Thermoreversible gelation and plasticization of polyacrylonitrile

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(Received 18 September 1991; accepted 13 January 1992)

The behaviour of highly concentrated polyacrylonitrile–propylene carbonate (PAN–PC) solutions with up to 70% polymer is reported. The PAN powder obtained from the slurry polymerization method was very porous and hence it was able to hold a large volume of liquid PC at room temperature, while remaining a free-flowing powder. On compression moulding the PC-blended powder, the PAN 'melted' like a thermoplastic and a moulded sheet was formed on cooling. X-ray diffraction showed that the plasticized sheets contained crystallites of PAN. There was a change in the crystallite structure in the PAN–PC moulded sheets compared with the reactor powder, and it is postulated that PC is incorporated in the crystallite lattice of the former. This would be an interesting case of polymer crystallization.

(Keywords: polyacrylonitrile; propylene carbonate; gels; plasticized films; X-ray diffraction; paracrystallinity; unit cells)

INTRODUCTION

In 1962, Holland *et al.* reported that chain-folded single crystals of polyacrylonitrile (PAN) could be grown from dilute propylene carbonate (PC) solution[1,2]. The polymer is only soluble in PC at elevated temperatures and it crystallizes when the solution is cooled. In a recent work, the behaviour of concentrated PAN–PC solutions was studied[3]. It was reported that 20% solutions formed gels on cooling[3].

The 20% PAN–PC gels were thermoreversible[3] and showed genuine first-order 'melting' (dissolution) endotherms and crystallization exotherms during calorimetry. This in itself was interesting, as pure PAN powder does not show any signs of fusion and it is stated in the literature that the polymer undergoes degradation reactions before the melting point is reached[4]. The presence of crystallites in these gels was confirmed by X-ray diffraction[3].

The previous work[3] was restricted to 20% polymer concentration, as it was difficult to add the polymer powder to the liquid PC and form a homogeneous, bubble-free solution at higher concentrations. However, a method was found subsequently for exploring solutions with polymer contents greater than 20%, and in this paper, PAN concentrations up to 70% are explored.

EXPERIMENTAL

Polymer and solvent

The polymer used was produced by free-radical polymerization of acrylonitrile. A slurry-type polymerization procedure was used, the details of which have been described previously[5]. The polymer was obtained as a dry white powder after washing and drying. The inherent viscosity measured in dimethylformamide at 25°C was 1.5 $\mathrm{dl\,g^{-1}}$. ^{13}C n.m.r. showed that the polymer was atactic with the following triad abundance: $(mm)=0.28$, $(rr)=0.22$ and $(mr)=(rm)=0.50$. The propylene carbonate used was obtained from Aldrich. The densities of crystalline PAN and PC are both 1.18 $\mathrm{g\,cm^{-3}}$.

Method of forming concentrated solutions

In the previous work, 20% wt/wt solutions were made by dissolving 2 g PAN powder in 8 g of PC with heating and stirring[3]. In order to make solutions with higher PAN concentrations, this method was unsuitable and a different approach had to be adopted. For example, to make a 30:70 PAN:PC solution, 3 g of dried PAN powder was ground to a fine dust in a mortar with a pestle, and then 7 g of PC was gradually dripped onto it; the liquid was subsequently mixed into the powder by mechanical grinding. This produced a dough-like material. Similarly, 40:60, 50:50, 60:40 and 70:30 PAN:PC blends were made; these were free-flowing powders. The PC-blended PAN could now be compression moulded to 'melt' (i.e. dissolve) the polymer. Heating under pressure gave a transparent solution without bubbles and cooling this gave a moulded sheet (i.e. thick film).

The PC-blended PAN powders were placed between aluminium foils and moulded at 190°C for 5 min; they were removed hot from the press at 190°C, so that they were still 'molten', and transferred to a metal box with a lid. The metal box was placed for 24 h in an oven preset at 75°C, in order to improve the crystallinity of the samples by annealing. The annealing temperature used was above the glass transition temperature of the various blends. When the samples were removed from the box and the metal foil was peeled off, a translucent film was obtained. The metal-foil wrapping and the closed box reduced PC evaporation during the annealing experiment.

Morphology of reactor powder PAN

To investigate the reason for the absorption of large amounts of PC by the PAN powder, the morphology of

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0032-3861/92/204304-10

the powder obtained from the reactor after slurry polymerization was studied by a Hitachi Field Emission Electron Microscope.

Wide-angle X-ray patterns from the moulded sheets

Wide-angle X-ray diffractograms were recorded at 20°C on the moulded and annealed sheets. For comparison, a diffractometer trace was obtained from the PAN reactor powder as well. Nickel-filtered Cu Ka radiation 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 $2\theta = 4°$ to $40°$. 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.

The average crystallite size (L_c) was determined from the broadening of the two main diffraction peaks centred around $2\theta \sim 17°$. The breadth at half height B was measured in radians and this was substituted into the Scherrer equation (equation (1)), which gives the crystallite size[6]:

$$L_c = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where K, the instrumental broadening factor, was determined and assigned a value of 1 by using silicon as a standard; θ is the Bragg angle, and $\lambda = 1.54$ Å is the wavelength of the X-rays.

RESULTS AND DISCUSSION

Single crystals precipitate from dilute (up to about 1% PAN–PC) solutions[1,2], but as the PAN concentration is increased above about 3% PAN, thermoreversible gels are obtained on cooling the solutions. *Figure 1* shows a 'wet gel' obtained from a 5% PAN–PC solution. From 10–20% PAN–PC solutions, firm 'dry gels' are obtained[3]. These can be cut neatly with a knife and some of their properties have been described previously[3]. The properties of PAN–PC compositions with greater than 20% PAN will be discussed.

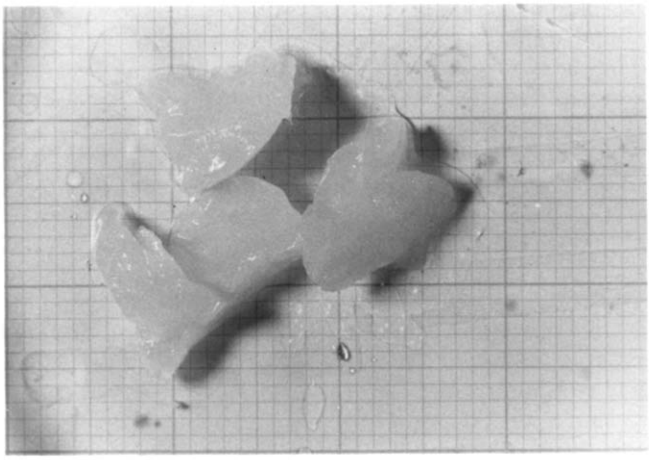

Figure 1 Glass tray containing the gel formed on cooling a 5% PAN–PC solution. The gel is thermoreversible and the presence of liquid is evident

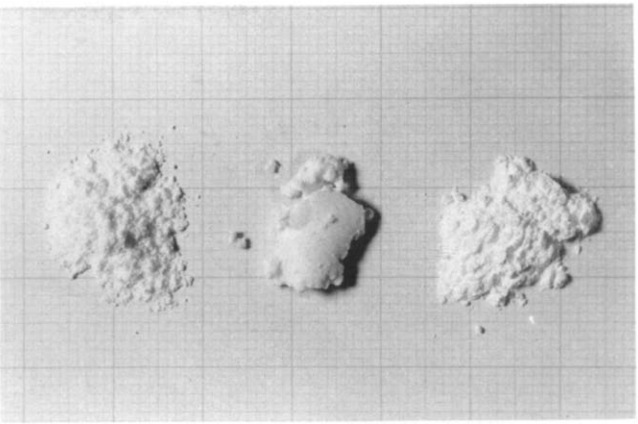

Figure 2 Left: dry PAN reactor powder. Centre: a 30:70 PAN:PC blend forms a dough-like material. Right: a 50:50 PAN:PC blend remains a remarkably free-flowing powder despite the fact that it contains 50% by weight of liquid (compare with powder on left). These have not been heated

PAN powder-morphology and the method of making high-concentration solutions

Normally, it is difficult to make very high-concentration solutions of any flexible-chain polymer. The high viscosity and elasticity of polymer solutions makes stirring difficult. Adding powder to the liquid PC to form the solution is appropriate for making solutions with up to about 20% PAN[3].

Above this concentration, apart from the difficulty in stirring, there are other problems. The powder is very porous and occupies a large volume. Adding this to a small volume of liquid and heating leads to an inhomogeneous, partially dissolved mass, which cannot be stirred and is full of air bubbles that are impossible to dislodge. The high viscosity of the medium after partial dissolution means that the bubbles cannot escape. Further, in polymer–solvent systems that require heating to form the solution, prolonged exposure to heat can cause degradation.

However, the method described here for making concentrated solutions without bubbles overcomes this problem. Instead of adding the powder to the liquid, the liquid was added to the powder and mechanically ground together. Between about 65 and 70% PC, a dough-like material was formed; however, PC contents less than, but up to, 65% led to surprisingly free-flowing powders (*Figure 2*).

The explanation for this phenomenon can be understood by referring to the micrograph of the PAN reactor powder in *Figure 3*. The powder produced by slurry polymerization has a remarkable 'cauliflower' morphology. The agglomerated powder particles have fine channels and interstices between them. On adding any non-solvent liquid, the powder acts like a sponge and absorbs and stores the liquid by capillary action. In doing so, the liquid displaces the air present in these channels. PC is a non-solvent at the temperature of mixing and this allows effective storing of the PC.

The transition state from a free-flowing powder to a dough-like material occurs at about 65% wt/wt PC. Below this concentration of PC, the voids are not totally filled with liquid and this leads to a free-flowing powder (compare *Figure 2*, right with left), but above this concentration, the voids in the powder have been completely filled with the liquid. A small surplus of PC

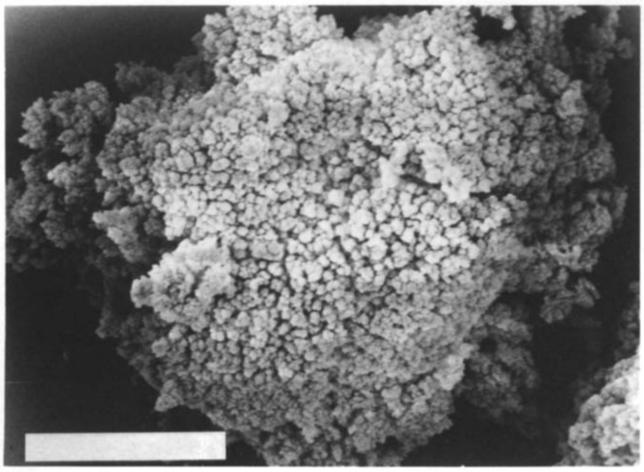

Figure 3 Micrograph showing the 'cauliflower' morphology of the PAN reactor powder particles in *Figure 2* (left). The empty volume is about 65%. It is this porous structure that allows a large volume of PC to be stored by capillary action. (White scale bar = 12.0 μm)

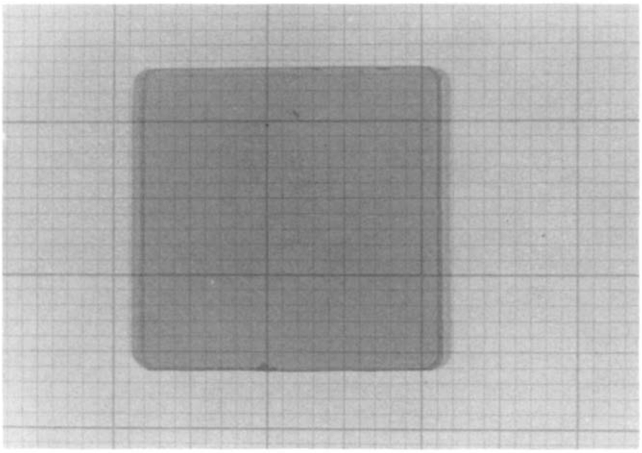

Figure 4 A 2 mm thick sheet made by compression moulding the 50:50 PAN:PC powder blend shown in *Figure 2* (right). Thus PAN–PC powder blends behave like a thermoplastic material; heating gives a plasticized 'melt' and cooling the 'melt' gives a plasticized sheet, which has the mechanical properties of a solid despite the presence of a large amount of liquid. The presence of solvent is less apparent now compared to the gel in *Figure 1*

above 65% leads to the binding of the powder particles into a dough (*Figure 2*, centre), but a large excess of PC above 65–70% (e.g. 10:90 PAN:PC) leads to the formation of a powder–liquid slurry at room temperature. In fact, as the density of PC and (crystalline) PAN are identical (1.18 g cm^{-3}), it may be concluded that the PAN reactor powder used here had a pore volume-fraction of about 65%. There can be differences in the particle size and the pore volume fraction of the powder depending on polymerization conditions, but generally the pore volume lies in the range 60–70%.

When the PC-blended powder was compression moulded at 190°C for a short time, an apparently homogeneous 'melt' was formed, which on cooling gave a plasticized sheet (*Figure 4*). It is emphasized that the transparent fluids formed by heating were concentrated solutions and are only referred to as 'melts' or 'plasticized melts' because they appeared to have a viscosity and consistency similar to melts of conventional thermoplastics such as polyethylene and polypropylene.

The moulded sheet had the mechanical properties of a solid, despite the presence of large amounts of solvent. All the sheets were translucent owing to the crystallization of the PAN, which caused light scattering (*Figure 4*). It is important to note that, while PAN–PC compositions with up to 30–35% PAN (i.e. from the slurry up to the dough-like material) dissolved easily and spontaneously on heating, blends with more than 30–35% PAN did not 'melt' and flow unless some pressure was applied. As long as some pressure was applied to the PC-blended powder, no stirring in the liquid state was needed to achieve an apparently homogeneous solution; this was because of the small powder particle size, which meant that the surface area to volume ratio was high. Moderate pressures were sufficient to fuse the solvent-soaked powder particles together.

Though only solutions spanning the range 30:70 to 70:30 PAN:PC were studied, in principle, it was possible to mould compositions with even higher PAN concentrations (for example, 80:20 PAN:PC), but it became difficult to distribute small volumes of PC evenly. This led to films with a patchy appearance, which was caused by unmelted powder particles that had not been exposed to PC.

Crystalline morphology of PAN powder and PAN–PC moulded sheets

The morphology and crystallinity of the reactor powder and the plasticized moulded films were studied by wide-angle X-ray diffraction. *Figure 5a* shows the X-ray diffractogram of the PAN powder, while *Figures 5b–f* show the traces from the PAN–PC films.

PAN reactor powder. The reactor powder (*Figure 5a*) produced by free-radical polymerization showed a broad peak centred around $2\theta = 16.7°$ and a weaker peak at $2\theta = 29.34°$. These correspond to d-spacings of 5.30 and 3.04 Å respectively (*Table 1*).

Various investigators have found different diffraction peaks in different types of PAN (for example, reactor powder, single crystals and oriented fibres) and the indexing of the reflections has led to much disagreement. Some authors have used a hexagonal lattice[7,8] while others have employed an orthorhombic lattice[9–14] to describe the crystal structure. Based on the fact that only equatorial reflections were found in diffraction patterns of oriented fibres and single crystals[1,12,13,15–19], most people have concluded that PAN has only two-dimensional order with no periodicity along the chain axis. This has been called a paracrystalline[12] or a 'laterally ordered'[15] type of structure. However, a few authors, notably Stefani *et al.*[11] and Colvin and Storr[14], found non-equatorial and equatorial reflections in drawn fibres and hence proposed a three-dimensional unit cell.

The PAN molecule has been described as adopting a stiff rod-like conformation due to the intramolecular repulsion of the nitrile dipoles[15,16]. Bohn *et al.*[15] and Olivé and Olivé[16] envisage these rod-like segments as being 'molecular cylinders' with a diameter of approximately 6 Å, with the nitrile groups protruding at all angles when viewed down the cylinder (chain) axis.

Here, a hexagonal packing of such cylinders[17] is assumed in the crystallites in the reactor powder. Crystals with a hexagonal lattice are often represented by one of three types of unit cell—the primitive hexagonal cell, hexagonal four-index cell or the pseudo-hexagonal cell[20].

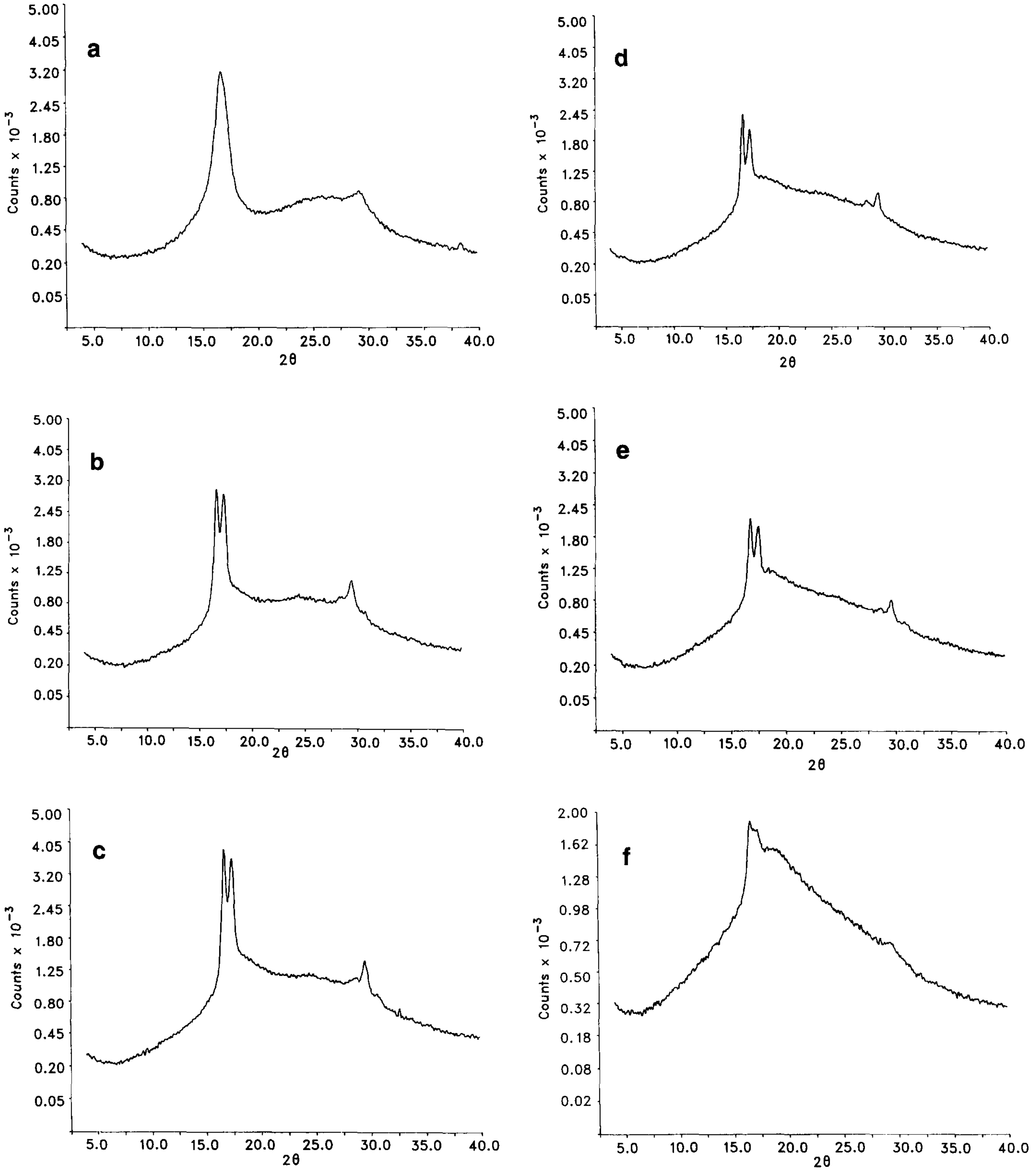

Figure 5 Wide-angle X-ray diffractometer traces showing intensity (counts) *versus* 2θ (deg): (a) PAN reactor powder. Only a singlet is observed at $2\theta \sim 17°$. A weaker peak occurs at $2\theta \sim 29°$. (b) 70:30 PAN:PC moulded film with doublet at $2\theta \sim 17°$. (c) 60:40 PAN:PC. (d) 50:50 PAN:PC. (e) 40:60 PAN:PC. (f) 30:70 PAN:PC moulded film. The doublet is still present but there is a good deal of amorphous scatter at higher angles

In this work, the hexagonal packing of the cylinders, representing rod-like segments of PAN molecules in the reactor powder, will be described by using a pseudo-hexagonal cell with rectangular axes a and b. For perfect, hexagonal packing $a/b = \sqrt{3}$. A plan view of the hexagonal packing of cylinders is shown in *Figure 6a*. The pseudo-hexagonal cell has the advantage that transformations to an orthorhombic lattice can be visualized as small deviations from a regular hexagonal lattice[20], leading to either $a/b < \sqrt{3}$ or $a/b > \sqrt{3}$.

According to this model, the reflection at $2\theta = 16.7°$ in *Figure 5a* can be assigned to $d_{010} = 5.30\,\text{Å} = b$. For regular hexagonal packing $a/b = \sqrt{3} = 1.73$, and hence $a = \sqrt{3} \times 5.3 = 9.18\,\text{Å}$ ($= d_{100}$). If these values of a and b are used, the remaining (weaker) reflections in *Figure 5a* can be indexed using equation (2) for the

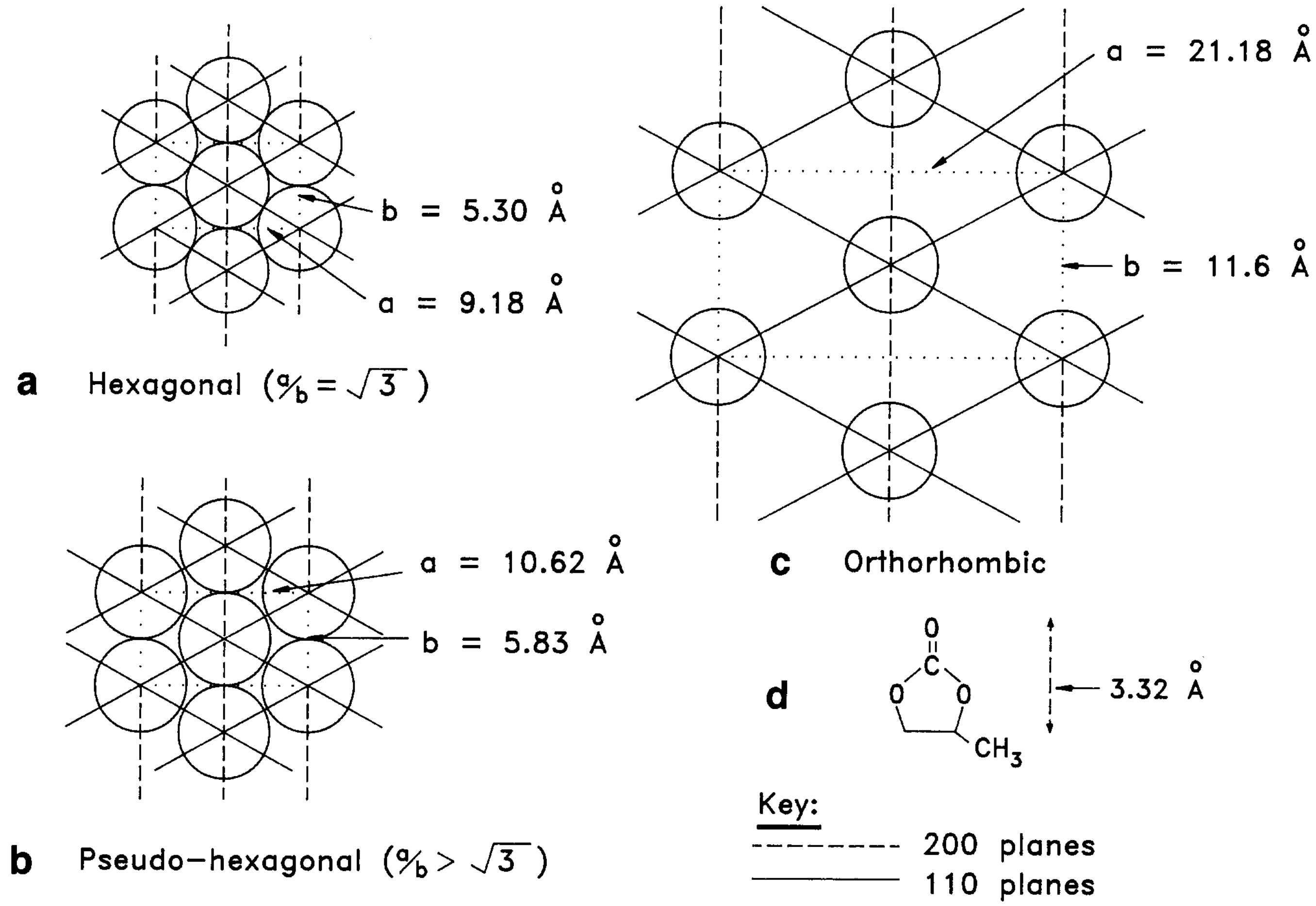

Figure 6 Schematic representation of the packing of rod-like PAN chains. The circles are cross sections of the 'molecular cylinders' representing the chains. Parts (a)–(c) are drawn to the same scale. (a) Hexagonal packing of 5.3 Å diameter cylinders with $a/b=\sqrt{3}$. The unit-cell parameters a and b were derived from the diffractogram in *Figure 5a* for the PAN reactor powder, and are indicated. (b) Pseudo-hexagonal (orthorhombic) packing of 5.83 Å diameter cylinders with $a/b>\sqrt{3}$. The values of a and b were computed for the moulded sheets from the diffractograms in *Figures 5b–f*, using Holland *et al.*'s[1] indexing system. This is a slight distortion of the regular hexagonal packing in (a). However, not all the peaks from the PAN–PC moulded films could be indexed on Holland's system. (c) Base-centred orthorhombic unit cell with the cell parameters of Klement and Geil[13]. It is assumed that the molecular cylinders are still no more than 6 Å in diameter. All the peaks from the PAN–PC moulded films could be indexed with this cell. (d) The PC molecule (not to the same scale). The dimension indicated refers to the distance between the carbonyl oxygen and the C–C bond in the ring. It is postulated that the size of the unit cell in (c) allows the PC molecule to be incorporated into the lattice

interplanar spacings in an orthorhombic or pseudo-hexagonal lattice[21]:

$$d_{hkl}=\left(\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right)^{-1/2} \qquad (2)$$

The experimentally measured and calculated d-spacings, as well as the indexing of all the peaks from the reactor powder, are collected together in *Table 1*. It can be seen that there is good agreement between calculated and experimental d-spacings based on a lattice with hexagonal packing of chains (with no c axis order). *Figure 6a* shows a schematic diagram of a hexagonal arrangement of 5.30 Å diameter cylinders in a lattice with the unit-cell parameters $a=9.18$ Å and $b=5.30$ Å derived from the diffractogram in *Figure 5a*.

The crystallite size estimated from the width at half height of the peak at $2\theta=16.7°$ (using equation (1)) gives a value of 73 Å. This corresponds to a lateral stacking of about 12 chains. Thus, the powder formed during slurry polymerization, though not amorphous, showed very short-range order. Owing to the very small crystallite size, the distinction between crystalline and amorphous regions is not as sharply delineated as in a semicrystalline polymer such as polyethylene.

Table 1 The d-spacings of the PAN reactor powder used in this study. The corresponding diffractogram is shown in *Figure 5a*. The peaks were indexed using a hexagonal lattice and a pseudo-hexagonal cell with $a=9.18$ Å and $b=5.30$ Å and $a/b=\sqrt{3}$. *Figure 6a* shows the packing of 5.3 Å diameter cylinders in hexagonal packing

	d_{hkl} (Å)		
hkl	Expt.	Calc.	Peak intensity
010	5.30	5.30	Strong
210	3.48	3.45	Very weak
300	3.04	3.06	Weak
220	2.34	2.29	Very weak

Here, we have used a two-phase model consisting of interlinked paracrystalline and amorphous regions to describe the reactor powder. An alternative view is that of Bohn *et al.*, who have described PAN as being a single-phase, 'laterally ordered' material with defects, which is in contrast to the conventional two-phase model for a semicrystalline polymer[15]. As the crystallite sizes in the reactor powder were extremely small, Bohn *et al.*'s view could also be a valid alternative model.

Table 2 The *d*-spacings from *Figures 5b–e* of the PAN–PC moulded films. In the far right-hand column, the peak indices based on Klement and Geil (*Table 3*) are included. The question marks indicate uncertainty about whether the peak is real

2θ (deg)	*d*-spacing (Å) of PAN:PC 70:30	60:40	50:50	40:60	$hk0$
16.71	5.31	5.30	5.31	5.28	4 0 0
17.33	5.11	5.09	5.09	5.09	2 2 0
24.36	3.64?	3.63?	3.67?	3.61?	2 3 0
28.40	3.14	3.14	3.14	3.14	4 3 0
29.44	3.03	3.03	3.02	3.01	6 2 0

PAN–PC moulded films. Figures 5b–e show the diffractograms from the 70:30, 60:40, 50:50 and 40:60 PAN:PC moulded sheets, all of which have similarities. There were four, possibly five, peaks in the moulded sheets, and these are listed in *Table 2* for convenient reference in the ensuing discussion. The most prominent feature of the moulded sheets compared to the reactor powder is a doublet at $2\theta = 17°$ (compare *Figure 5a* with *Figures 5b–f*). It is uncertain whether the peak at $2\theta = 24.6°$ corresponding to 3.61 Å is genuine and hence it has been listed with a question mark.

The 30:70 PAN:PC sheet showed a different trace and this is shown in *Figure 5f*. Though this also showed an underlying doublet at $2\theta \sim 17°$, there was substantial diffuse scattering at higher angles due to the large amount of solvent present. The 30:70 PAN:PC sheet will be discussed separately in the following subsection.

Normally, a singlet at $2\theta \sim 17°$ is observed not only in reactor powders (as in *Figure 5a*) but also in oriented fibres made from homopolymers and copolymers of PAN[14,15,18,19]. A doublet has been observed only under special conditions. X-ray diffraction work by Stefani *et al.*[11] on oriented and annealed fibres, electron diffraction studies by Holland *et al.*[1] on single crystals grown from propylene carbonate, X-ray diffraction studies by Klement and Geil[13] on single-crystal mats and X-ray diffraction studies by Sokół *et al.*[22–24] on PAN swollen with various polar liquids, have all shown a doublet, indicating that in these cases the packing of the chains becomes orthorhombic[12]. Here, the reflections from the PAN–PC moulded films will be compared with the results of Stefani *et al.*, Holland *et al.* and Klement and Geil, and comments will also be made on the swelling studies of Sokół *et al.*

The first six of Stefani's peaks were reported as 5.26, 5.10, 3.60, 3.00, 2.64 and 2.54 Å. These were indexed as 1 1 0, 2 0 0, 1 1 1, 0 2 0, 2 2 0 and 4 0 0 respectively, Using equation (2) and substituting $d_{110} = 5.31$ Å and $d_{200} = 5.11$ Å from *Table 2* gives the unit-cell parameters $a = 10.22$ Å and $b = 6.32$ Å for the PAN–PC samples (Stefani *et al.*'s values were $a = 10.20$ Å and $b = 6.10$ Å). However, Stefani's indexing leads to a problem. He recorded a peak at 3.00 Å, which was indexed as 0 2 0. Here, *Table 2* shows that there are two closely spaced peaks, one at 3.01–3.03 Å, and another at 3.14 Å In fact, it was found that the 3.14 Å peak indexes better as 0 2 0, but this leaves the 3.01–3.03 Å peak unindexable as an $hk0$ reflection.

Holland *et al.*[1] quoted a total of five spacings having values of 5.3, 5.1, 3.0, 2.9 and 2.6 Å from electron diffraction experiments on PAN single crystals grown from dilute propylene carbonate solution. Unlike Stefani[11], Holland *et al.* found no evidence for *c*-axis periodicity in the single crystals. As their single-crystal research was the impetus for this work and the previous one on thermoreversible PAN–PC gels[3], it is also worth looking at their peaks and the assignments made by them.

The first two of Holland's five spacings (5.3 and 5.1 Å) correspond to the doublet at $2\theta \sim 17°$ and are the same as those shown in *Table 2* for the moulded sheets. From considerations of the multiplicities of the reflections at 5.3 and 5.1 Å in the single crystals, Holland *et al.* concluded that these should be indexed as d_{200} and d_{110} respectively, instead of the reverse, which was used by Stefani[11]. This gives $a = 10.60$ Å and $b = 5.82$ Å, instead of $a = 10.20$ Å, $b = 6.10$ Å (Stefani). The last three peaks were not explicitly indexed by Holland *et al.*, but using his lattice parameters, the 3.0, 2.9 and 2.6 Å peaks can be indexed as 3 1 0, 0 2 0 and 2 2 0 reflections respectively.

When Holland's indexing scheme is applied to the peaks in *Table 2* from the moulded films, assigning $d_{200} = 5.31$ Å and $d_{110} = 5.11$ Å gives $a = 10.60$ Å and $b = 5.82$ Å. However, the 3.61–3.67 Å and the 3.14 Å peaks in *Table 2*, which were not found by Holland, cannot be indexed using his scheme.

Stefani's lattice parameters lead to a/b being slightly less than $\sqrt{3}$, while Holland's lead to a/b being slightly greater than $\sqrt{3}$. However, both cases represent distortions from the hexagonal packing shown in *Figure 6a*; *Figure 6b* shows the packing of 5.82 Å diameter cylinders using Holland's lattice parameters with $a/b > \sqrt{3}$.

Klement and Geil[13] observed 13 equatorial reflections in X-ray diffraction studies on single-crystal mats. The mats were prepared by growing single crystals from 0.02–0.04% PAN–PC solutions at 98°C, which were then sedimented by filtering, dried and powdered[13]. Two important new peaks with large spacings of 10.07 and 7.81 Å were found. Like Holland, they did not find any evidence for *c*-axis periodicity[13]. Using Holland's values of $a = 10.6$ Å and $b = 5.82$ Å, they found that not all of the 13 peaks could be indexed as $hk0$ reflections. However, by doubling Holland's values for the lattice constants (i.e. putting $a = 21.18$ Å and $b = 11.60$ Å), a satisfactory indexing was achieved. Thus, the indexing they used was different from that of Stefani or Holland. The peaks of the doublet (5.3 and 5.1 Å) are now classified as 4 0 0 and 2 2 0 as opposed to 1 1 0 and 2 0 0 (Stefani) or 2 0 0 and 1 1 0 (Holland). It is also noted that Klement and Geil observed many peaks that were not found by Stefani *et al.* in oriented fibres, or by Holland *et al.* in the single crystals.

The 13 reflections found by Klement and Geil are tabulated in *Table 3*, along with their indexing. Examining the peaks in *Table 2* from the PAN–PC moulded films shows that these peaks are a subset of Klement and Geil's peaks in *Table 3*. Hence, Klement and Geil's indexing has been placed in *Table 2*, alongside the peaks from the moulded sheets.

Since Klement and Geil's single crystals were grown from propylene carbonate, and the presence of crystallites was identified as the cause for the gelation of concentrated PAN–PC solutions, it seems reasonable to seek a connection between their work and the crystallites in the gel. It should be noted that Klement and Geil's single crystals[13] had much larger dimensions (1 μm wide and 5.8 μm long) than the crystallites in the moulded sheets. The former were grown from very dilute solution (< 1% PAN), while the latter were formed from extremely concentrated (up to 70% PAN) solutions where the

Table 3 The 13 d-spacings observed by Klement and Geil[13] in single-crystal mats of PAN grown from PC. As there was no evidence for non-equatorial reflections, they indexed all peaks as $hk0$ reflections. The indexing used by them employed $a = 21.18$ Å and $b = 11.60$ Å. The peaks found in the PAN–PC plasticized films form a subset of these peaks (cf. *Table 2*)

	d_{hkl} (Å)	
hkl	Calc.	Expt.
110	10.18	10.07
210	7.83	7.81
400	5.30	5.36
220	5.09	5.05
420	3.91	3.91
230	3.63	3.64
430	3.13	3.14
620	3.02	3.02
040	2.90	2.90
240	2.80	2.87
800	2.65	2.65
440	2.54	2.53
550	2.03	2.03

chains were highly entangled. It is to be expected that in the PAN–PC gels[3] and moulded sheets, the crystallites would be much smaller and they would be interlinked by chains. Hence, it would be difficult to observe some of the weaker peaks from these samples compared to the single-crystal mats. Further, scattering from the large amount of solvent present in the PAN–PC films could obscure the weak peaks.

If Klement and Geil's large lattice is assumed to apply to the crystallites in the PAN–PC moulded films (though the 10.07 Å spacing was not observed in the moulded sheets), then it leads to an interesting question. *Figure 6c* shows the packing of cylindrical rod-like molecular segments in an orthorhombic lattice with Klement and Geil's values of a and b. The authors did not include a sketch of their lattice in their paper[13] or specify the type of orthorhombic lattice, but a base-centred one is assumed here. Though Holland's (or Stefani's) lattice in *Figure 6b* represents only slight deviations from the hexagonal lattice in *Figure 6a*, *Figure 6c* shows a significant enlargement. If it is assumed that the molecular cylinders are still about 5.3 Å in diameter[15,16], then the interchain distance in *Figure 6c* has increased greatly. The question is, why should such a large lattice be needed?

Klement and Geil[13] did not comment on the unusually large size of the unit cell they proposed, but it is surprising when other crystallizable vinyl polymers have smaller cells. For example[25], syndiotactic poly(vinyl chloride) has an orthorhombic unit cell with $a = 10.4$ Å, $b = 5.3$ Å and $c = 5.10$ Å, while atactic poly(vinyl fluoride) has an orthorhombic cell with $a = 8.57$ Å, $b = 4.95$ Å and $c = 2.52$ Å. The nitrile group is not particularly large and even after allowing for the atactic nature of free-radical PAN, there is no intrinsic reason for the lattice to be so large, especially when it is remembered that in the polymerized powder (*Table 1*) and in oriented fibres[11] the chains are able to pack closer as in *Figure 6a*.

One possibility is that the chain adopts a more contracted conformation in the gels and plasticized films than in the reactor powder or in the oriented fibres, so that the diameter of the rod is much greater than 5.3 Å A second possibility is that any propylene carbonate molecules that may be attached to the nitrile groups by dipolar interactions could be accommodated in such a lattice. Many crystalline materials exclude extraneous molecules from the lattice, but there are cases where solvent molecules may co-crystallize with a compound.

Klement and Geil's single-crystal mats were dried at room temperature and then ground in a mortar with a pestle. No mention was made of how (or whether) the residual propylene carbonate content in the dried mat was checked[13]. PC has a high boiling point (240°C) and other work has shown that it is difficult to remove PC below about 5% wt/wt, as the molecule is paired to the nitrile group by dipolar interactions[26]. In terms of moles of PC, this is a much greater percentage. Thus, it is possible that there was bound solvent present in Klement and Geil's single-crystal mats; at the time their work was carried out, there was no reason to consider any effect that this would have on the crystallites. On the other hand, Holland *et al.*'s single crystals (also grown from PC) were deposited on an electron microscope grid, so that a thick multilayer of crystals was not formed. It is possible that these were dried better than the single-crystal mat, and this may be the reason why they observed a smaller lattice.

In the PAN–PC gels[3] and moulded sheets of this work, it is certain that the solvent is still present in large quantities; most of it would be located in amorphous regions, but it is possible that if the unit cell in the crystallites forming the junction points in the gel[3] or moulded films is as large as that shown in *Figure 6c*, some PC molecules could be incorporated in it. Subsequent work on these gels and moulded films support this possibility[26,27]. Certainly, the size of the PC molecule shown in *Figure 6d* allows it to be conveniently fitted into the lattice in *Figure 6c* but not into the lattices in *Figures 6a* or *6b*, where the chains are more closely packed. It is envisaged that the PC molecules are oriented 'horizontally' with respect to the polymer chain axis[26], so that there is dipolar interaction between the carbonyl group of the propylene carbonate and the nitrile of the polymer.

There is a third possibility to explain the diffractograms of the moulded films in *Figures 5b–e*. If the peak at 3.64 Å in *Table 2* is considered to be spurious and is ignored, leaving just the peaks 5.31, 5.11, 3.14 and 3.04 Å, then the peaks 5.31 and 3.14 Å and 5.11 and 3.03 Å, when taken in pairs, are in the ratio 1.69:1. This is very close to the ratio $\sqrt{3} = 1.73:1$, which is characteristic of the peaks in a hexagonally packed system[9]. Thus, the diffraction pattern could be interpreted as arising from a biphasic material with two hexagonally packed assemblies, one with a molecular rod diameter of 5.31 Å and the other with 5.11 Å. However, it is not clear how this could arise physically due to crystallization from a homogeneous solution.

Sokół *et al.*[22–24] made solvent-swollen PAN by a different approach. PAN powders and films (made by an undisclosed method) were swelled with polar liquids such a nitromethane, nitrobenzene and pyridine, at various temperatures. Structural changes were examined by n.m.r. spectroscopy and X-ray diffraction. The swollen films made by them were in principle the same as the PAN–PC films in that both contain solvent; the only difference is that the PAN–PC films were made by forming concentrated solutions and then solidifying to form a solvent-swollen film.

Sokół *et al.*'s[22–24] X-ray diffractograms from the unswollen films showed the usual singlet at $2\theta = 17°$ and $2\theta = 29.5°$, similar to those in *Figure 5a*, but after swelling, the peak at $2\theta = 17°$ became a doublet, similar to those in *Figures 5b–e*. In order to explain this solvent-induced transformation, they proposed that the solvent entered not only the amorphous regions but also the paracrystallites themselves. Removal of the solvent from the swollen film caused the structure to revert back to that of the original unswollen polymer. (This is good evidence that the presence of solvent is the direct cause for the changes in the X-ray diffraction peaks.)

Though Sokół *et al.*[22–24] invoked a change from hexagonal packing of 6 Å diameter molecular cylinders to an orthorhombic arrangement on swelling, their interpretation was different. They proposed that swelling caused a decrease in the diameter of the molecular cylinders in the crystallites, which was achieved by the chains adopting a more extended zig-zag (i.e. *trans*) conformation; it was implied that this was necessary to accommodate the solvent. However, no lattice parameters were derived, nor was there any indication of the final (reduced) diameter of the cylinders, or the intercylinder spacing and how it compared with the molecular size of the swelling agent.

With their model, presumably there would be a reduction in the conformational entropy of the chain. It would imply that if a drawn PAN film were to be swelled, it would spontaneously elongate, but experience shows that stretched fibres of flexible-chain polymers usually shrink when dissolved.

Thus, while Sokół's swelling experiments support the postulate reached here that solvent can be incorporated in the crystallites, it is felt that the size of the PC molecule and the orientation it adopts when paired to the nitrile[26] would require a significant increase in the interchain distance but this is unlikely to be achieved by the PAN molecule adopting a zig-zag conformation. Sokół *et al.* noted that their three reflections coincided with Klement and Geil's results (they would also fit Holland's or Stefani's peaks), but failed to notice that the latter's[13] lattice parameters were so large that it was not even necessary to invoke a lengthening of the molecular cylinders to accommodate the solvent.

Crystallite size measurements. The average crystallite sizes in the moulded sheets, L_{c1} and L_{c2}, were estimated using equation (1) from the broadening of the peaks at $2\theta_1 = 16.7°$ and $2\theta_2 = 17.4°$ in *Figures 5b–f*. Different values of size can be obtained from different peaks because the crystal size varies in different directions[28].

The variation of crystallite size as a function of PAN content is plotted in *Figure 7*. It can be seen that the apparent crystallite size is about three times greater in the moulded sheets than in the PAN reactor powder (~200–260 Å *versus* 70 Å). However, this does not necessarily mean that more chains are involved in the crystallites of the PAN–PC moulded sheets, if the lattice has expanded compared to the reactor powder. The crystallite size rises to a maximum at 50:50 PAN:PC and then decreases (*Figure 7*).

Only one annealing temperature and time were used in these experiments, and it is possible that the optimum crystallite size and perfection are dependent on composition (as is evident from *Figure 7*), annealing temperature and time. The variation in crystallite size with respect to these factors needs to be explored.

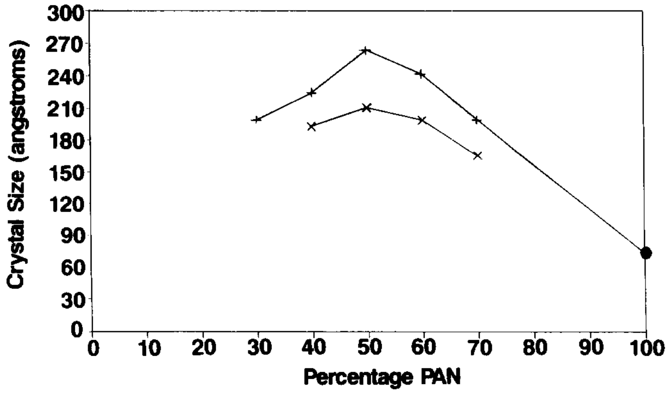

Figure 7 Variation of crystallite size with composition in PAN–PC moulded films. The crystallite sizes L_{c1} (+) and L_{c2} (×) were estimated from the broadening of the doublet at $2\theta = 16.7°$ and 17.4° in *Figures 5b–e*. For the 30:70 PAN: PC, only one peak could be used (*Figure 5f*). In general, the peak at $2\theta = 16.7°$ gave higher values than the peak at $2\theta = 17.4°$. For the 100% PAN, the L_c value (●) was taken from the reactor powder where only one peak at $2\theta = 16.7°$ was found

For a polymer with crystallites having a paracrystalline type of order, the line broadening of the peaks occurs due to both the small crystallite size and lattice distortions[28,29]. Thus, the crystallite sizes shown in *Figure 7*, which were estimated from the Scherrer equation, are lower bounds, as broadening due to lattice distortions was not taken into account[28,29].

The 30:70 PAN:PC sheet showed a different X-ray pattern compared to the other moulded sheets, which can be seen by comparing *Figure 5f* and *Figures 5b–e*. It is clear that the appearance of the trace in *Figure 5f* is not just due to small crystallite size because the trace in *Figure 5a* for the reactor powder, where the average crystallite size was extremely small (~70 Å), does not show such a diffuse background near the main peak at $2\theta = 17°$. *Figure 5f* shows an intensity loss of the higher reflections and the appearance of a diffuse background that is concentrated in the vicinity of the strongest peaks at $2\theta \sim 17°$. This is characteristic of the presence of first-order-type of crystal lattice defects[28]; thermal motion is one ever-present source of this type of defect. Note that paracrystallinity is a second-order-type defect[28]. A first-order type of defect does not lead to significant line broadening but it causes a diminishing of the diffracted intensity.

The reason for the presence of the first-order type of defect (in addition to paracrystallinity) in the 30:70 PAN:PC sheet was not investigated. It is possible that there was more PC present in the lattice of the PC-rich samples such as the 30:70 PAN:PC sheet, and this may have allowed increased thermal motion in the crystallites at room temperature compared with the other moulded sheets.

General comments on gels and plasticized solids

From the results reported here and in the previous work on 20% PAN–PC gels[3], it may be concluded that the gels and plasticized sheets exhibit a continuous spectrum of mechanical properties, with the former representing the low polymer content and the latter the high polymer content end of the composition range. Thus, the dividing line between gels and plasticized solids is arbitrary.

The PC-rich sheets (30:70 PAN:PC) showed obvious signs of wetness due to the presence of solvent, but the

PAN-rich sheets (70:30 PAN:PC) appeared to be quite dry (*Figure 4*). The former warped if left overnight in the open due to plasticizer evaporation, but the latter were more dimensionally stable at 20°C over extended periods of time.

Though the PC-rich sheets were rubbery at room temperature, the PAN-rich samples were similar in appearance to a moulded sheet of a conventional thermoplastic polymer such as polyethylene or polypropylene (*Figure 4*). Normally, PAN is not processed as a thermoplastic, because its melting point is considered to be above the degradation temperature[4,16]. A true thermoplastic such as polyethylene does not need a solvent to depress the melting point to make it processable. Solvent processing of polyethylene is only used in exceptional cases such as the gel spinning of ultra-high-molecular-weight polyethylene[30].

It is interesting to compare the behaviour of PAN–PC solutions with solutions of other crystallizable polymers. Polymers such as polyethylene and polypropylene are not soluble at room temperature in any liquid, but they dissolve in hydrocarbon solvents such as xylene at elevated temperature. Thus, on cooling a dilute polyethylene solution, the polymer crystallizes as single crystals[31]. From concentrated solutions of polyethylene, thermoreversible gels are formed.

In comparison, PAN is insoluble in non-polar solvents at any temperature. Though it dissolves in polar solvents such as dimethylsulphoxide (DMSO) and dimethylformamide (DMF), it is soluble at all temperatures in these solvents, even on cooling below ambient temperature. For example, a 20–30% PAN solution in DMSO is viscous but pourable and it would not gel at ambient temperatures if kept free from moisture. If cooled, the solvent itself will crystallize before the PAN does (the freezing point of DMSO is 19°C). In other words, DMSO and DMF are good solvents for PAN at all temperatures above the freezing point of the solvent. Propylene carbonate, on the other hand, is unusual in that it is a polar solvent that only dissolves PAN at elevated temperatures, and hence with this solvent there is a parallel with the dissolution and crystallization of polyethylene from xylene. PC is in fact one of the few solvents from which PAN crystallizes[32].

At low solvent concentration (less than 30% PC), one may view the PC as a plasticizer for PAN, in the same way that dioctyl phthalate is a plasticizer for poly(vinyl chloride) (PVC). A plasticizer depresses both the glass transition temperature T_g and the flow temperature T_f (ref. 33). In addition, a good plasticizer should have a large value for the difference $T_f - T_g$, to extend the service range of the articles made from the plasticized polymer[33]. The plasticizers for PVC such as dioctyl phthalate have boiling points in excess of 300°C and low freezing points. PC, however, has a boiling point of 240°C and a freezing point of −55°C. Thus, PC is probably not suitable for making permanently plasticized articles from PAN unless the PC content is less than 10%, but it allows PAN to be processed as a thermoplastic type of material[26].

CONCLUSIONS

The behaviour of PAN–PC solutions up to a concentration of 70% PAN has been established. From dilute solutions (up to 1% PAN), single crystals are obtained[1,2,13], but between 1 and 20% PAN, thermoreversible gels are formed on cooling the solution[3]; above 30% PAN, PC-plasticized films could be made by moulding.

The PAN powder produced by slurry polymerization had a surprisingly high pore volume-fraction of about 65%. The porosity of the powder could be used advantageously to hold a latent solvent like PC in the powder particles, till the solvent was activated by heating. This allowed the formation of transparent, essentially bubble-free 'melts' by merely heating and compressing the PC-blended powders.

The solidification on cooling of PAN–PC solutions due to partial crystallization enabled the polymer to be moulded like a thermoplastic. In this respect, PAN–PC solutions are different from solutions of the polymer in most of the common solvents used for its processing. Thus, this allowed the possibility of processing PAN like a thermoplastic polymer[26].

The powder produced from the polymerization reactor had chains packed in a hexagonal arrangement but the crystallite sizes were extremely small. Dissolution in PC and crystallization led to a rearrangement into orthorhombic packing.

The X-ray diffraction peaks in the PAN–PC films were compared with those found by Stefani *et al.*[11], Holland *et al.*[1] and Klement and Geil[13]. It was found that not all the diffration peaks coincided with or could be indexed on Stefani's or Holland's schemes. However, all five peaks from the PAN–PC films coincided with five of the 13 reflections found by Klement and Geil in single-crystal mats grown from propylene carbonate. However, it must be pointed out that the 10.08 Å peak, which led to Klement and Geil's large cell, was not observed in these moulded sheets. An alternative interpretation in terms of the formation of a biphasic material was also considered but it was felt that this was unlikely to occur.

If the crystallites indeed have the unit-cell dimensions quoted by Klement and Geil, then it is postulated that some PC molecules are incorporated in the crystallites. This is not a possibility that has been considered previously, and more generally would also represent an interesting case of polymer crystallization. It would also imply that there may not be a unique lattice, as it could depend on the amount of solvent.

It would seem that the crystal structure of PAN can be influenced by the type of sample studied—reactor powder, oriented fibres, single crystals grown from dilute solution, gels with solvent present and swollen films. It is possible that the puzzling differences in unit cell found by different investigators are due to the incorporation of residual solvent in the crystallites. More evidence will be presented to support this view.

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