. It is also noted that PC can be removed by alternative methods such as by extracting with acetone or hot water.

3.5. Properties of PAN films

3.5.1. *Transparent and pearlized films*

It has been pointed out that the drawn PAN homopolymer films could be obtained with a transparent or pearlized finish (Fig. 5). The pearlized films were opaque, but had a beautiful lustrous sheen (Fig. 5b). The pearlized films had a microporous texture consisting of voids with nominal diameters of 10–15 μm which were bridged by fibrils. This is shown in the scanning electron micrograph in Fig. 6. The voids were too small to be seen individually by eye, but this texture caused light scattering and gave the lustrous, pearlized finish. If the pearlized film was soaked in water, it became more transparent, as the pores filled with the liquid; there was a better refractive index match between polymer and liquid and so scattering was reduced. Alternatively, heat-pressing the drawn pearlized films at 170 °C caused the film to become more transparent as the voids were closed.

It was not fully established why micro-voiding sometimes occurred during drawing, but it is felt that it depended on the primary film and the drawing temperature. The polymer powder was dissolved in the PC by a compression-moulding technique and though this gave an apparently homogeneous primary film, it is felt that at the microscopic level, there were concentration gradients, with the core of the original powder particles containing less PC. On drawing such a film, there would be stress concentrations which could lead to micro-tearing.

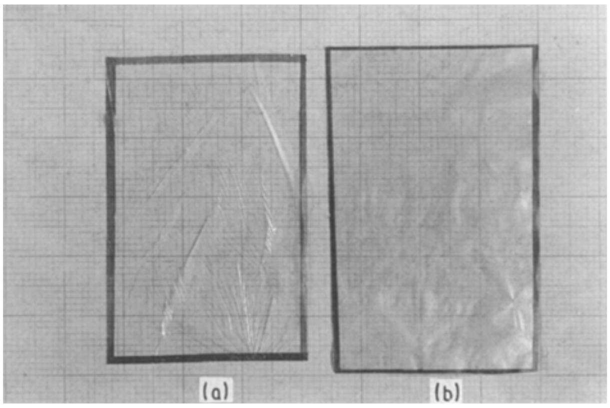


Figure 5 (a) Transparent biaxially drawn film. (b) Pearlized biaxially drawn film. The borders of the films were marked with ink to make them visible.

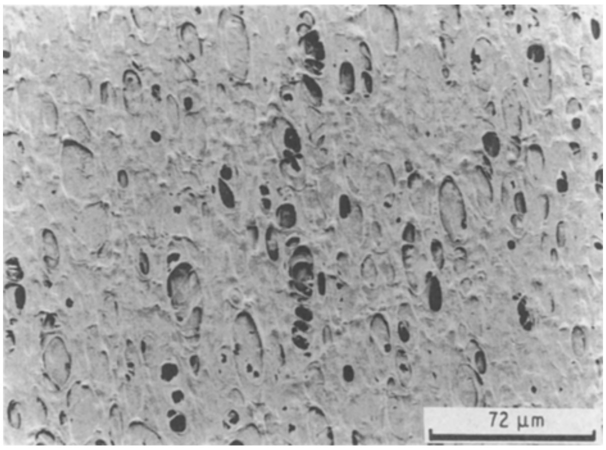


Figure 6 Scanning electron microscope picture of the pearlized biaxially drawn film of Fig. 5b. The voids are often bridged by fibrils. Light scattering occurs due to the micro-void texture and causes the pearlized effect.

TABLE I The mechanical properties of biaxially stretched PAN films with pearlized and transparent finishes. All films contain about 5% residual PC. The mechanical properties quoted are an average of the values measured for the two principal draw directions. Thus, for a 2 × 2 film, the moulus was 1.75 GPa in both draw directions

Draw factor	Young's modulus (GPa)	Ultimate tensile strength (MPa)	Elongation to fracture (%)	Film type
2 × 2	1.75	49	10.9	Pearlized
4 × 4	3.01	70	4.9	Pearlized
5 × 5	3.40	91	4.2	Pearlized
4 × 4	3.50	101	4.6	Transparent

In principle, better shearing during melting should give a more homogeneous primary film. This would be feasible during a continuous extrusion operation using a screw extruder, but with compression moulding, there is little opportunity for shearing. The other factor which could influence the drawing behaviour and the morphology of the drawn film could be the degree of crystallinity in the primary film. It was observed that whitening occurred if the film was drawn at too low a temperature.

Further work is required on finding the factors required in making transparent or pearlized films, as both types of material would have interesting properties and applications. The majority of this work, including the mechanical property studies, was conducted on pearlized films.

3.5.2. Mechanical properties of biaxially drawn films

With uniaxially drawn films, the maximum draw factor obtained was about × 15, before the film splintered. Owing to the tendency for highly drawn uniaxial films to fibrillate, they would not be of much practical use and hence their mechanical properties will not be reported. However, uniaxially drawn films were useful for X-ray and for orientation studies. This is discussed later.

Biaxially drawn films did not have the same tendency to splinter as the uniaxial films. The mechanical properties of biaxially drawn films as a function of draw factor are shown in Table I. For the pearlized film, an average maximum modulus of 3.4 GPa and a strength of 91 MPa were obtained. These films could be folded and crumpled repeatedly without damage, but they could be torn like paper. The 4 × 4 transparent film showed a similar modulus but a higher strength of 101 MPa.

The moduli values in Table I for the biaxial films are comparable with those of commercial biaxially oriented polypropylene and polyethylene terephthalate. The strengths were somewhat on the low side, but this is to be expected because the films tested were microvoided.

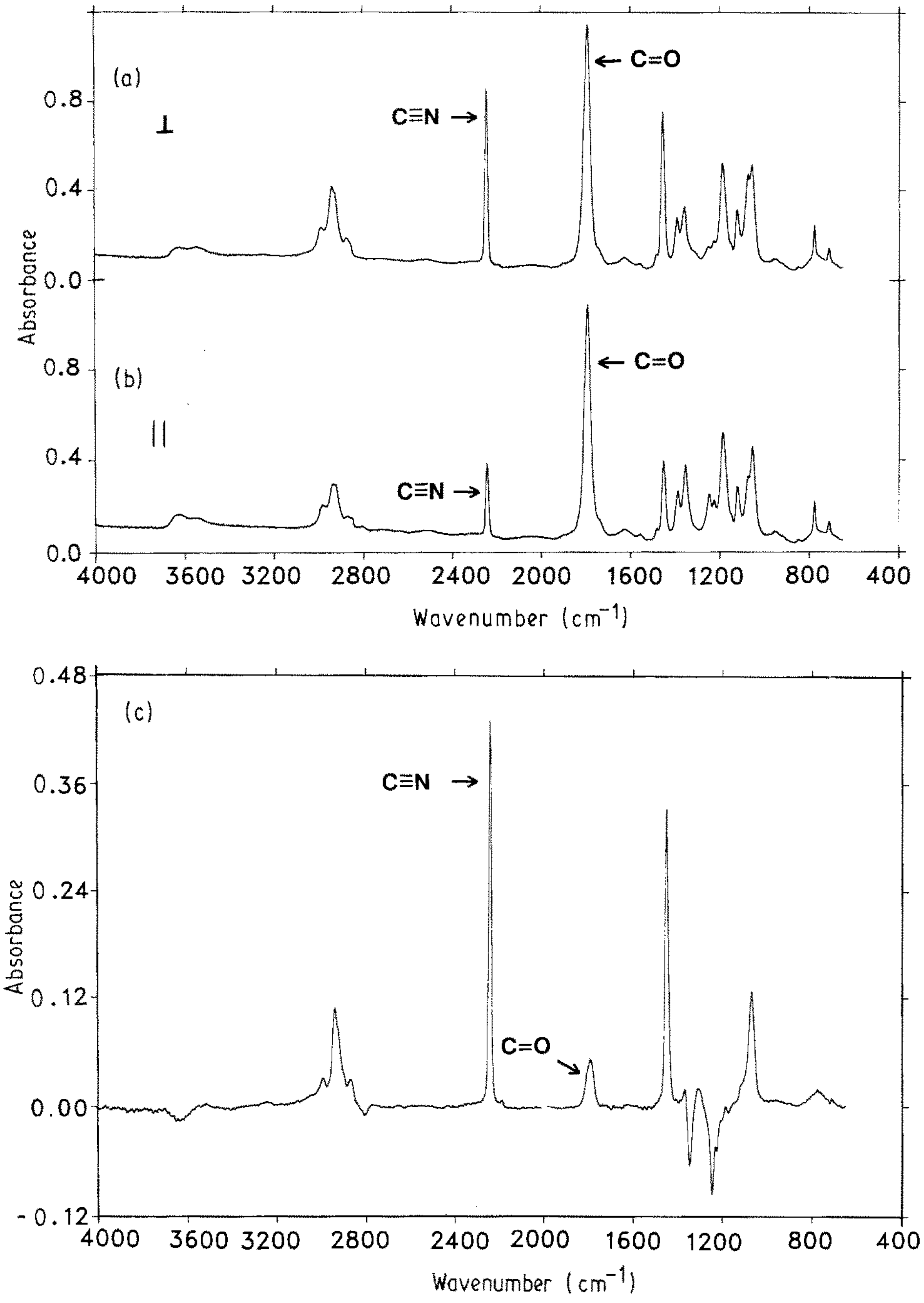
3.6. IR dichroism and dipolar interactions between polymer and solvent

There is evidence from IR dichroic measurements for dipolar interactions between the nitriles of the PAN and the carbonyl groups of the PC molecules.

Fig. 7a and b show the polarized IR spectra of a × 10 uniaxially drawn PAN film containing 5% PC, for perpendicular and parallel polarizer directions. The dichroic ratio of the nitrile band is given by $DR_{C\equiv N} = A_x/A_y$, where A_x and A_y correspond to the integrated absorbance values for perpendicular and parallel polarized radiation, respectively. Similarly, the dichroic ratio of the carbonyl band $DR_{C=O}$ was obtained from the ratio of the absorbances at 1790 cm^{-1} using perpendicular and parallel polarized IR radiation (Fig. 7a and b).

The partial dichroic spectrum provides a graphic representation of polarized IR spectra and is a plot of $(A_x - A_y)$ versus wavenumber. This is shown in Fig. 7c. For an unoriented sample, both polarizer positions would give an identical spectrum and so the difference will be zero, but if the bands show dichroism, then the partial dichroic spectrum will show some peaks above and some below the zero baseline (Fig. 7c).

The nitrile band at 2244 cm^{-1} in Fig. 7a and b clearly shows dichroism with the nitrile absorption being greater when the IR beam is polarized perpendicular to the draw direction. In a uniaxially drawn film, the polymer chain axes tend to align parallel to the draw direction while the nitrile groups will tend to align perpendicular to it (Fig. 2). This explains why the absorbance of the nitrile is greater when the beam is polarized perpendicular to the draw axis. The nitrile dichroic ratio ($DR_{C\equiv N}$) measured for this film was 2.56. Although this value does not appear to be particularly high, it should be pointed out that the IR dichroism of oriented PAN is intrinsically low compared with other oriented polymers [20, 21]. Because the transition moment angle (the angle between the direction of the dipole moment change and the polymer chain axis) for the nitrile stretch is about 70° [22],



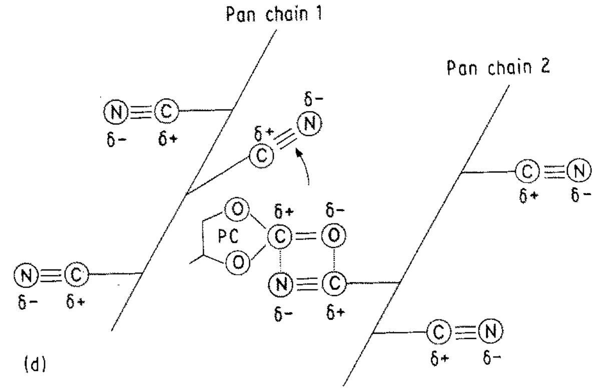


Figure 7 Polarized IR spectra showing the dichroism of the PAN nitrile band and the PC carbonyl band. (a) Electric vector of IR radiation polarized perpendicular to draw axis. Note that the nitrile and carbonyl absorbances are greater with this polarization compared to (b). (b) Electric vector of IR polarized parallel to draw axis. The nitrile and carbonyl absorbances are diminished with this polarization, compared to (a). (c) Partial dichroic spectrum (note: different scale from (a) and (b)). The nitrile band shows greater dichroism than the carbonyl band. (d) Schematic diagram showing the dipolar interaction of the PC molecule with the nitrile group of the PAN. The breaking of intermolecular nitrile dipole pairs by the PC molecules allows the chain segments to move by bond rotation, which leads to the dissolution of the PAN.

the maximum nitrile dichroic ratio corresponding to a perfectly oriented sample would be only 3.77.

Interestingly, the carbonyl band at 1790 cm^{-1} from the residual PC also showed similar dichroism with the perpendicular absorption being greater than that parallel to the draw axis (Fig. 7a and b). The IR dichroic ratio for the PC was however very low (1.06) but it was reproducible. This suggested that the carbonyls of the PC molecules were oriented in the same way as the nitriles and because there is no way of preferentially orienting the PC molecule by mechanical deformation (as one can a polymer molecule), it is proposed that the carbonyl group forms a dipole pair with the nitrile. This is illustrated in Fig. 7d. It is suggested that the pairing of nitrile dipoles from adjacent chains is broken by the insertion of the carbonyl portion of the PC molecule. The breaking of the intermolecular nitrile dipolar bonds, in effect, lowers the melting point of the PAN and makes it "melt" or dissolve in the PC at moderate temperatures.

There are several possible reasons why the carbonyl vibration shows less dichroism than the nitrile band. Firstly, the PC molecules in oriented films may be excluded from the denser, more ordered crystallites and are probably concentrated in the amorphous regions of the polymer and so are not as oriented. A second explanation may be that the carbonyl–nitrile dipole pairing is not perfectly anti-parallel as drawn in Fig. 7d but exists at various angles. Another possibility is that the transition moment direction for the carbonyl vibration may be only slightly greater than 54.7 °. This is the angle where no dichroism is observed regardless of the degree of orientation in the molecules [23].

3.7. Wide-angle X-ray diffraction studies

3.7.1. PAN reactor powder

Fig. 8a shows the diffractogram of the PAN reactor powder used in this work. The polymer was not amorphous but there were only two peaks. These *d*-spacings are listed in Table II. In accordance with the previous findings [3], the crystallites in the polymer powder obtained from the reactor can be described by a hexagonal packing of cylinders representing rod-like PAN molecules. This is shown in Fig. 9a.

It is feasible to describe the order in PAN powder by a two-phase model consisting of a series assembly of crystallites and amorphous regions with the qualification that the type of order in PAN crystallites is of a two-dimensional kind which has been called paracrystalline or "laterally ordered" [21, 24]. The crystallites in the reactor powder, however, were extremely small as suggested by the broadness of the peaks.

3.7.2. The 40:60 PAN:PC gel film

In the previous study, the nature of the crystallites in the 70:30, 60:40, 50:50, 40:60 and 30:70 PAN:PC moulded sheets was extensively discussed [3]. Here, the 40:60 PAN:PC sheet is reconsidered in order to compare, not only with the reactor powder, but with the drawn film made from it.

The striking feature of the 40:60 PAN:PC moulded film, in comparison with the reactor powder, is the appearance in Fig. 8b of two strong peaks instead of one peak in the vicinity of $2\theta = 17°$. This has been explained as arising from a rearrangement of the hexagonally packed chains in the powder into an orthorhombic lattice after dissolution and recrystallization from PC [3].

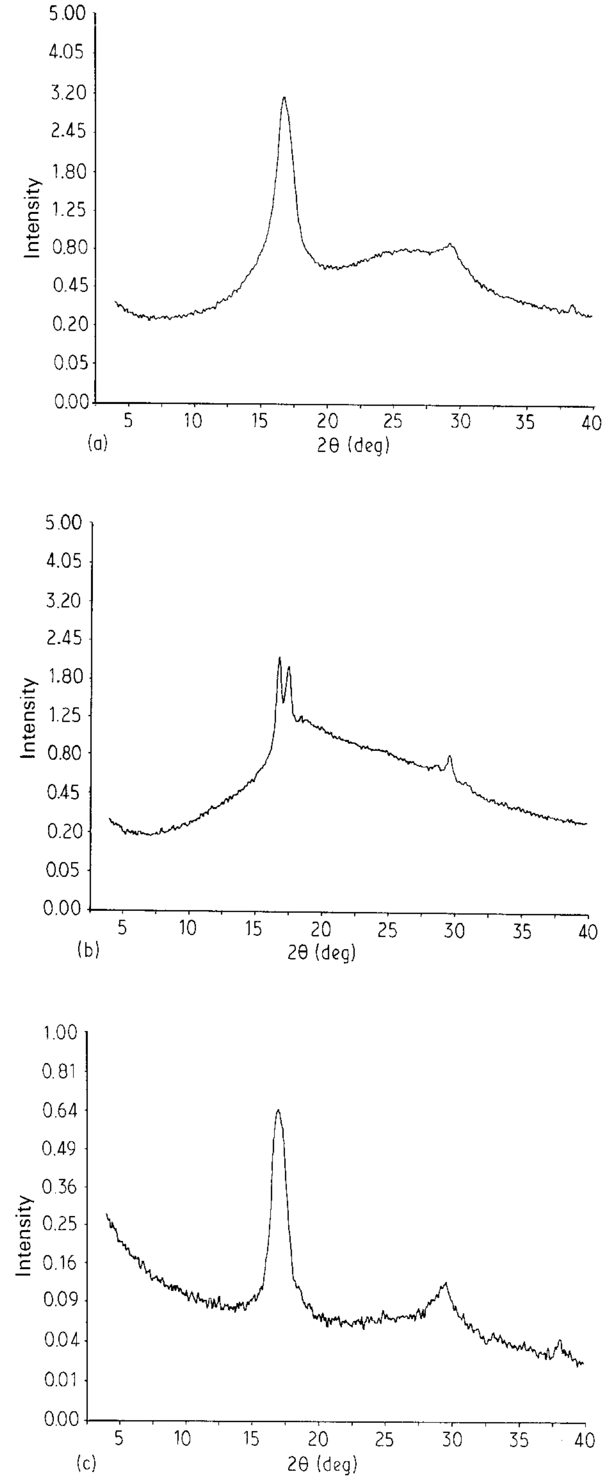


Figure 8 Wide-angle X-ray diffractograms showing diffracted intensity versus 2θ (deg). (a) Reactor powder, (b) 40:60 PAN:PC plasticized gel film, (c) equatorial scan of 40:60 uniaxially drawn film with 20% residual PC. After drawing, the trace resembles that of the reactor powder.

In addition, the moulded gel films showed additional weaker reflections [3] which were found to coincide with reflections obtained by Klement and Geil [25] in single-crystal mats grown from PC. Hence the peaks from the moulded films were indexed as $h\,k\,0$ reflections [3] according to Klement and Geil's scheme [25], which involved a rectangular cell with $a = 2.118$ nm and $b = 1.160$ nm (see Table III). This cell and one possible chain-packing scheme is

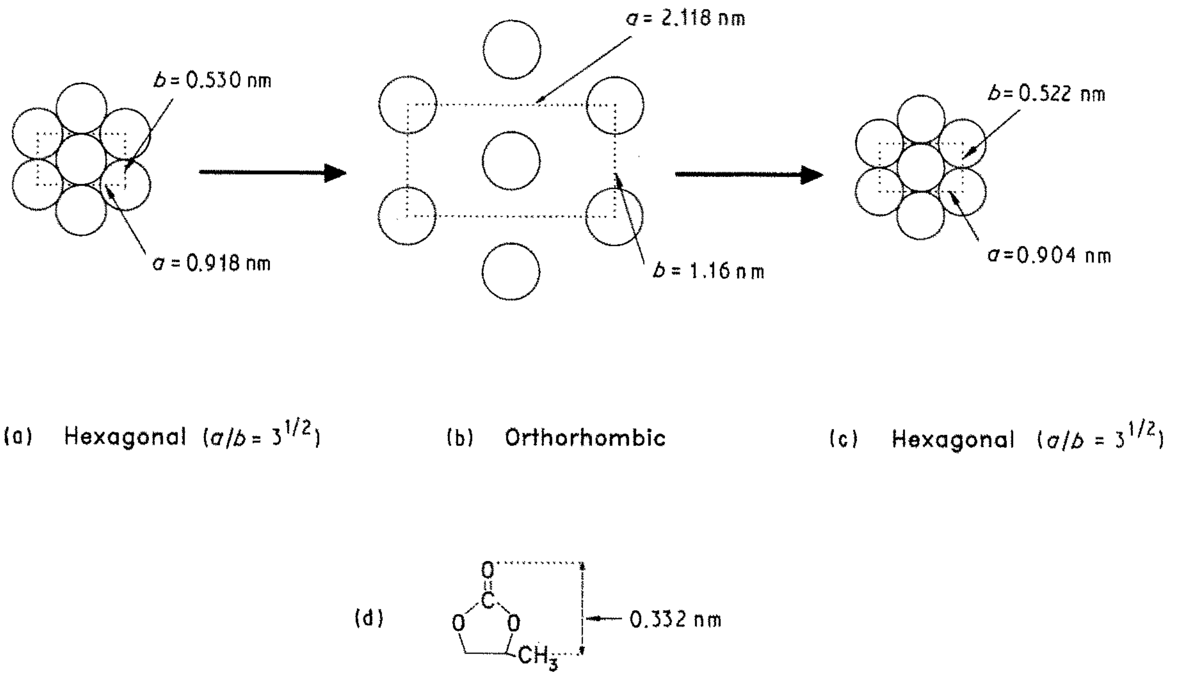


Figure 9 Model of the packing of rod-like cylinders representing PAN molecules, seen in cross-section. (a) Reactor powder with hexagonal packing of molecular rods. (b) Packing in the 40:60 PAN:PC primary gel film. The peaks from the primary film could be indexed using the large rectangular cell which is based on Klement and Geil [25]. (c) Packing in the 40:60 PAN:PC uniaxially drawn film. The packing reverts back to hexagonal, suggesting that PC is now excluded from the crystallites. (d) Size of the PC molecule. Comparison with the cell in (b) shows that the PC molecule could be conceivably fitted into the lattice by dipolar interactions with the nitrile [3].

TABLE II The d-spacings of the PAN reactor powder used in this study. The corresponding diffractogram is shown in Fig. 8a. The peaks were indexed using an hexagonal lattice and a pseudo-hexagonal cell with $a = 0.918$ nm and $b = 0.530$ nm and $a/b = 3^{1/2}$.

hkl	d_{hkl} (expt.)	d_{hkl} (calc.)	Peak intensity
010	0.530	0.530	Strong
300	0.304	0.306	Weak

TABLE III The reflections in the 40:60 PAN:PC primary film are compared with the thirteen d-spacings observed by Klement and Geil [25] in PAN single-crystal mats grown from dilute propylene carbonate solutions. The corresponding diffractogram is shown in Fig. 8b. The peaks were indexed as $hk0$ reflections using $a = 2.118$ nm and $b = 1.160$ nm [25].

hkl	Klement and Geil Single-crystal mat		PAN:PC film 40:60;
	d_{hkl} (calc.) (nm)	d_{hkl} (exp.) (nm)	d_{hkl} (exp.) (nm)
110	1.018	1.007	–
210	0.783	0.781	–
400	0.530	0.536	0.528
220	0.509	0.505	0.505
420	0.391	0.391	–
230	0.363	0.364	0.361
430	0.313	0.314	0.314
620	0.302	0.302	0.301
040	0.290	0.290	–
240	0.280	0.287	–
800	0.265	0.265	–
440	0.254	0.253	–
550	0.203	0.203	–

sketched in Fig. 9b. Owing to the unusually large size of the unit cell parameters and the size of the PC molecule (Fig. 9d), it was postulated in the previous work that PC may be incorporated in the crystallites of the PAN–PC moulded sheets [3].

Sokół and co-workers [26, 27] have conducted post-swelling studies on PAN films and powders which were exposed to polar solvents such as nitrobenzene, nitromethane and pyridine. They also found that the single peak at $2\theta = 17°$ changed to two close peaks after swelling. When the solvent was removed from the swollen film, a single peak was re-obtained. Thus, it was clear that it was the presence of the solvent in the crystallites that caused the changes in the diffraction peaks. However, they proposed that the chains adopted a more extended conformation in the crystallites when the material was swelled, and this created space for the solvent. Thus, the diameter of the rods became smaller. However, our interpretation [3] is that solvent is incorporated by lattice expansion as shown in Fig. 9b. Note, however, that the loose packing of chains shown in Fig. 9b is tentative, as it is not based on an analysis of peak intensities.

3.7.3. Uniaxially drawn 40:60 PAN:PC film

Fig. 8c shows an equatorial scan of a uniaxially drawn PAN–PC film. It can be seen that this has a resemblance to the diffractogram of the reactor powder in Fig. 8a with the double peaks at about $2\theta = 17°$ in

TABLE IV Indexing of the equatorial reflexions in Fig. 8c from unaxially drawn PAN–PC film. The film was drawn × 10 and contained about 20% PC. A hexagonal packing of the chains was assumed, with $a/b = 3^{1/2}$. A rectangular cell with $a = 0.904$ nm and $b = 0.522$ nm was used to index the reflexions.

2θ (deg)	*hkl*	*d* (exp.) (nm)	*d* (calc.) (nm)
16.96	010	0.522	0.522
29.44	300	0.303	0.301

the primary film reverting to a single peak at $2\theta = 17°$ in the drawn film. Thus, on drawing, the packing reverts from orthorhombic back to hexagonal. However, the peak positions in Fig. 8c have been shifted slightly compared with the reactor powder. Table IV lists and indexes the equatorial peaks of the drawn film with the lattice parameters derived on the basis of hexagonal packing (i.e. with a rectangular cell and $a/b = 3^{1/2}$). As a consequence of the drawing, the rods are slightly smaller in diameter than in the reactor powder which means that the chains adopt a slightly more extended conformation (the rod diameter is 0.522 nm, instead of 0.530 nm). Also the peaks from the drawn film are less broad than those from the reactor powder, indicating improved crystallinity. The overall transformation that occurs in the crystallite structure, in going from reactor powder to PC-plasticized gel film and then to the drawn film, is summarized in Fig. 9.

A diffraction pattern of the drawn film obtained by a flat plate photographic technique (not shown) also confirmed that there were only two equatorial reflections. This result is in accordance with that of most investigators [20, 21, 28]. Only a few authors such as Stefani *et al.* [29, 30] and Colvin and Storr [31] have found meridional reflections in drawn PAN fibres, and hence proposed a three-dimensional orthorhombic unit cell.

Thus, our results suggest that on drawing, a fringed-fibrillar structure with hexagonal packing of the chains is obtained. In fact, further investigations on drawn films made from a number of different solvents give similar *d*-spacings as the ones shown in Table IV, so this appears to be a general result for drawn films [32].

4. Conclusion

PAN crystallizes from propylene carbonate to give single crystals, thermoreversible gels and plasticized solids, depending on the polymer concentration [1–3]. It was reported in a previous work that propylene carbonate was a good plasticizer for PAN. Here, PC plasticization was used to produce biaxially oriented PAN films. No coagulation was involved and the drawing was done in the presence of the solvent. The method of film production involved flow-induced chain extension and crystallization. The principle is not restricted to propylene carbonate and can be used with other solvents or solvent mixtures from which the polymer crystallizes.

IR dichroism results on uniaxially oriented films indicated that not only were the nitriles preferentially oriented perpendicular to the draw axis but the residual PC molecules were similarly oriented, suggesting that there was dipolar pairing between the nitriles of the PAN and the carbonyl groups of the PC molecule.

The X-ray results indicated that the reactor powder was not entirely amorphous; it showed the presence of small crystallites, with hexagonal packing [3]. Moulded primary gel films which were made by dissolving in PC and recrystallizing showed that a rearrangement of the crystallite lattice occurred. The change in the diffraction pattern observed in the moulded film compared with the reactor powder appears to be due to incorporation of PC molecules into the crystallites. On drawing the moulded film, the crystallite structure reverted back to hexagonal packing of chains, suggesting that the PC molecules were now removed from the crystallites. Only equatorial peaks were found in the diffraction pattern of the drawn films, which indicated that there was no chain-axis order.

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