Interaction of water and hydrated crystallization in water-plasticized polyacrylonitrile films

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It is known that pure water can be a solvent for polyacrylonitrile (PAN), but only at temperatures above its boiling point at atmospheric pressure. Thus, a PAN powder which had been blended with water could be compression moulded at 210°C like a thermoplastic material. The water-plasticized films were flexible and could be uniaxially drawn. X-ray diffraction studies on the dry (as-polymerized) powder and the plasticized film showed that there was a remarkable transformation in the diffraction pattern of the latter, which suggested the formation of a new hydrated polymorph. On drawing the plasticized film, the water was mostly expelled from the film and the *d*-spacings in the diffraction pattern reverted to those in the original, dry polymer. Infra-red dichroism studies led to the conclusion that the residual water molecules in the drawn film were preferentially oriented in a way which suggested hydrogen bonding to the nitriles. Raman spectroscopy showed that the nitrile vibration-band was shifted to higher frequency in the water-plasticized PAN compared with the dry polymer, and this was also indicative of hydrogen bonding of the water to the nitriles. Chain orientation factors were computed from the dichroism of the nitrile and water vibration-bands.

(Keywords: polyacrylonitrile; water plasticization; solvated crystallites)

INTRODUCTION

Polyacrylonitrile ($-[CH_2-CH(CN)]_n-$) is soluble in polar organic solvents such as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) as well as in aqueous ionic solvents such as NaSCN(aq) and $ZnCl_2$(aq). As the polymer is not considered to be melt processable, it is often processed from solutions in the above-mentioned solvents.

Pure water is not a solvent for polyacrylonitrile (PAN) at any temperature up to its normal boiling point. However, in 1948 Coxe reported that water-impregnated PAN powder could be extruded into filaments at temperatures above the boiling point of water at atmospheric pressure[1]. There are several patents describing water-plasticized melt spinning of fibres[2–6] and extrusion of films[7]. The patent literature deals chiefly with engineering problems. For example, one difficulty is how to maintain the high pressures needed to extrude water-plasticized PAN; evaporation of water by back-venting through the feed zone of the extruder can be a problem and has to be overcome[8]. The controlled depressurization needed after extrusion, in order to draw the fibres on-line while preventing the water from flashing off abruptly and leaving porous fibres, is another technical problem that has to be surmounted[9]. However, in some cases, applications are disclosed for fibrillated 'plexifilaments' formed by deliberately letting the water flash off[10].

In the scientific literature, there is much less work reported on the plasticization of PAN by water. This is probably due to the intrinsic difficulty in making fibres and films by water-plasticized melt extrusion of PAN. The engineering problems are more daunting than in ordinary wet spinning, and hence such work appears to have been usually carried out in industrial laboratories. Frushour[11,12] has, however, described the 'melting' of PAN by water at temperatures above 185°C. When PAN powder and water were heated in a sealed, thick-walled glass tube, the PAN dissolved and formed a transparent solution at 185°C; on cooling, the solution transformed into a solid plug[12]. This would not occur if dry PAN powder were heated to similar or even higher temperatures. These visual observations are clear proof that water does dissolve PAN at these temperatures. Further, Frushour[11,12] showed that during differential scanning calorimetry (d.s.c.), water-plasticized PAN exhibited 'melting' endotherms and crystallization exotherms. In contrast, dry PAN powder does not normally manifest any evidence for melting in a d.s.c. experiment, unless exceptionally high heating rates are used[13].

Frushour's work was restricted to d.s.c. studies involving a few milligrams of polymer. In this work, we have found an easy way of making 10 × 10 cm pieces of water-plasticized PAN film without extrusion. The plasticized films were supple due to the presence of the water and so were amenable to drawing. The morphology of the plasticized films and the changes induced by uniaxial drawing were studied by X-ray diffraction, infra-red (i.r.) and Raman spectroscopy.

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EXPERIMENTAL

Materials

PAN was made by suspension polymerization of acrylonitrile using the free-radical initiator azoisobutyronitrile, yielding a white powder after washing and drying. The polymer was essentially atactic, as described in a previous paper[14]. The inherent viscosity measured in DMF at 25°C was 1.5 dl g^{-1}.

Method of blending water with PAN powder

Around 5 g of dry PAN powder were ground to a fine dust with a pestle and mortar. A 50:50 PAN/water blend was made by simply distributing 5 g of distilled water as evenly as possible over the powder from a pipette and grinding. This method has been used successfully by us in previous work for blending small volumes of liquids with large volumes of PAN powder[15]. It relies on the porous powder absorbing the liquid by capillary action.

Formation of primary films by compression moulding of powder/water mixtures

The 50:50 PAN/water blend was a moist powder. This was spread out on a piece of aluminium foil; the foil was folded back so that the powder was sandwiched. This was then weighed. Next, the folded foil with the enclosed moist powder was placed between steel plates and compressed in a hot press at 210°C. The holding pressure was 15 MPa and the moulding time was 3 min. It was important to cool the sample to room temperature under pressure so as to avoid gross blistering due to the formation of steam. After releasing the pressure, the foil containing the moulded film was reweighed in order to establish the amount of water lost. On peeling the foil, a smooth, flexible, cream-coloured film was obtained. This film was trimmed at the edges and stored in a bottle of distilled water to prevent dehydration.

Drawing of the moulded films

The moulded sample will be referred to as the primary film or the water-plasticized film. Rectangular strips of the primary film (5 cm long and 1 cm wide) were cut out with a punch. Ink marks were placed 1 cm apart to measure the draw ratio. These strips of film were drawn manually to various draw ratios over a hot bar. The temperature of the hot bar was controlled by a Eurotherm temperature controller, which monitored the temperature of the surface to an accuracy of ±1°C[16]. The draw rate was about 0.5 cm s^{-1}.

Films with draw factors of 3 ×, 4 ×, 6 ×, 8 × and 10 × were produced by drawing the primary film at 120°C. A film with a draw factor of 1.2 × was also made by carefully drawing the primary film at a lower temperature of 90°C in order to avoid sharp necking. This film was needed to determine the nature of the X-ray diffraction peaks in the primary film.

X-ray diffraction

Wide-angle X-ray diffraction was used to study and compare the type of long-range order in the PAN reactor powder, the primary film and the uniaxially drawn films.

CuKα radiation (Ni-filtered) was generated using a Philips PW 1730 generator operating at a voltage of 40 kV and a current of 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 interval $2\theta = 4$–$50°$. 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, but were also verified by visually inspecting the trace in order to check that the peaks were real.

The two-dimensional diffraction pattern of each sample was also recorded on photographic film (flat plate); the results will be shown where appropriate.

Infra-red dichroism

Dichroic infra-red (i.r.) spectra of uniaxially drawn films of various draw ratios were recorded on a Nicolet 740 *FT*i.r. spectrometer equipped with a Spectra-Tech wire-grid polarizer.

The theory of i.r. dichroism has been described elsewhere[17,18]. We shall use the standard equations for a uniaxially drawn polymer, namely

$$D = \frac{A_{\parallel}}{A_{\perp}} \tag{1}$$

$$D_0 = 2\cot^2\alpha \tag{2}$$

$$D = \frac{f\cos^2\alpha + \frac{1}{3}(1-f)}{\frac{1}{2}f\sin^2\alpha + \frac{1}{3}(1-f)} \tag{3}$$

$$f = \tfrac{3}{2}\langle\cos^2\sigma\rangle - \tfrac{1}{2} = \frac{(D-1)(D_0+2)}{(D_0-1)(D+2)} \tag{4}$$

In equation (1), D is the measured dichroic ratio and $A_{\parallel}$ and $A_{\perp}$ are the absorbances of the selected vibration using radiation which was polarized parallel and perpendicular, respectively, to the draw axis. Spectra were measured from the drawn films with the electric vector of the polarized i.r. radiation set first parallel and then perpendicular to the draw direction. From the absorbances for the two polarizer settings, D values were determined using integrated band intensities for two of the vibration bands in the spectrum. Owing to the thickness of the drawn films used in this study, it was not possible to use the unreliably high absorbance of the C≡N stretching vibration at 2244 cm^{-1}. However, previous work by one of us[19] has shown that the dichroism of the satellite band (^{13}C≡N) at 2192 cm^{-1} mimics exactly the behaviour of the main C≡N vibration. This band was therefore chosen for the dichroic ratio measurements (integrated absorbance from 2205 to 2170 cm^{-1}) and the subsequent determination of the chain-orientation factor f for each draw ratio. It was found that the water molecules remaining in the drawn film were also oriented, and hence dichroic ratios D were measured for the vibration band corresponding to the water deformation mode at 1625 cm^{-1}.

In equation (2), D_0 is the dichroic ratio of the vibration in the perfectly oriented polymer and α is the angle the transition-moment vector of the vibration makes with the polymer chain-axis. For flexible molecules, α is a conformationally averaged quantity (see Bashir *et al.*[20] for a detailed discussion of this topic). A transition moment angle of 73° was used[20] for both of the chosen vibrations (i.e. the nitrile-satellite band and the water deformation band). The choice of 73° for α will be discussed later.

If D is measured for each draw ratio and α is known, then they can be used in equations (3) and (4) to calculate the chain orientation factor *f*. The quantity *f* is related to σ, the average angle the polymer chain-axes make with the draw axis, and therefore it is a measure of chain axis orientation; its value ranges from 0 for random to 1 for perfect axial orientation. Thus, it was possible to plot an orientation factor *versus* draw ratio curve.

Raman spectroscopy

The i.r. dichroism results suggested that the water molecules could be hydrating the nitriles of the polymer. For probing this interaction in the undrawn films, Raman spectroscopy was used. The relatively thick primary film with its high water content was more amenable to the Raman method, particularly as water is a weak Raman scatterer. Raman spectra were thus acquired from the undrawn films in order to see if there was a shift in the frequency of the nitrile-stretching vibration, both before and after drying the films.

Thermogravimetric analysis showed that the as-moulded, water-plasticized film contained about 17% by weight of water. The Raman spectrum was first recorded on this film. Next, the water was removed from the film using a microwave oven. The quantity of water removed after microwave drying was established to be 16.7% by weight. The Raman spectrum was re-recorded for the dried film. Thus, any shift in the nitrile band after the removal of water could be monitored.

Satisfactory i.r. measurements were not possible from the primary film owing to its excessive thickness and the strong water absorptions which were caused by the high (17%) water content. However, by drying the starting film to 1% water content and recording the spectrum, then further drying the film to 0.2% water content and re-recording the spectrum, we were able to test for any shifts in the nitrile band in the i.r. spectrum.

RESULTS AND DISCUSSION

PAN/water fusion melts

The starting point of the work was the 'phase' diagram in *Figure 1*, disclosed originally by Porosoff in a Cyanamid patent[2]. The fields in the diagram were described[2] as follows: field 1 corresponds to a single liquid phase which is a homogeneous PAN/water solution; field 2 contains two liquid phases – a concentrated PAN/water solution and excess water; field 3 consists of a solid-like PAN/water phase; and field 4 is a two-phase composition with a solid-like PAN/water phase and excess water. For extrusion and processing operations, clearly one has to operate in field 1. Strictly speaking, *Figure 1* is not a phase diagram (though it has been referred to as such[2]), for in a binary system in which high pressures are involved this will be a three-dimensional plot depending on the three state variables temperature, composition and pressure[21]. Thus a simple, two-dimensional temperature–composition plot would be merely a section through the PAN/water phase diagram.

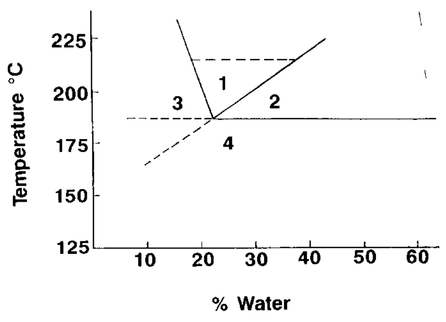


Figure 1 'Phase diagram' of the PAN/water system as reported by Porosoff[2]

The study from which *Figure 1* was derived was conducted by heating various compositions of PAN and water to different temperatures in a sealed, thick-walled glass tube but at an unspecified pressure[2]. Nevertheless, it was felt that *Figure 1* must have a resemblance to the phase behaviour and so it was used as a guide to choose the water composition and moulding temperature in this work. Although a 70:30 PAN/water blend could be moulded at 190°C, empirically it was found that better-plasticized films were formed if a 50:50 PAN/water powder blend was moulded at 210°C; hence, the latter composition was adopted for this work. Neither composition, however, seems to fit the single-phase fusion melt region (field 1) of *Figure 1*.

Production of primary films by compression moulding

The primary film was produced by compression moulding powder which had been blended with 50% water. It was indeed very surprising that 10 × 10 cm films of good quality could be made by such a simple operation. Despite the applied pressure and the aluminium foil used to enclose the moist powder during moulding, it was found that only 17% water was left in the moulded film, even though the original composition in the blended powder contained 50% water. Firstly, some of the water was lost by evaporation from the powder during the time it took to close the platens of the press. Secondly, a layer of free water was left on the surfaces of the film when the sample was cooled, and this was wiped away with paper. This behaviour corresponds to field 4 in *Figure 1*, where a two-phase composition with a solid-like PAN/water phase and excess water is formed at low temperatures[2].

The water-plasticized films were very different in appearance from films cast from PAN solutions in dimethyl sulfoxide or dimethylformamide[20]. In contrast to cast films which are generally transparent, these films were opaque and had a distinctive cream colour. The films were surprisingly smooth and flexible, and could be bent or even folded without snapping. It is clear that the water at high temperatures and pressures had 'melted' the PAN and allowed it to form a smooth film instead of a sintered sheet. The 17% water remaining in the film made it flexible, allowing it to be cut cleanly with scissors or with a guillotine. (If the moulded sheet was dried completely in an oven it became brittle, and cutting led to crazing and cracking; thus, the presence of the water has an effect on the mechanical properties.)

For the drawing experiments, rectangular strips (5 × 1 cm) were cut from the primary film with a punch. On heating and applying a tensile stress, the plasticized film-strip necked sharply and drew smoothly. As the film contracted in thickness and width during stretching, the drawing could be considered uniaxial. The maximum draw factor here was about 10 × . However, this depended on other factors such as the molecular weight. For example, using a polymer with a different molecular weight gave a maximum draw factor of 15 × .

The films lost most of the water during drawing and the residual water content in the drawn material was estimated to be about 1% by weight. However, no blistering occurred due to water removal, provided that the drawing temperature was not much higher than 120°C.

The drawn film had a beautiful glossy, 'pearlized' texture. This arose due to micro-voiding (long, needle-like pores) which caused light scattering. There appeared to be micro-tearing during drawing, but the cause was not investigated. However, despite the presence of micro-voids, the drawn films did not splinter and were surprisingly tough. In contrast, in a previous work using cast films, we found that uniaxially drawn films splintered easily[20].

X-ray diffraction and long-range order

Dry and moist PAN powder. The diffractogram in *Figure 2a* of the dry PAN powder is the conventional one frequently cited in the literature[22,23]. It contains only two peaks with spacings of 5.30 Å (1 Å = 0.1 nm) and 3.05 Å whose ratio is close to $\sqrt{3}$:1. Such a diffractogram has been interpreted as arising from a hexagonally packed assembly of rod-like polymer chains[15,24,25]. With just two peaks, there is more than one way of indexing the hexagonal lattice. One may use a pseudo-hexagonal (rectangular) cell[15] with dimensions $a = 9.18$ Å, $b = 5.30$ Å and $a/b = \sqrt{3}$; alternatively[26], it is possible to use a pseudo-hexagonal cell with $a = 10.69$ Å, $b = 6.17$ Å, and $a/b = \sqrt{3}$. The hexagonal packing using the latter cell is shown in *Figure 6a*. *Figure 2a* also indicates that an amorphous halo is present (between $2\theta = 10$ and 35°, reaching a maximum at about $2\theta = 25°$) in the case of the dry powder.

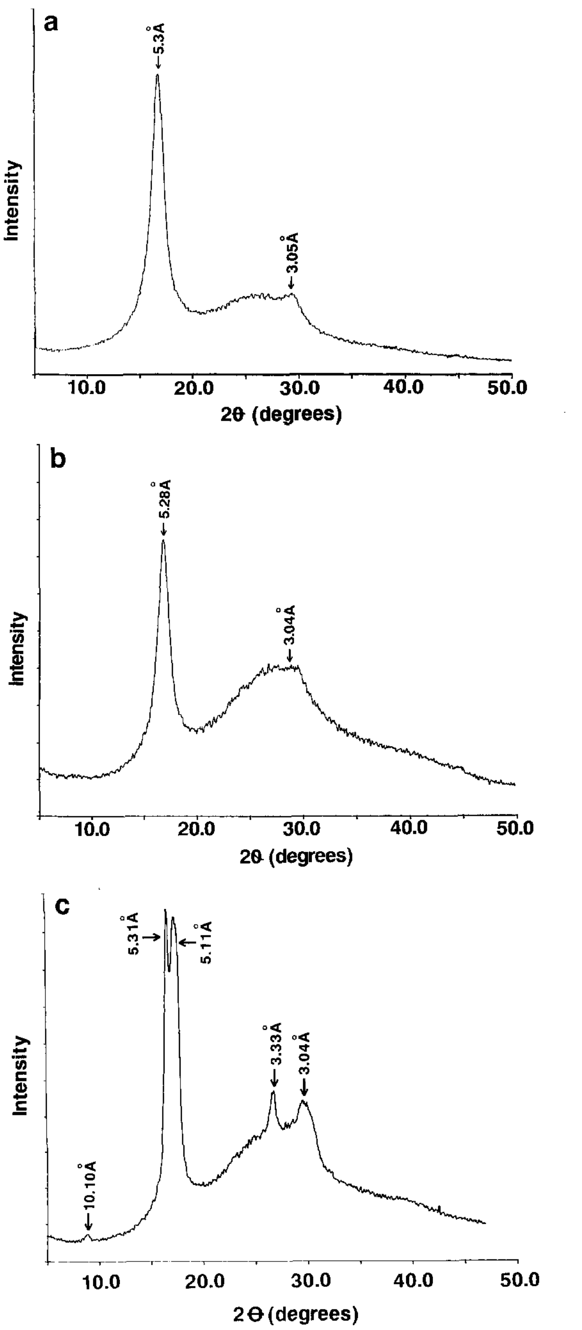


Figure 2 Wide-angle X-ray data: (a) diffractogram of dry PAN powder; (b) diffractogram of moist PAN powder, with 50% water by weight; (c) diffractogram of water-plasticized PAN film

Table 1 The d spacings obtained in the water-plasticized PAN films containing 17% water. A rectangular cell with $a = 21.18$ Å and $b = 11.60$ Å was used to index the peaks as *hk*0 reflections

hkl	d_{hkl} experimental (Å)	d_{hkl} calculated (Å)
110	10.10	10.07
400	5.31	5.30
220	5.11	5.09
610	3.33	3.37
620	3.04	3.02
040	2.90	2.90

The diffractogram of PAN powder that was blended with 50% water (but not heated) is shown in *Figure 2b*. Comparison with the dry powder diffractogram in *Figure 2a* shows that this trace is essentially the same, except that the absorbed liquid produced diffuse scattering that obscured the peak at 3.04 Å. Hence, the interaction between the water and the PAN powder at room temperature does not lead to a rearrangement of the chain packing. In previous work, it was shown that the powder produced by slurry polymerization was very porous[15], and it would appear that the 50% water was merely held in the pores of the powder by capillary action.

Clearly, PAN does not significantly swell in pure water at room temperature, and all the changes observed in the diffraction pattern (described next) only occur when the polymer is dissolved in the water at elevated temperatures and then crystallized.

Water-plasticized PAN films. Figure 2c shows that there is a remarkable transformation when the water-filled PAN powder is compression moulded. While there are many diffractograms of the type displayed in *Figure 2a*[22,23,42,43], we have never seen a diffractogram such as that in *Figure 2c* shown in the literature.

Table 1 lists all the peaks found in the water-plasticized film. Note that a 2.90 Å peak is also listed because it occurs as a shoulder to the peak at 3.04 Å; this is not evident in *Figure 2c* but it was better resolved in films where the water content was reduced slightly by drying. Compared with the polymer powder, there were two close d-spacings near $2\theta = 17°$, instead of the single peak found in the powder; in fact, the weaker peak of the doublet showed a shoulder, so there may well be three close peaks. Of particular interest is a weak peak at 10.1 Å, which was found to be reproducible and genuine. In the literature, Frushour[11], who conducted d.s.c. studies on water-plasticized PAN, briefly noted (in passing) that

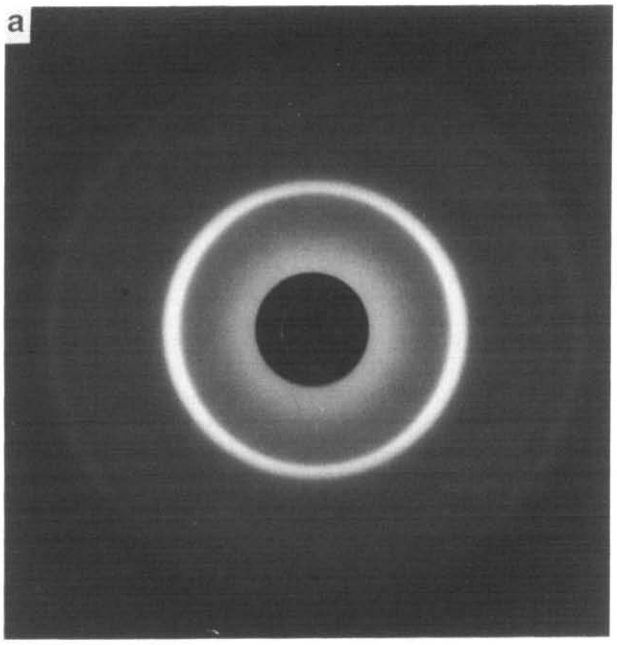
X-ray analysis of the polymer pellet that was left in the calorimeter after dissolution in water showed an unusual peak at 3.36 Å. Curiously, he did not give details of any other peaks, though he concluded that an unknown structure must have been formed[11]. *Figure 2c* shows that the peak mentioned by Frushour is probably the 3.33 Å spacing in the water-plasticized film.

The diffractogram of *Figure 2c* represents a transformation from hexagonal (*Figure 2a*) to orthorhombic packing[27]. It has to be stated that the hexagonal polymorph is most commonly observed while the orthorhombic polymorph has been reported relatively rarely. Further, the literature does not make clear what conditions lead to the orthorhombic form. In our previous work on gel films made from PAN plasticized with propylene carbonate, which is an organic solvent, a similar transformation to an orthorhombic form was observed in the diffraction pattern of the gel compared with that of the polymer powder[15]. Thus, from our experience, we tentatively link the orthorhombic form to solvent-containing gels or plasticized films of PAN.

In order to establish the nature of the peaks in the diffractogram in *Figure 2c*, the water-plasticized film was drawn 1.2 × and the diffraction pattern was recorded photographically. *Figure 3a* shows that the 5.31 Å, 5.11 Å, 3.33 Å, 3.04 Å and 2.90 Å peaks were equatorial. Owing to the great difference in intensities of the peaks, and the closeness of the 5.31 Å and 5.11 Å as well as the 3.04 Å and 2.90 Å spacings, this is difficult to show with one exposure. In *Figure 3b*, the sample to film distance was increased and this clearly shows that the 5.31 Å and the 5.11 Å spacings were equatorial peaks. However, we had trouble establishing the nature of the 10.10 Å peak because of its weakness and its closeness to the central beam. This was made worse by the fact that we did not have a vacuum tank to hold the camera, so that any weak peak with a large *d*-spacing would have been obscured by air scattering.

Nevertheless, it is reasonable to assume that the 10.10 Å peak would also be an equatorial one. Usually, only equatorial peaks are observed in PAN because the polymer is atactic and hence lacks any periodicity along the chain axis. There appear to be two cases where such large spacings have been reported for PAN in the literature. The first is in single-crystal mats grown from propylene carbonate solution by Klement and Geil[28], and the second is in single-crystal mats grown from a mixed solvent by Kumamaru *et al.*[29]. In both cases, this large spacing (10.08 Å, Klement and Geil and 10.5 Å, Kumamaru *et al.*) was an equatorial peak. A 10.10 Å equatorial peak would lead to a large cell, as both Klement and Geil and Kumamaru *et al.* found for their single-crystal mats[28,29]. Note, however, that the 3.33 Å peak listed in *Table 1* was not found by Klement and Geil or Kumamaru *et al.* in their single-crystal mats. All the peaks in *Table 1* (including the 3.33 Å spacing) could be indexed by using Klement and Geil's rectangular cell, with $a = 21.18$ Å and $b = 11.60$ Å, assuming they were all *hk*0 reflections[28].

In our previous work, we put forward the postulate that such a large cell arose in certain solvent-containing samples such as PAN gels owing to the formation of solvated crystallites[15,16]. In the present case, such a large cell should allow water to be incorporated in the lattice by bonding with the nitriles. However, a sufficient number of reflections were not present in *Figure 2c* to allow a more definitive picture of the arrangement of the polymer chains and the water molecules in the proposed cell to be deduced. The model of chain packing shown in *Figure 6b* is thus tentative, and is not based on any intensity calculations. More direct evidence for water molecules being bound to the chains comes from the i.r. dichroism experiments, discussed later.



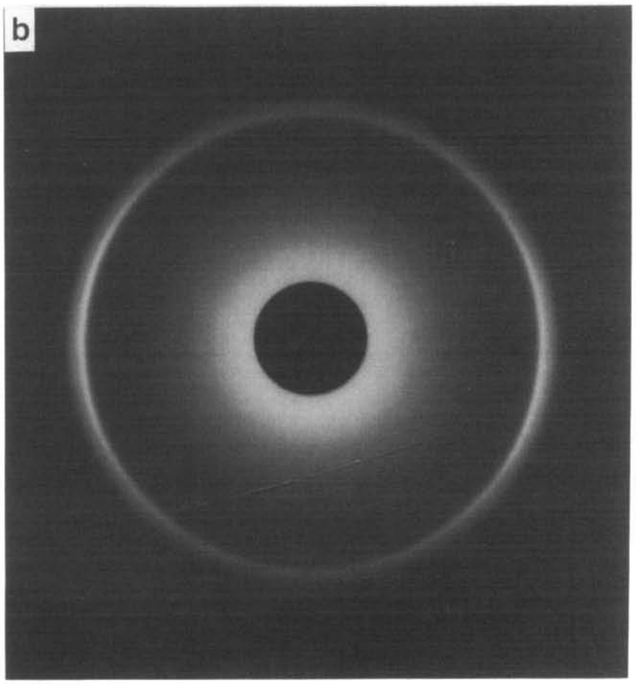


Figure 3 (a) The diffraction pattern of slightly drawn plasticized film (draw axis vertical). (b) The diffraction pattern of the slightly drawn film (draw axis vertical) with the sample to film distance adjusted to show clearly the two close, intense spacings. The 5.31 Å and 5.11 Å peaks shown in this photo are equatorial

It seems that the hexagonal to orthorhombic transition is directly associated with the presence of water. This was confirmed when a water-plasticized film (originally containing 17% water) was dried out over a period of a year and its X-ray diffraction pattern was recorded. It was found that the dried film, which had become very brittle by then, showed a diffractogram which was identical to that of the dry powder (*Figure 2a*); that is, on drying, there was a reverse orthorhombic to hexagonal transition.

The possibility of solvated crystallites was first postulated by us in studies on the gelation of PAN/propylene carbonate solutions[15,16]. The observations reported here with water lead to the conclusion that the formation of solvated crystallites may be a more general phenomenon with this polymer.

Uniaxially drawn PAN/water films. As mentioned before, very slight drawing led to the 5.31 Å, 5.11 Å, 3.33 Å, 3.04 Å and 2.90 Å peaks concentrating on the equator of the diffraction pattern. Remarkably, the equatorial diffractogram of the 10 × drawn film in *Figure 4* shows that after drawing to higher draw ratios (3 × or higher) the diffraction pattern only contains two equatorial peaks. For the 10 × drawn film, the spacings were 5.22 Å and 3.02 Å. The diffraction pattern of a 6 × drawn film is shown in *Figure 5*. This clearly demonstrates the presence of two equatorial arcs with similar spacings to those shown in the diffractogram in *Figure 4*.

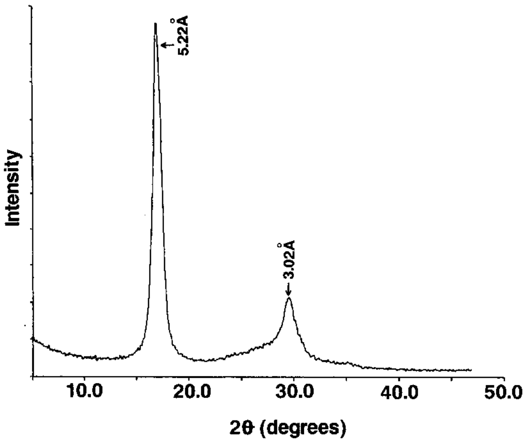


Figure 4 Equatorial diffractogram of a 10 × drawn PAN/water film

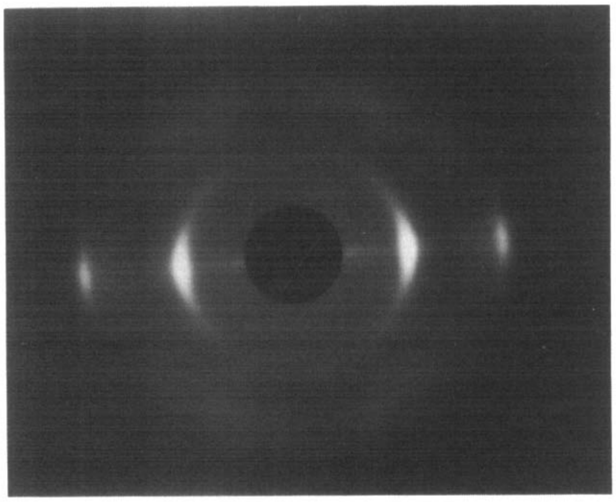


Figure 5 Fibre diffraction pattern of a 6 × drawn film (draw axis vertical). There were only two equatorial reflections; there is also an amorphous ring and diffuse scattering in the quadrants

Figure 5 shows that some non-equatorial scattering was also present in the 6 × drawn film, but, as noted by Bohn *et al.*[25], it was too diffuse to be regarded as a diffraction peak.

Figure 5 is in fact the standard diffraction pattern of the hexagonal polymorph[25,30,31]. Compared with *Figure 2a*, which is the diffractogram from the hexagonal polymorph in PAN powder, both *d* spacings (5.22 Å and 3.02 Å) have decreased, but they still remain in the ratio $\sqrt{3}$:1. The peaks in the highly oriented film can thus be indexed on the basis of hexagonal packing[24]. Again, with just two peaks, more than one indexing scheme is possible[26]. One could use a rectangular cell[15] with $a = 9.02$ Å, $b = 5.21$ Å and $a/b = \sqrt{3}$, or alternatively[26] it is possible to use a rectangular cell with $a = 10.42$ Å, $b = 6.02$ Å and $a/b = \sqrt{3}$. The latter was adopted in *Figure 6c* and it corresponds to the hexagonal packing of 'molecular rods' with a diameter of 6.02 Å. Note that in the drawn films, the cell of the hexagonal polymorph is slightly smaller in dimensions compared with the unoriented PAN powder, whichever of the two alternatives is used for indexing.

These results can be interpreted as follows. On drawing very slightly, the solvated orthorhombic polymorph becomes oriented, but further drawing leads to the water being largely squeezed out and the chains repacking in a hexagonal mode. The molecular rods in the highly drawn film are slightly smaller in diameter compared with the powder, which is to be expected because drawing extends the polymer chains. Hence, the cell size for the hexagonal polymorph in the drawn film is slightly smaller than it is in the unoriented powder. Note that the amorphous scattering present in the dry powder (*Figure 2a*) is also reduced in the 10 × drawn film (*Figure 4*).

The overall changes that occur in the molecular packing during the process of going from the reactor powder to the plasticized film and then to the drawn film are shown by the schematic model in *Figure 6*. The following transformation takes place: hexagonal form (dry PAN)→hydrated orthorhombic form (plasticized PAN)→hexagonal form (highly drawn PAN). The last transformation is particularly interesting – generally, drawing leads to orientation of the crystallites, but here drawing to a high draw ratio leads to both orientation and a phase change. Drawing brings the chains closer together and this knocks the water molecules off from the nitriles. This is supported by the fact that most of the water is lost during hot drawing.

We have always found only two equatorial peaks in the diffractograms of highly drawn PAN films (as in *Figures 4* and *5*), regardless of the initial casting solvent[20] or plasticizer[16] used in producing the primary film. This is the same situation as in the diffraction patterns reported by Bohn *et al.*[25], Statton[30], Houtz[31], and Warner *et al.*[32], but it differs from the work of a few authors such as Stefani *et al.*[33] and Colvin and Storr[34]. The lack of sharp, non-equatorial reflections in *Figure 5* has been interpreted as indicating a two-dimensional type of order with a lack of periodicity in the chain axis direction[16,24–27,30,32]. The lack of *c*-axis order is to be expected because the polymer produced by free-radical polymerization is atactic and hence there is an absence of periodicity along the chain axis[14]. Stefani *et al.*[33] and Colvin and Storr[34], however, proposed a three-dimensional unit cell, but our results do not substantiate their findings.

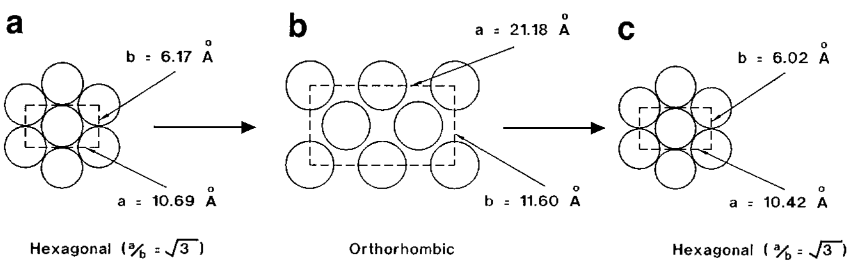


Figure 6 Schematic model of the molecular packing, showing the transformations that occur when PAN powder is blended with water and drawn: (a) hexagonal, reactor powder; (b) orthorhombic, hydrated polymorph in water-plasticized film; (c) return to the hexagonal polymorph after drawing

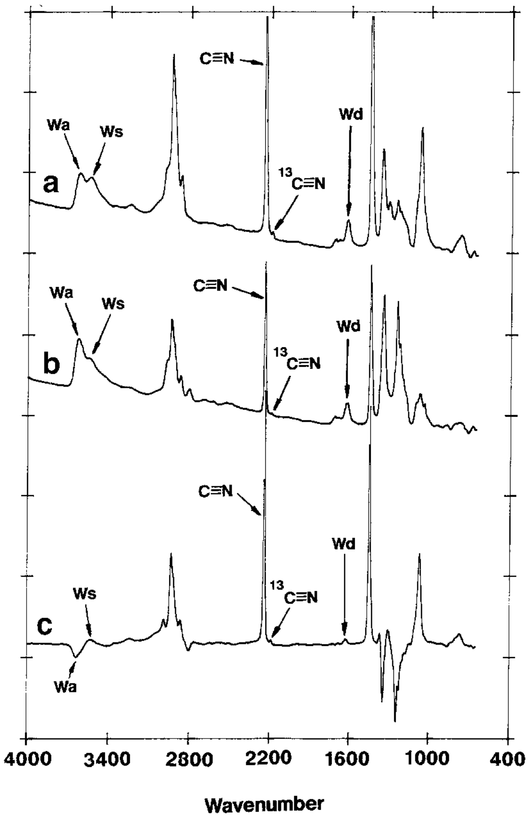


Figure 7 Polarized i.r. spectra of drawn PAN films. W_s is the symmetric stretch, W_a is the asymmetric stretch and W_d is the bond angle deformation mode of the water molecules: (a) electric field vector perpendicular to draw axis; (b) electric field vector parallel to draw axis; (c) partial dichroic spectrum (perpendicular minus parallel spectrum)

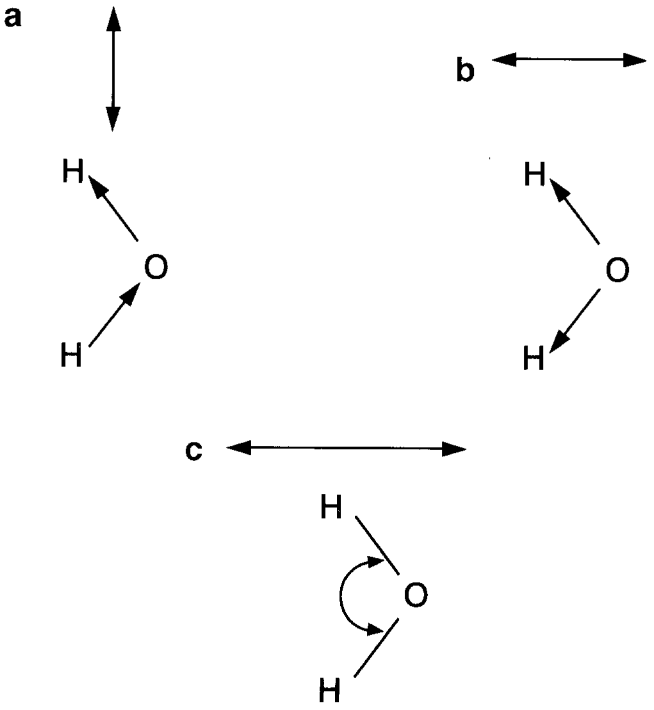


Figure 8 The modes of vibration of the water molecule and the directions of the associated transition moment vectors: (a) asymmetric stretch; (b) symmetric stretch; (c) bond angle deformation

Interactions between water molecules and nitrile groups

The dichroic i.r. spectra of the uniaxially drawn PAN/water film are displayed in *Figure 7*. The partial dichroic spectrum, which is a plot of $A_{\perp} - A_{\parallel}$ *versus* wavenumber, gives a graphic, qualitative illustration of orientation effects and is also displayed in *Figure 7*.

Frushour has mentioned that prolonged exposure to water at high temperatures can lead to the conversion of PAN to water-soluble polyacrylamide[12]. However, the i.r. spectra show that this has not occurred in the timescale of the moulding operation.

The dichroism in the PAN absorptions was as anticipated, with the characteristic $^{13}C{\equiv}N$ stretching vibration at 2192 cm^{-1} showing perpendicular dichroism. Most interestingly, the orientation of residual water in the film could also be discerned. The directions of dichroism of the characteristic water bands at 3632, 3545 and 1625 cm^{-1}, corresponding to asymmetric H–O–H stretch (parallel), symmetric H–O–H stretch (perpendicular) and H–O–H deformation (perpendicular), respectively, can be found by inspecting the spectra in *Figure 7*. Based on the transition-moment directions of these vibrations (*Figure 8*), this dichroic behaviour allows the preferred orientation of the water molecules with respect to the draw direction to be deduced. As a mechanical drawing cannot permanently orient water molecules, one has to assume that they are attached at some points to the polymer chain.

Four conceivable interactions between the water molecules and the chain are depicted in *Figure 9*. *Figure 9a* shows a hydrogen-bonding interaction between the oxygen of the water and the methine proton of the polymer chain; *Figures 9b* and *9c* involve hydrogen bonding of the water with the nitrile nitrogen; and *Figure 9d* involves an anti-parallel interaction between

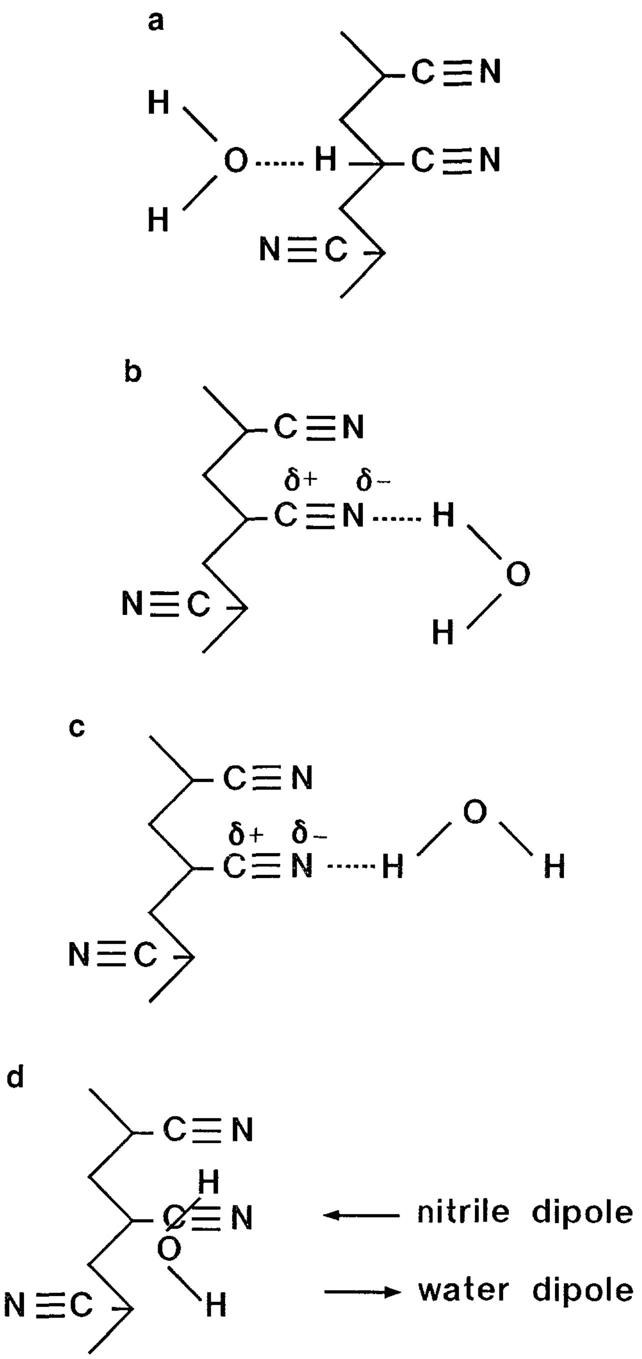


Figure 9 (a) Orientation of the water molecule with respect to the draw axis (vertical), allowing hydrogen bonding to the methine proton of the polymer. (b) Orientation of the water molecule with respect to the draw axis, indicating the possibility of hydrogen bonding to the nitrile. The water molecule can be rotated about the hydrogen bond axis, giving a distribution of orientations which would all be consistent with the dichroic behaviour seen in *Figure 7*. (c) Another orientation of the water molecule involving hydrogen bonding. However, this orientation is not consistent with the observed dichroism of the water bands seen in *Figure 7*. (d) Another orientation consistent with the spectra of *Figure 7* involves dipole–dipole interaction. An ideal, anti-parallel arrangement of dipoles is shown. The arrows indicate the respective dipole moment vectors of the nitrile and water

the dipole moment of the water molecule and the nitrile dipole. Note that the hydrogen-bonding interactions generally involve the proton of A–H and the lone pair of B, where A and B are electronegative atoms such as O or N; hence, *Figures 9a* to *9c*, but not *Figure 9d*, come under this category. In *Figure 9d*, the dipole moment vector of the water is the vector sum of the two O–H bond-moment vectors, which themselves are directed along the bond axis from O to H.

The dichroism results of *Figure 7*, when taken together with the transition moment directions of the vibrations of the water molecule shown in *Figure 8*, indicate that *Figure 9c* can be excluded. However, the dichroism results by themselves cannot distinguish between the hydrogen-bonding configurations of *Figures 9a* and *9b* or the dipole–dipole interaction in *Figure 9d*. Hence, it is necessary to look at other evidence to decide between these three alternatives.

The hydrogen-bonding arrangement in *Figure 9a* will be considered first. In earlier times, it was believed that the methine proton (H–C–CN) took part in hydrogen bonding with the nitrile on an adjacent chain, and this interaction was considered as mainly responsible for the fibre-forming capacity of PAN[35]. However, this is now thought to be unlikely and the nitrile–nitrile dipole pairing is considered to be the dominant interaction[35]. Note that it has been shown that the methine proton in PAN can be abstracted by a strong base, because the resulting negative charge can be stabilized by delocalization on to the nitrile group[14]. On the other hand, the methine proton is not polarized sufficiently for hydrogen bonding because it is not directly attached to the electronegative nitrogen atom, but instead is separated from it by two carbon atoms. This is similar to the case of acetylene (H–C≡C–H), where the H atoms are acidic (compared with the H atoms in ethane, for example) owing to the delocalization of the charge resulting from proton abstraction, yet acetylene does not hydrogen bond to electron donors. In summary, we may dismiss the hydrogen-bonding interaction of the water molecule with the methine proton of PAN.

It still remains to decide between the interactions shown in *Figures 9b* and *9d*. It is generally found that in complexes between an electron acceptor and the nitrile (which acts as an electron donor through the lone pair on the nitrogen), the nitrile-stretching band shifts to higher frequency[35]. The electron acceptor may be a proton that forms a hydrogen bond or a Lewis acid such as BCl_3. Thus, the C≡N stretching frequency shifts from 2254 cm^{-1} in acetonitrile to 2261 cm^{-1} in acetonitrile/water mixtures[35]. Similarly, in complexes of acetonitrile with BCl_3[35], the nitrile band shifts to 2355 cm^{-1}. The fact that the complexed nitrile has a higher stretching frequency than the free nitrile is surprising; however, it has been shown that the C≡N bond is slightly shorter in such complexes and the force constant of the bond is actually increased[36]. Based on the data from complexes of organic nitriles, it has become customary to regard the increase in the nitrile-stretching frequency as being diagnostic of complex formation via the lone pair of the nitrogen atom, even if no single-crystal X-ray structural data are available[35]. Conversely, a shift to a lower frequency, observed in certain complexes with organic nitriles, is taken as indicating that the bonding takes place through the π orbitals of the C≡N bond[35].

Likewise, the H–O–H stretching bands near 3500–3600 cm^{-1}, which are normally very broad in pure water, shift to higher frequency, sharpen and split into well-defined, symmetrical and anti-symmetrical components in mixtures of acetonitrile and water where the level of water is low[37]. This behaviour has again been rationalized in terms of hydrogen-bonding interactions[37].

However, it has also been proposed by Attard[38] that water binds to nitriles not by hydrogen bonding but by a dipole–dipole interaction as shown in *Figure 9d*. In order to establish whether such a dipole–dipole interaction occurred in preference to a hydrogen-bonding interaction in the primary film (i.e. *Figure 9d* or *9b*), the Raman spectra of the as-moulded film and the same film after drying were acquired. In the water-plasticized film containing 17% water, the nitrile band occurred at 2242.8 cm^{-1}. After drying the film, the nitrile band had shifted to 2240.9 cm^{-1}. This is shown in *Figure 10*. Thus, in the water-plasticized film, where we believe a proportion of the water is interacting with the nitriles, the nitrile band occurs at a higher frequency, which, as in the case of organic nitriles, suggests hydrogen bonding as in *Figure 9b*.

A similar shift of the nitrile band to higher frequency was observed in the i.r. spectra when a plasticized film with 1.0% water and a dried film with 0.2% water were used. Further, in the i.r. spectra, it was found that there was a small but measurable increase in the extinction coefficient of the nitrile band in the wet film. This again is consistent with the configuration in *Figure 9b* rather than *Figure 9d* because in the former arrangement, the dipole-moment vectors of the nitrile and the water would add and reinforce, while in the latter the vectors would cancel or reduce in magnitude.

Goodman and Suwyn[39] described a shift of the nitrile band to higher frequency as PAN/water mixtures were heated. However, they reported that there was no shift at temperatures below about 140°C, but above this temperature the nitrile band at 2234 cm^{-1} started to reduce in intensity, and finally disappeared at 225°C; concurrently, at 140°C a new band started to appear at 2250 cm^{-1} and reached a maximum at 225°C – that is, there was a high-frequency shift of 16 cm^{-1}. Such a large shift was observed because at high temperatures, where water dissolves PAN, most of the nitriles are hydrated. However, Goodman and Suwyn[39] did not report on whether there was a shift in the nitrile band when the PAN/water composition was cooled to room temperature after fusion. The context of their work was different, being a patent, where it was used as a diagnostic tool to determine the extent of nitrile hydration.

In our case, a 2 cm^{-1} shift of the nitrile band to higher frequency in the Raman spectrum of the water-plasticized film was observed, but this occurred at room temperature. This is consistent with some of the water co-crystallizing with the PAN when it was cooled from a PAN/water solution under pressure; the magnitude of the shift was smaller than that reported by Goodman and Suwyn because only a fraction of the 17% water is actually involved in the crystal hydrates. Much of the water is 'free' and is not involved in the hydration at room temperature, as it resides in small pores of various sizes (see also Price and Bashir[40]).

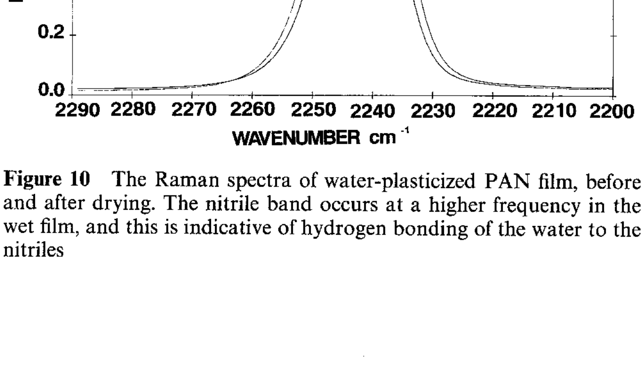


Figure 10 The Raman spectra of water-plasticized PAN film, before and after drying. The nitrile band occurs at a higher frequency in the wet film, and this is indicative of hydrogen bonding of the water to the nitriles

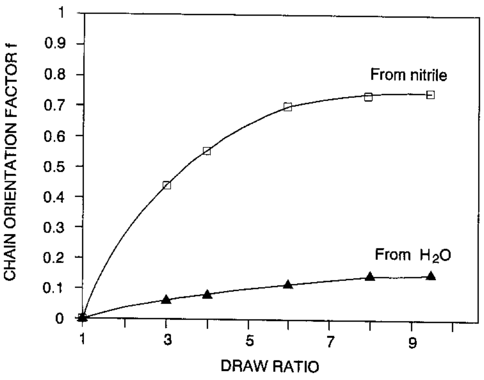


Figure 11 Chain orientation factors, calculated from the dichroism of the nitrile vibration band and the vibration band from the bond angle deformation mode of the water molecules bound to the nitriles, as a function of draw ratio. A common transition-moment angle of 73° was used for both vibrations

Finally, we must comment on the H–O–H stretching bands (in the vicinity of 3600 cm^{-1} in *Figure 7*) of the water in the plasticized film. As in the acetonitrile/water mixtures mentioned earlier, we observe that these bands are shifted to higher frequency, sharpened and split into symmetrical and anti-symmetrical components (*Figure 7*), in contrast to the relatively broad and featureless O–H bands in bulk water[37]. This effect is also found in other polymers that absorb a small amount of water, such as polyesters. Our primary evidence for hydrogen bonding to the nitriles is, however, the shift in the nitrile band, rather than the shift in the H–O–H stretching bands.

Chain orientation factors measured from i.r. dichroism

Figure 11 shows the chain orientation factor, measured from the dichroic behaviour of the nitrile band, as a function of the draw ratio. It can be seen that the chain orientation rapidly increases at low draw ratios initially and then begins to level off. This is reminiscent of the orientation behaviour of crystallites during the solid-state drawing of semi-crystalline polymers such as polyethylene, where high crystal orientation is achieved at low draw ratios[41].

The orientation factors computed from the dichroism of the bond angle deformation band of the water remaining in the film after drawing turned out to be different from those based on the nitrile dichroism. This computation was based on the assumption that the transition-moment angle for this vibration was also 73° (i.e. the same as that of the nitriles). From the i.r. dichroism and the Raman results, we have deduced that the configuration of the water molecules was as shown in *Figure 9b*. With this disposition, the transition-moment vector of the bond-angle-deformation mode (*Figure 8*) may be assumed, as a first approximation, to be parallel to the axis of the nitrile-stretching vibration. As a transition-moment angle of 73° for the nitrile-stretching vibration was employed (see ref. 20 for a detailed discussion of this choice), the same value was adopted for the deformation mode of the water.

Based on the assumption that the water is attached in such a way that it can be regarded as being part of the chain, the orientation factor computed from the water vibration in *Figure 11* can be regarded as a chain orientation factor. It also follows the same pattern as the chain orientation factor curve from the nitrile band; that is, the orientation factor increases monotonically, with an initially rapid rise which tends to level off at higher draw ratios. However, if the transition-moment angle is the same for both vibrations, then one should obtain the same values for the dichroic ratios and the chain orientation factors as those obtained from the nitrile band. *Figure 11* shows that this is not the case. This probably arises from the fact that the angular distribution function of the water is broader than for the nitriles (i.e. the water is less ordered than the nitriles). Thus, a true measure of the chain orientation can only be obtained from the nitrile band.

CONCLUSIONS

Uniaxially oriented PAN films were made by drawing compression-moulded, water-plasticized sheets. The moulded sheets were prepared by blending the reactor powder with 50% by weight of water and moulding under pressure at 210°C.

X-ray diffraction studies showed the following changes in the long-range order in the reactor powder, the water-plasticized, moulded sheets and the drawn films made from the moulded sheets:

1. The diffractogram of the reactor powder was characteristic of the hexagonal polymorph, often cited in the literature.
2. On moulding the water-blended PAN powder, the lattice expands with a transformation from hexagonal to a new, orthorhombic form. It is suggested that the water molecules are incorporated in the lattice.
3. On drawing the water-plasticized PAN films, the water is expelled (as evidenced by weight loss) and the chain packing reverts from orthorhombic back to hexagonal. There was no evidence for *c*-axis order and it is concluded that the PAN crystallite has only a two-dimensional kind of order.

I.r. spectroscopic studies showed not only dichroism in the nitrile band but also in the vibrations associated with the water molecule. The latter indicated that the water molecules had a preferential orientation. Furthermore, a shift to higher frequency of the nitrile band was detected in the Raman spectrum of the water-plasticized film and this supported hydrogen bonding of the water to the nitriles. Chain-axis orientation factors computed from the nitrile vibration indicated that the orientation increased very rapidly up to a draw factor of about 6 × and thereafter tended to a plateau value.

Since this work was performed, we have conducted d.s.c. studies on the freezing behaviour of the water in the plasticized film. Surprisingly, two distinct freezing peaks were observed during the formation of ice. This result shed further light on the morphology of water-plasticized films made by compression moulding. The results are disclosed in a further publication[40].

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