

# The formation of polymer-solvent complexes of polyacrylonitrile from organic solvents containing carbonyl groups

Z. Bashir\*, S.P. Church and D.M. Price

The crystallisation behaviour on cooling of concentrated solutions of polyacrylonitrile (PAN) in two organic solvents, gamma butyrolactone (gBL) and ethylene carbonate (EC), was investigated. gBL is a liquid but EC is a crystalline solid at 20 °C. Wide angle X-ray diffraction studies showed that the peaks from the solvent-containing gel films were different from those in the dry PAN powder. Polarised-infrared spectroscopy measurements conducted on uniaxially-drawn gel films indicated not only preferential orientation of the nitriles perpendicular to the draw direction but also orientation of the residual solvent in such a way as to suggest pairing of the gBL or EC molecule with the nitriles on the chains. It is suggested that the X-ray diffractograms of the gels may be due to the formation of polymer-solvent complexes during crystallisation of PAN from solvents with carbonyl groups. Differential scanning calorimetry showed gel-melting endotherms on heating and crystallisation exotherms on cooling.

## 1 Introduction

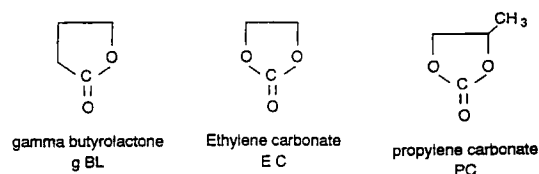
The solvents for polyacrylonitrile (PAN) generally belong to two classes. The first type consists of aqueous ionic-media such as  $ZnCl_2$  (aq.) and  $NaSCN$  (aq.). Secondly, polar organic liquids containing carbonyl (C=O) groups, such as dimethyl formamide and dimethyl acetamide, are solvents. PAN-based fibres for textiles and for carbon-fibre precursors are usually wet-spun from these two types of solvents in industrial processes. Non-polar organics such as pure hydrocarbons do not dissolve the polymer at any temperature.

Propylene carbonate (PC) is an organic solvent for PAN which contains a carbonyl group. However, unlike dimethyl formamide and dimethyl acetamide (which also possess a C=O group), PC does not dissolve PAN at room temperature but only becomes a solvent at elevated temperatures. The thermoreversible gelation of concentrated polyacrylonitrile (PAN) solutions in propylene carbonate was recently investigated by us [1-3]. It was shown that 5-30% PAN solutions could be made by dissolving the polymer powder in hot PC at about 130-160 °C; when the solution was cooled, it gelled very quickly. Partial crystallisation of the polymer was identified as the cause for the gelation – X ray diffraction, nuclear magnetic resonance spectroscopy and differential scanning calorimetry supported this conclusion [1-3]. These studies also led to the plasticised-melt extrusion of fibres and films of PAN [4-6].

The most interesting scientific feature of the previous work was the suggestion that the crystallites in the gel might be a solvated polymorph. That is, propylene carbonate molecules were believed to be bound to the polymer chains in the crystallites by dipolar interactions between the carbonyl group of the solvent and the nitriles of the PAN. Evidence for this was obtained from infrared dichroism studies on drawn PAN-PC gel films which indicated that the solvent was oriented [5]. It was also shown that the diffraction pattern of PAN-PC gels was different from that of dry polymer powder, and the change was directly associated with the presence of the solvent [3, 5, 6].

If this conclusion is correct, then it would be reasonable to expect a similar behaviour with other carbonyl-containing solvents in which the PAN has limited solubility

at room temperature but which dissolve the polymer at elevated temperatures. Gamma-butyrolactone (g-BL) and ethylene carbonate (EC) are two such solvents for PAN. The molecular structures of g-BL, EC and PC are shown below:



In this work, the crystallisation behaviour of PAN from concentrated gBL and EC solution was investigated in order to see if the results reported previously for propylene carbonate are more general.

## 2 Experimental

### 2.1 Polymer and solvent

The polymer was prepared by the free-radical polymerisation of acrylonitrile using a slurry method. The details are given in a previous work [7]. The inherent viscosity of the polymer was measured in dimethyl formamide at 25 °C and this gave a value of 1.7 dL/g. Carbon-13 nuclear magnetic resonance spectroscopy of the polymer showed that it was essentially atactic [7].

The gamma-butyrolactone was obtained from Aldrich and was used as received. It has a boiling point of 205 °C and a freezing point of -45 °C. Ethylene carbonate was obtained from BDH. It has a melting point of 37 °C and a boiling point of 245 °C.

### 2.2 Preparation of gel films

The PAN-gBL and PAN-EC gel films were made by a technique developed in the previous work on the PAN-propylene carbonate gels [2]. This was because at high polymer concentrations it becomes difficult to add a voluminous powder to a small volume of liquid and form a homogeneous bubble-free solution. The method disclosed earlier depended on blending the liquid with PAN powder and compression-moulding the resulting plasticised

[\*] Z. Bashir, S.P. Church and D.M. Price  
Courtaulds Research  
72 Lockhurst Lane, Coventry, CV6 5RS, United Kingdom

powders to form gel films [2]. Thus, compositions of 80 : 20, 70 : 30, 60 : 40, 50 : 50 and 40 : 60 PAN : gBL were made by mixing the liquid with the polymer powder in a mortar and grinding with a pestle. In the case of the PAN-EC compositions, the EC had to be first melted. The liquid EC was then added to PAN powder and again mechanically mixed by grinding. PAN : EC compositions used were 70 : 30, 60 : 40, 50 : 50, 40 : 60 and 30 : 70. The numbers quoted are weight ratios of polymer and solvent.

The solvent-plasticised powder was next placed between aluminium foil, which was then inserted between two steel plates for compression moulding. The moulding temperature and time were 180 °C and 5 minutes, respectively. A moderate moulding pressure was used for the 40 : 60 and 50 : 50 PAN : gBL compositions as excessive pressure caused the "melt" to run out of the mould. The compositions with higher polymer content had a higher "melt" viscosity and required higher moulding pressures. After cooling, the foil was peeled to obtain the turbid gel film.

### 2.3 X-ray diffraction studies on PAN-gBL and PAN-EC gel films

Wide-angle X-ray diffractograms of the unoriented gel films were recorded. Cu  $K_{\alpha}$  (nickel filtered) 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 beam. The radial scans on the samples were carried out in the region  $2\theta = 4^{\circ}$  to  $50^{\circ}$ . The data were collected at  $0.02^{\circ}$  intervals with counting for 1 second at each step. Peak positions were determined by the APD 1700 (Version 4) software controlling the system.

The diffractograms from the following samples were recorded:

- PAN reactor powder (for comparison).
- PAN-gBL gel films containing 40, 50, 60, 70 and 80 % polymer.
- PAN-EC gel films, containing 30, 40, 50, 60 and 70 % polymer.

### 2.4 Calorimetric studies

Calorimetric measurements were carried out using a DuPont 910 Differential Scanning Calorimeter (DSC) interfaced to a 9900 Computer Thermal Analyzer.

The instrument was fitted with a liquid nitrogen cooling accessory in order to permit controlled cooling. The DSC cell was calibrated for temperature and enthalpy response according to the melting point and the heat of fusion of pure indium. Hermetically-sealed pressure-resistant sample pans were employed in order to reduce evaporation of solvent during the experiment. A heating and cooling rate of  $10^{\circ}/\text{min}$  was used throughout. Samples were heated up to 200 °C and then cooled to  $-100^{\circ}\text{C}$ , followed by two repetitions of the cycle to test reproducibility.

### 2.5 Infrared dichroism studies on uniaxially drawn gel films

The aim of this experiment was to examine the orientation of the PAN chains and to see whether the solvent mole-

cules also became oriented after drawing. A 50 : 50 PAN : gBL and a 40 : 60 PAN : EC gel film were drawn at 115 °C to a draw ratio of 10 : 1. For this experiment, the solvent-content had to be reduced to about 5 % by drying the drawn film at 70 °C for 24 hours in a fan-oven. This is because the carbonyl peak of the solvent has a large extinction coefficient. The film was dried by hanging it vertically, with a paper clip attached as weight.

The infrared (IR) dichroic behaviour was established using polarised IR spectroscopy. The instrument used was a Nicolet 740 FTIR spectrometer, equipped with a Spectra Tech wire-grid polariser. The IR spectrum of the uniaxially-oriented gel film was first recorded with the polarisation direction perpendicular to the draw direction. The spectrum was next recorded at the same position in the film with the polarisation direction now parallel to the draw direction. This allowed bands showing perpendicular dichroism (i.e. higher absorbance for the perpendicular polarisation-state) and parallel dichroism (i.e. higher absorbance for the parallel polarisation-state) to be determined.

## 3 Results and discussion

Before embarking on a comparison of the long-range order found in dry PAN and the polymer precipitated from organic solvents containing carbonyl groups, clarifications on the terminology used in this paper to describe this order will be made here. Generally, most investigations on PAN have suggested to the presence of only two-dimensional order; periodicity along the chain axis appears to be absent because of the atactic nature of the polymer produced by the free radical polymerisation of acrylonitrile. Though various terms such as "laterally-ordered" or "directional crystallisation" have been coined to describe this [8, 21], we shall use the less cumbersome words "crystallise" and "crystallisation", which are normally applied to systems that have the more common three-dimensional order. However, it should be understood that when we use these words here in the context of PAN, we mean in fact two-dimensional order.

### 3.1 Polyacrylonitrile-gamma butyrolactone gel films

Fig. 1 shows the typical diffractogram of PAN reactor powder. This is characterised by peaks near  $2\theta = 17^{\circ}$  ( $5.30 \text{ \AA}$

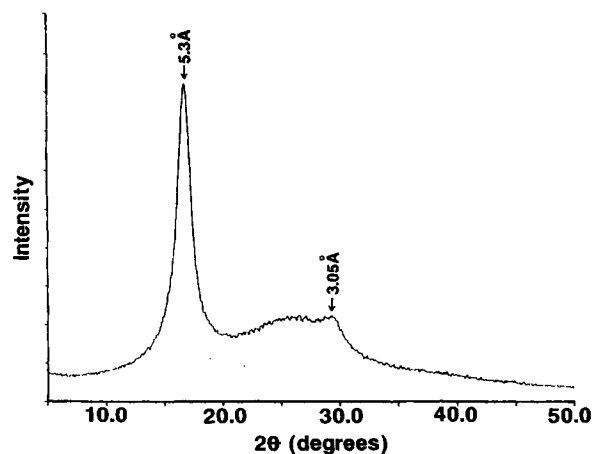


Fig. 1. The wide angle diffractogram of PAN reactor powder typically shows two prominent peaks corresponding to  $5.30 \text{ \AA}$  and  $3.05 \text{ \AA}$ . This is associated with the hexagonal polymorph.

spacing,  $1 \text{ \AA} = 0.1 \text{ nm}$ ), and  $2\theta = 29.5^\circ$  ( $3.05 \text{ \AA}$ ). The PAN chain is believed to adopt a rod-like conformation due to the intramolecular repulsion of the nitrile dipoles [8]. Thus, the diffractogram of Fig. 1 has been attributed to a hexagonal packing of "molecular rods" [2, 8-10]. This is the most commonly cited diffractogram of PAN in the literature and it is needed here for comparison with the diffractograms produced from the samples crystallised from solution.

We were unable to obtain diffractograms revealing diffraction peaks in PAN-gBL gels where the polymer content was less than about 30%. This is because of the diffuse scattering from the solvent which obscured any peaks from the polymer crystallites that might have been present in the gel. In earlier works by other authors [11, 12], the causes of the gelation of PAN polymers in various solvents, including gBL, were discussed. Though it has been suggested in these works that polymer crystallisation might be the principal reason for the gelation of certain PAN solutions, obtaining X-ray evidence was hampered because the diffuse scattering from the large amount of liquid obscured any diffraction peaks [11, 12]. These authors did not make gels with very high polymer content and hence the diffuse scattering from the liquid was unavoidable [11, 12].

In this work, our method of making gel films by moulding plasticised powders allow specimens with high polymer content to be prepared. It was only on going to the PAN-gBL gel films with PAN content greater than 40% that the scattering from the liquid solvent in the vicinity of  $2\theta = 17^\circ$  was reduced and the diffraction peaks from the polymer became visible.

Fig. 2 shows the diffractogram of the 80 : 20 PAN : gBL film. The most striking feature is the appearance in Fig. 2 of two close peaks near  $2\theta = 17^\circ$  compared with the single peak in the reactor powder (Fig. 1). The spacings of these two reflexions correspond to  $5.30 \text{ \AA}$  and  $5.10 \text{ \AA}$ ; there appear to be also three peaks in the vicinity of  $2\theta = 30^\circ$ , corresponding to spacings of  $3.14 \text{ \AA}$ ,  $3.03 \text{ \AA}$  and  $2.90 \text{ \AA}$ . The 70 : 30 PAN : gBL gel film showed a diffractogram that was virtually identical to that in Fig. 2, with the same five peaks. The 60 : 40, 50 : 50 and 40 : 60 PAN : gBL gel films also displayed similar peaks, but as the solvent content increased, the diffuse scattering from the liquid started to obscure the peaks (not shown). By slightly stretching the gel films and

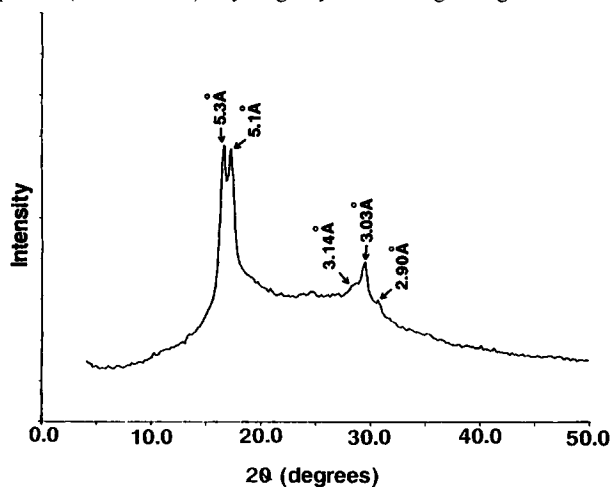


Fig. 2. Diffractograms of a 80 : 20 PAN : gBL gel film. This shows the appearance of new peaks compared with the dry PAN powder in Fig. 1 and indicates the formation of an orthorhombic polymorph.

recording the diffraction pattern on photographic film, it was established that all the peaks were equatorial.

As Fig. 1 shows, in the hexagonal polymorph, only a single peak near  $2\theta = 17^\circ$  is found. However, twin peaks near  $2\theta = 17^\circ$  have been noted in certain PAN samples. For example, it has been reported in electron diffraction studies on single crystals by Holland et al. [13] and by Lindenmeyer and Hosemann [14], in X-ray studies on single-crystal mats made from dilute propylene carbonate solutions by Klement and Geil [15] and also by Hinrichsen and Orth [16], and in our previous work on PAN-propylene carbonate gels and gel films [1, 2]. Sokoř et al. [17-19] also observed diffractograms with double peaks near  $2\theta = 17^\circ$  after post-swelling (originally dry) PAN with liquids such as nitrobenzene, pyridine and nitromethane.

The diffractogram in Fig. 2 has been interpreted as being caused by an orthorhombic chain-packing which is different from the hexagonal polymorph [2, 3, 13-19]. The peaks in Fig. 2 cannot be indexed as  $hk0$  reflexions on the hexagonal system but can be indexed using the large rectangular cell proposed by Klement and Geil ( $a = 21.18 \text{ \AA}$  and  $b = 11.60 \text{ \AA}$ ). The peaks observed in Fig. 2 are a subset of the peaks found by Klement and Geil in single-crystal mats grown from propylene carbonate. Note however that Klement and Geil's cell was based on the observation of a  $10.08 \text{ \AA}$  equatorial spacing; such a peak is not observable in Fig. 2 and hence the adoption of this cell for indexing the peaks in Fig. 2 has to be regarded as tentative. In our previous work [2, 3], it was additionally proposed that a solvated orthorhombic polymorph (rather than a normal crystalline polymorph) may be the cause of the new diffraction pattern and the enlarged cell.

Figs. 3 (a) and 3 (b) show the IR spectra of an uniaxially-drawn PAN-gBL film with the polarisation direction

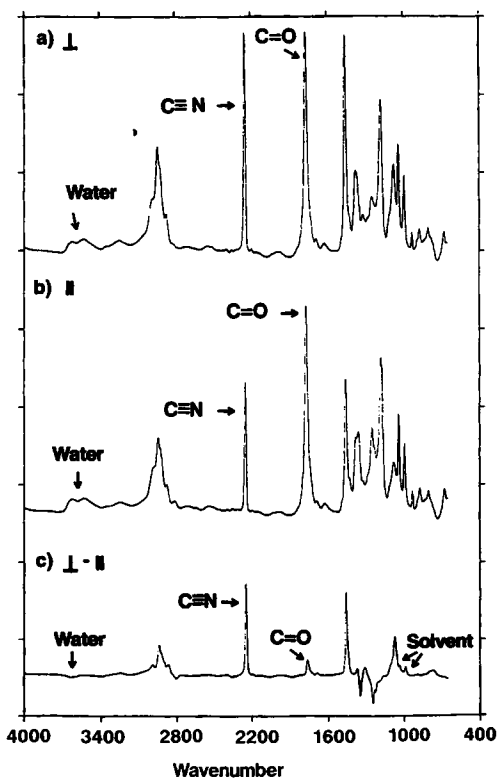


Fig. 3. IR dichroism behaviour of uniaxially drawn PAN-gBL films: (a) Polarisation perpendicular to draw axis, (b) polarisation parallel to draw axis, (c) partial dichroic spectrum which is (a) - (b).

perpendicular and parallel to the draw direction, respectively. The band at  $2244\text{ cm}^{-1}$  due to the  $\text{C}\equiv\text{N}$  stretching vibration of PAN shows perpendicular dichroism. Further, as with our previous work using propylene carbonate, the carbonyl vibration-band at  $1767\text{ cm}^{-1}$  of the gBL-solvent molecules shows dichroism. Moreover, the direction of dichroism is the same as that of the nitrile band – that is, it manifests perpendicular dichroism. As a small molecule such as gBL cannot normally become permanently oriented due to a mechanical deformation, we must postulate that there is dipolar pairing of this molecule with the nitrile group of the polymer. Thus, orienting the polymer chains by mechanical drawing preferentially orients the solvent molecules as well. This is shown schematically in Fig. 4 (a) with an anti-parallel arrangement of nitrile and carbonyl dipoles.

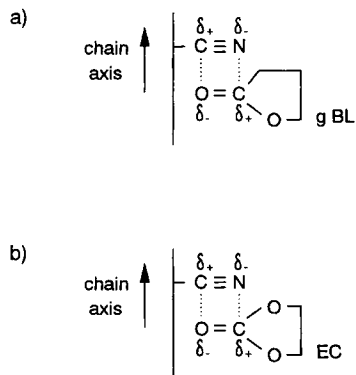


Fig. 4. Schematic anti-parallel arrangement of nitrile and carbonyl dipoles a) PAN-gBL b) PAN-EC. This is based on the dichroic behaviour shown by the nitrile and the carbonyl ( $\text{C}=\text{O}$ ) bands in Fig. 3 and Fig. 8.

The spectra in Fig. 3 also indicate the dichroism of the other gBL bands. Further, Fig. 3 shows that the small amount of water present in the system becomes oriented [22]. Fig. 3 (c) exhibits the partial-dichroic spectrum obtained by subtraction of the parallel spectrum from the perpendicular spectrum – that is, Fig. 3 (a) minus Fig. 3 (b). This instantly shows the dichroism and its direction for all the bands; in this representation, bands showing perpendicular dichroism appear above the baseline, those that show parallel dichroism appear below the baseline and bands that show no dichroism do not deviate from the baseline.

Thus, it can be seen that the solvent orientation observed with propylene carbonate in the previous work [5] appears to be more general. PAN is a polymer with a linear functional group (i.e. the nitrile) which is highly polar, and therefore liquids that have functional groups such as carbonyls which can form dipole-dipole pairs will tend to be solvents or plasticisers for the polymer. Though the existence of solvent orientation and dipolar pairing can be demonstrated only in oriented gel films, it is reasonable to assume that such pairing of the solvent molecules with the nitriles would be present in the polymer solution and thus it is conceivable that the solvent could co-crystallise with the polymer when a hot polymer solution is cooled. Hence, the IR result would be consistent with the idea of an expanded lattice with solvent incorporated by dipolar interactions.

Finally, we shall discuss the DSC studies on the “melting” and crystallisation behaviour of PAN-gBL films. It is well

known that when dry PAN powder is heated, there is no sign of melting in the DSC under normal heating rates (below about  $40^\circ/\text{min.}$ ) [23]. The powder does not appear to melt and flow. Instead, a violent, exothermic reaction occurs at about  $300^\circ\text{C}$  when the polymer is heated in air [23].

Paul’s work on the gelation of PAN copolymers [12] showed somewhat ambiguous indications of first-order phase transitions during gel melting and gel formation. The results were not definitive, probably because he used a PAN copolymer and solvents from which the polymer had an intrinsically low tendency to crystallise [12]. Less ambiguous evidence was produced later by Frushour [24, 25], who demonstrated “melting” endotherms when water-plasticised PAN was heated in a DSC experiment. Crystallisation exotherms were also exhibited on cooling of the PAN-water mixture. Similarly, “melting” endotherms and crystallisation exotherms have been reported by us in PAN-PC gels [1].

Though most investigators do not believe that PAN possesses a truly crystalline (three-dimensional) order, the separate results of Frushour [24, 25] and Bashir [1] indicate that even a material with only two-dimensional order can show a first-order phase transition. (In this respect, it is similar to other materials with intermediate order such as liquid crystals, where the change from a mesophase to an isotropic liquid is accompanied by an enthalpy of transition). On the other hand, if there was no long-range order at all in PAN, one could have expected a glass transition, but not any endothermic or exothermic transitions. Thus, the apparent lack of a melting endotherm when dry PAN powder is heated does not appear to be due to a lack of true crystalline order, but seems to be because the melting point is far higher than the degradation temperature.

The DSC studies reported in the current work reinforce these previous conclusions. The PAN-gBL gel films also showed “melting” endotherms on heating and crystallisation exotherms on cooling with associated enthalpies of transition. This is illustrated in Figs. 5 (a) and 5 (b), which show the heating of a 50 : 50 gel film and its subsequent cooling.

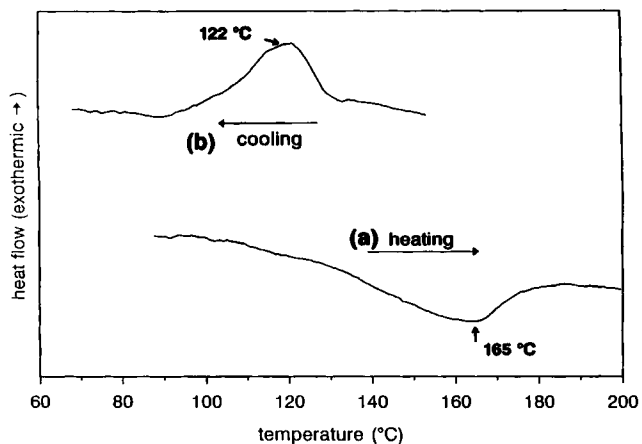


Fig. 5. DSC “melting” (dissolution) and crystallisation behaviour of 50 : 50 PAN : gBL gel film. Heating and cooling at  $10^\circ/\text{min.}$

On the first heating run, all the PAN-gBL gel films always showed a broad “melting” endotherm between about  $125^\circ\text{C}$  and  $175^\circ\text{C}$ . On the cooling run, if the cooling rate was too fast, a “crystallisation” exotherm was not observed;

consequently, if the cooled sample was reheated a second time immediately afterwards, a smaller melting endotherm was observed. This indicates that fast cooling does not allow crystallisation and hence, on the second heating-run, a melting endotherm was barely observable. On the other hand, if the cooling rate (after the first melting) was not too high, a crystallisation exotherm was observed on cooling, and a melting exotherm was found on the second heating run. For the particular sample in Fig. 5 (b), a cooling rate of  $10^{\circ}/\text{min.}$  was sufficient for a crystallisation exotherm to be observed. Comparing with our previous work however, it was found that crystallisation appeared to occur less readily from gBL solutions than from the propylene carbonate solutions. Unlike PAN-gBL solutions, the PAN-PC solutions appeared to crystallise quickly at all attainable cooling rates. The difference is particularly notable in solutions with low polymer content.

In Fig. 5 (a), the enthalpy of the "melting" transition in a 50 : 50 gel film was 10 J per gram of gel (20 J per g of PAN). However, it was pointed out in a previous work on PAN-PC gels that the heat of fusion of PAN cannot be simply equated to the enthalpy of the endothermic transition obtained from the gel during heating [1], as has been done in some works [24, 25]. This is because the enthalpy measured during the "melting" of the gel film is actually the combination of two terms: the heat of fusion and the heat of mixing ( $\Delta\bar{H}_{\text{dissolution}} = \Delta\bar{H}_{\text{mix}} + \Delta H_{\text{fusion}}$ ). In Fig. 5 (a), the heat of dissolution was 10 J/g, but as we do not know the partial heat of mixing, the heat of fusion cannot be calculated.

It is interesting to recall the melting-point-depression study of Krigbaum and Tokita (1960) using gBL as the diluent [26]. By employing a dilatometric method to measure volume changes of PAN-gBL solutions, they estimated the enthalpy and entropy of fusion of pure PAN. Solutions of PAN were made by dissolving the powder in gBL at elevated temperatures, after which they were held at a certain temperature for crystallisation. Samples with PAN concentrations greater than 35% by wt. were made by evaporating solvent from initially more dilute solutions. The "melting points" were measured by heating the samples (which presumably were gels of varying stiffness) and observing the volume change with temperature; at the "melting point", there was a step-wise increase in volume as would be expected at a first-order phase transition. In Krigbaum and Tokita's experiment, the volume change was measured, and the enthalpy and entropy were calculated from Flory's relationship for the melting-point depression due to a diluent [26].

Our results raise the possibility that when the PAN powder is dissolved in a solvent such as gBL and crystallised by cooling, solvated crystallites are formed, which act as the junction points in the gels. Remelting would then involve dissolution of the solvated crystallites rather than the pure polymer crystallites. Thus, any heat of fusion calculated from the diluent method (either calorimetrically or through dilatometry) could refer to the heat of fusion of the solvated polymorph rather than to the crystallites in the dry PAN powder.

We have not as yet resolved the problem of finding the heat and entropy of fusion of PAN directly. Due to the possible complications raised by the formation of solvated crystallites, there is a measure of doubt about the validity of estimating these thermodynamic quantities for this polymer from the indirect method involving diluents.

### 3.2 Polyacrylonitrile-ethylene carbonate gel films

In contrast to the PAN-gBL system, the PAN-EC combination is different because the solvent is a crystalline solid at room temperature (taken as  $20^{\circ}\text{C}$ ). Due to this, the polymer solution has the possibility of freezing separately when the polymer solution is cooled to room temperature. Here, the DSC results will be discussed first, followed by the X-ray and IR results.

We shall first illustrate the essential DSC results, just using the two extremes of the concentration regime studied. These are the 30 : 70 PAN : EC (i.e. the solvent-rich composition) and the 70 : 30 PAN : EC (i.e. the polymer-rich composition) gel films. The first heating scan of the 30 : 70 PAN : EC sample in Fig. 6 (a) shows the melting of the pure EC crystals at  $29^{\circ}\text{C}$  and the melting of the PAN : EC complex at higher temperatures. This sample had been stored for about two weeks after moulding. The melting point of pure EC crystals in the bulk is  $37\text{--}39^{\circ}\text{C}$  but the crystals in the gel film are small and hence they melt at a lower temperature. It is well known that small crystals melt at temperatures lower than the equilibrium melting point [27]. The bulk EC crystals obtained from the manufacturer of the chemical were very large in dimensions (typically 15 mm long and 2-3 mm wide). In contrast, in the EC microcrystals which were formed in the amorphous regions of the gel, the largest dimension would be no more than 100-1000 Å. Thus, the peak at  $29^{\circ}\text{C}$  in Fig. 6 (a) can be correctly

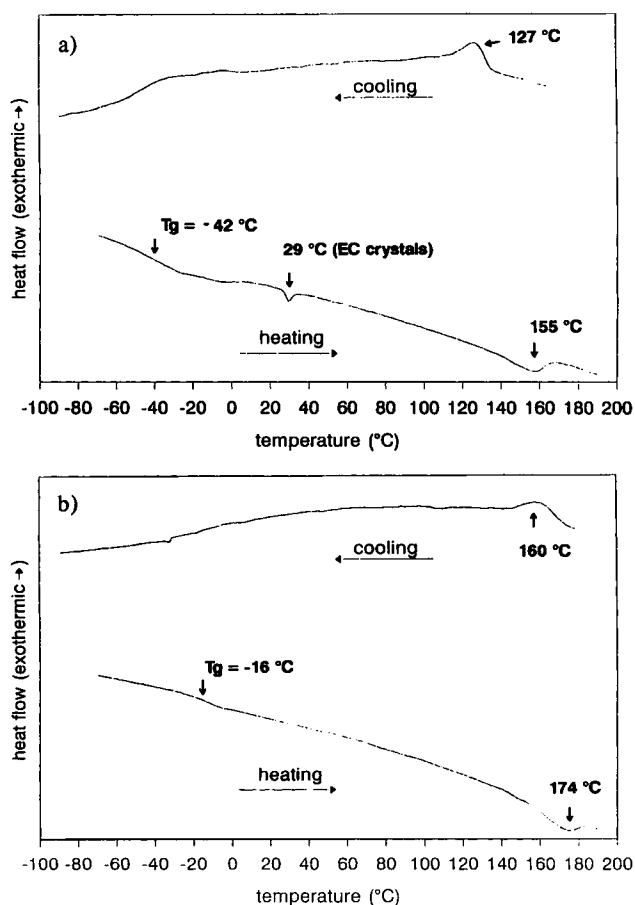


Fig. 6. DSC heat-cool cycle for PAN-EC gel films. Heating and cooling at  $10^{\circ}/\text{min.}$   
 (a) 30 : 70 PAN : EC  
 (b) 70 : 30 PAN : EC

attributed to the melting of pure EC microcrystals. The heat associated with this endotherm was 1.5 J per gram of gel, which amounts to 2.14 J per gram of EC. The heat of fusion of pure EC was measured independently and found to be 162 J/g. Hence, the endothermic peak at 29 °C represents the crystallisation of only about 1.3 % EC.

We shall attribute the high temperature peak at 155 °C in Fig. 6 (a) to the dissolution of the crystallites of the polymer-solvent complex rather than to the dissolution of crystallites of pure PAN. It can be seen that the peak associated with the polymer is characteristically broader than the peak linked with the pure EC microcrystals.

Fig. 6 (a) also shows that on cooling after the first melting, the crystallisation of the PAN : EC complex was observed at 127 °C. However, at the cooling rate used, crystallisation of the pure EC was not observed and instead, a glass transition was found at -55 °C. Crystallisation of the free EC (that is, EC which is not part of the polymer-solvent complex) does eventually take place in the solvent-rich composition. This manifests itself visually in the form of needle-like crystals of EC which can be seen in the gel film a few days after moulding. Further, if a DSC heating scan is conducted after storing the cooled sample obtained after the first melting run, a peak at 29 °C is observed once again due to the melting of pure EC crystals. Thus, EC supercools and crystallises very slowly.

Similarly, the 40 : 60 PAN : EC film manifested on heating an endothermic peak at 32.5 °C due to the melting of pure

EC and a peak at 152.6 °C for the PAN-EC complex (not shown here). On cooling at 10 °/min to -100 °C immediately after melting, the material supercooled to a glass: neither the crystallisation of the PAN-EC complex nor that of the pure EC was observed. Reheating immediately afterwards did not result in any endotherms. However, if the sample was stored for a few days, a heating thermogram similar to that in Fig. 6 (a) was obtained.

The thermograms of the 50 : 50, 60 : 40 and 70 : 30 PAN : EC will be illustrated by showing the behaviour of just the 70 : 30 composition. This is shown in Fig. 6 (b). These compositions showed no melting endotherms for the EC crystals during heating, but a melting endotherm for the polymer-solvent complex was observed at 173 °C. On cooling, a crystallisation exotherm was observed at about 160 °C for the polymer-solvent complex, but no low-temperature crystallisation-exotherm for the EC was found. The fact that the solvent showed neither melting endotherms (even in aged gel films) nor crystallisation exotherms below a certain EC content in the gel film suggests that most of the EC is "used" in forming the solvated complex and the surplus solvent is not present in sufficient quantities to crystallise separately in the polymer-rich specimens.

The X-ray results are in accord with the DSC results in Fig. 6. Figs. 7 (a)-(c) display the diffractograms of various PAN-EC gel films. They all show a transition to the orthorhombic polymorph from the hexagonal polymorph found in the original polymer powder (Fig. 1). The diffractogram

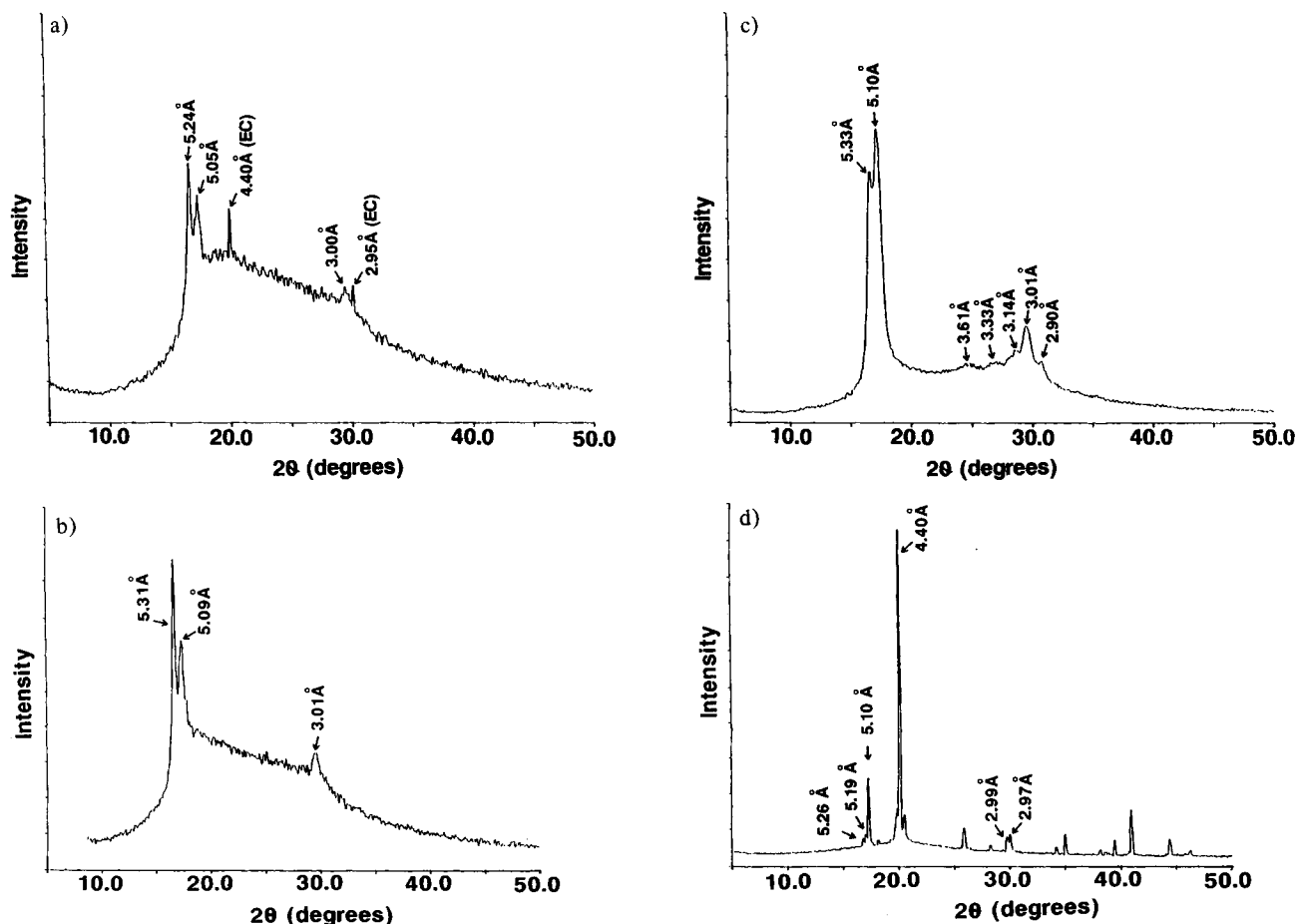


Fig. 7. X-ray diffractograms of PAN : EC gel films. (a) 30 : 70 PAN : EC. (b) 50 : 50 PAN : EC. (c) 70 : 30 PAN : EC. (d) Pure polycrystalline ethylene carbonate; a non-linear intensity scale is used in (d) so that the weaker peaks are shown. Only the peaks that could appear in the 30 : 70 PAN : EC gel film in Fig. 7 (a) are labelled.

of the solvent-rich 30 : 70 PAN : EC film in Fig. 7 (a) needs to be studied in conjunction with Fig. 7 (d) which shows the diffractogram of pure (polycrystalline) ethylene carbonate. In the 30 : 70 PAN : EC gel film in Fig. 7 (a), the strongest peaks from the pure EC crystals (4.05 Å and possibly 2.95 Å) are present; these peaks are much sharper than the polymer peaks, and are typical of crystals of organic compounds. The peaks from the polymer-solvent complex occur at 5.24 Å and 5.05 Å and again indicate the formation of the orthorhombic polymorph. Note that in Fig. 7 (d), peaks at 5.26 Å, 5.19 Å and 5.10 Å are also present in the pure EC crystals. While these three peaks in Fig. 7 (d) could contribute towards the intensity of the 5.24 Å and 5.05 Å peaks in Fig. 7 (a), the latter are chiefly due to the polymer rather than the pure EC crystals, as the strongest peak in the EC is the 4.05 Å spacing while the 5.26 Å, 5.19 Å and 5.10 Å peaks in Fig. 7 (d) are very weak in comparison. In any case, we have always observed the twin peaks at about 5.2 Å and 5.1 Å (characteristic of the orthorhombic polymorph) in the PAN-PC and the PAN-gBL gel films, where there is no question of the solvent crystallising at room temperature. There is also a considerable amount of diffuse scattering in Fig. 7 (a) between  $2\theta = 20^\circ$  and  $30^\circ$ ; this indicates that there is also liquid EC present. Thus, the diffractogram in Fig. 7 (a) can be regarded as a superposition of the scattering from three components: the PAN-EC complex, pure EC crystals and liquid EC. This is in accord with the DSC results in Fig. 6 (a), which show the melting of the pure EC crystals as well as the PAN-EC complex.

Fig. 7 (c) shows the typical diffractogram of the polymer rich 60 : 40 and the 70 : 30 PAN : EC compositions. Only one diffractogram is reproduced as the two had virtually identical traces. Now, the diffraction peaks from the pure EC crystals were not detectable as the solvent that may have been present in the amorphous regions did not crystallise. This result also co-relates well with the DSC results in Fig. 6 (b) because with this composition the melting of the polymer-solvent complex and its subsequent crystallisation was observed, but the melting or crystallisation of the pure solvent was never found. In Fig. 7 (c), the weaker peaks from the polymer-solvent complex in the region  $2\theta = 20^\circ$  to  $30^\circ$  could be detected as the diffuse scattering was reduced due to the low content of free liquid in these samples.

In fact, the PAN-EC gel films in Fig. 7(c) showed more peaks than the PAN-gBL films in Fig. 2 or the PAN-PC gel films previously reported by us [2]. The photographic diffraction pattern of slightly stretched gel films showed that all the peaks associated with the polymer were equatorial. All these peaks can be indexed as  $hk0$  reflexions with Klement and Geil's cell ( $a = 21.18 \text{ \AA}$  and  $b = 11.60 \text{ \AA}$ ). Again we emphasize that we have not observed the 10.08 Å equatorial spacing (which leads to Klement and Geil's cell) in these PAN-EC gel films.

The diffractograms from the intermediate compositions such as the 50 : 50 PAN : EC were also distinctive. By way of example, Fig. 7 (b) shows a typical diffractogram. In these compositions, the EC was present in large amounts, yet the excess liquid that was not incorporated in the polymer-solvent complex had not crystallised during cooling, and was stored in liquid form in the amorphous regions of the gel. Thus, the peaks from the pure EC crystals observed in the 30 : 70 PAN : EC gel film (Fig. 7 (a)) did not appear in Fig. 7 (b). This could be deduced from the DSC results as well, which showed only the melting of the PAN-EC complex (that is, pure EC crystals were not present). The diffracto-

gram in Fig. 7 (b) only shows the characteristic peaks of the orthorhombic form which we have attributed to the PAN-EC complex. Unlike the 70 : 30 PAN : EC compositions, these intermediate compositions however showed enhanced amorphous scattering in the interval of  $2\theta = 20^\circ$  to  $30^\circ$  (Fig. 7 (b)) due to the presence of large amounts of liquid EC.

Finally, the polarised IR spectra of an oriented PAN-EC gel film are shown in Fig. 8. The nitrile band as usual showed perpendicular dichroism. Unexpectedly, there were two bands at  $1802$  and  $1776 \text{ cm}^{-1}$ , instead of the single peak associated with the carbonyl vibration in this region of the spectrum. This was not observed with PC [5] or gBL (Fig. 3 of this work). For the further interpretation of the spectra in Fig. 8, we were fortunate to be able to draw upon the work of Angell, who assigned the bands in the (unpolarised) infrared spectrum of pure ethylene carbonate in the vapour, liquid and crystal states [28]. The  $1802 \text{ cm}^{-1}$  peak is the carbonyl ( $\text{C}=\text{O}$ ) vibration-band of the EC molecule [28] and as with the PC and the gBL, this band shows the same perpendicular dichroism as the nitrile. As before, this indicates preferential solvent orientation with respect to the draw axis and again we infer that this occurs due to anti-parallel dipole-dipole pairing between the nitriles of the polymer and the carbonyls of the solvent (Fig. 4 (b)).

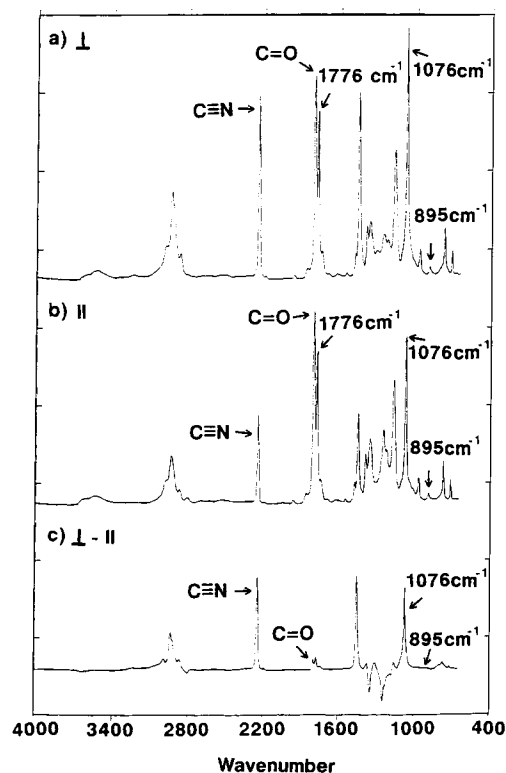


Fig. 8. Polarised IR spectra of uniaxially oriented PAN : EC films. (a) Polarisation perpendicular to draw axis, (b) polarisation parallel to draw axis and, (c) partial dichroic spectrum.

The  $1776 \text{ cm}^{-1}$  peak is a Fermi resonance band [28]. This band is the overtone of the  $\nu_1$  ( $895 \text{ cm}^{-1}$ ) skeletal-breathing vibration of the EC ring with symmetry class  $a_1$  in the  $C_{2v}$  point group. The dichroism of this band must therefore mimic the  $\text{C}=\text{O}$  band since this is also of  $a_1$  symmetry. The overtone of an  $a_1$  band must necessarily be  $a_1$  as the direct product of the two irreducible representations is of course  $a_1$ ; that is,  $a_1 \times a_1 = a_1$ . The perpendicular dichroism of the

895 cm<sup>-1</sup> EC band could also be detected by careful inspection of the spectra. Perpendicular dichroism is also observed in the 1076 cm<sup>-1</sup> ( $\nu_5$ ) skeletal stretch of the EC ring. (This band is overlapped with the broader 1073 cm<sup>-1</sup> PAN band which also displays perpendicular dichroism). Again, this dichroic behaviour is as anticipated, based on the  $a_1$  symmetry of the  $\nu_5$  EC-vibration.

These data give a self-consistent set of dichroic behaviour, which fits the proposed orientation of the EC molecule with respect to the chain axis (Fig. 4 (b)). Whereas with the PC and gBL systems, the solvent orientation was deduced solely from the dichroism of the carbonyl vibration (we did not have assignments of the other solvent bands), with the EC, the dichroism of the carbonyl band as well as the vibrations associated with the EC ring concur with the orientation of the molecule shown in Fig. 4 (b).

Incidentally, these polarised IR results, acquired in an entirely different context, also provide an independent confirmation that Angell's [28] assignments of the aforementioned bands in the unpolarised IR spectrum of pure ethylene carbonate are correct.

In summary, the IR results in this work and the previous one [5] have consistently pointed to solvent orientation with several solvents containing carbonyl groups. Moreover, the nature of the dichroism is always the same in all the solvents examined and it strongly suggests complexing with the nitrile groups on the chains [5]. It provides circumstantial evidence for the possibility of formation of solvated crystallites, whose X-ray diffractograms are different from that of the hexagonal polymorph found in dry PAN.

#### 4 Conclusions

These are the principal conclusions:

- (a) Concentrated PAN-gBL and PAN-EC solutions gelled on cooling.
- (b) The gel films showed sharp X-ray diffraction peaks, indicating that crystallisation involving the polymer chains was the principal cause of gelation.
- (c) The diffractograms of the gel films were different from that of the dry polymer powder. There appeared to be a transition from hexagonal packing of chains to an orthorhombic form.
- (d) DSC experiments showed first-order phase transitions on heating and cooling of the gel films. This is consistent with a polymer which, though not crystalline in the conventional sense, is not amorphous either. In the PAN-EC gel films, melting of the pure solvent crystals was also observed in solvent-rich specimens.

- (e) IR dichroism studies showed that uniaxial drawing leads not only to polymer orientation but to orientation of the solvent molecules. The orientation adopted by the solvent molecules was suggestive of dipolar interactions between the carbonyl group of the solvent molecule and the nitrile group of the polymer. The binding of the solvent with the polymer would support the possibility of formation of solvated crystallites when a PAN solution in these solvents is cooled.

These results parallel those found with PAN-propylene carbonate solutions originally [1-3].

#### References

- [1] Z. Bashir, *J. Polym. Sci. (Phys.)* **1992**, *30*, 1299.
- [2] Z. Bashir, *Polymer* **1992**, *33*, 4304.
- [3] Z. Bashir, A. Tipping, I.R. Herbert, *in print, J. Polymer Sci. (Phys.)*.
- [4] Z. Bashir, *patent application WO. 92/0/830 to Courtaulds plc 1991*.
- [5] Z. Bashir, S.K. Atureliya, S.P. Church, *J. Materials. Sci.* **1993**, *28*, 2721.
- [6] S.K. Atureliya, Z. Bashir, *in print, Polymer*.
- [7] Z. Bashir, G. Manns, D.M. Service, D.C. Bott, I.R. Herbert, R.N. Ibbett, S.P. Church, *Polymer* **1991**, *32*, 1826.
- [8] C.R. Bohn, J.R. Schaeffgen, W.O. Statton, *J. Polymer Sci.* **1961**, *55*, 531.
- [9] G. Natta, G. Mazzanti, P. Corradini, *Rendiconti delle sedute della Accademia Nazionale dei Lincei, XXV*, *3 (Ferie 1958)*.
- [10] S.B. Warner, D.R. Uhlmann, L.H. Peebles, Jr. *J. Materials Sci.* **1979**, *14*, 1893.
- [11] A. Labudzinska, A. Wasiak, A. Ziabicki, *J. Polym. Sci. Part C*, **1967**, *16*, 2835.
- [12] D.R. Paul, *J. Appl. Polym. Sci.* **1967**, *11*, 439.
- [13] V.F. Holland, S.B. Mitchell, W.L. Hunter, P.H. Lindenmeyer, *J. Polym. Sci.* **1962**, *62*, 145.
- [14] P.H. Lindenmeyer, R. Hosemann, *J. Appl. Phys.* **1963**, *34*, 42.
- [15] J.J. Klement, P.H. Geil, *J. Polym. Sci.* **1968**, *A2 (6)*, 1381.
- [16] G. Hinrichsen, H. Orth, *Kolloid-Z u. Z. Polymere* **1971**, *247*, 844.
- [17] M. Sokoł, J. Grobelny, E. Turska, *Polymer* **1987**, *28*, 843.
- [18] M. Sokoł, E. Turska, *Acta Polymerica*, **1984**, *35*, 135.
- [19] M. Sokoł, J. Grobelny, E. Turska, *Polymer* **1991**, *32*, 2161.
- [20] R.C. Houtz, *Textile Res. J.* **1950**, *20*, 786.
- [21] W.O. Statton, *Ann. N.Y. Acad. Sci.* **1959**, *83*, 27.
- [22] Z. Bashir, S.P. Church, D. Waldron, *in print, Polymer*.
- [23] N. Grassie, R. McGuchan, *European Polym. J.* **1971**, *7*, 1091.
- [24] B.G. Frushour, *Polym. Bull.* **1981**, *4*, 305.
- [25] B.G. Frushour, *Polym. Bull.* **1982**, *7*, 1.
- [26] W.R. Krigbaum, N. Tokita, *J. Polym. Sci.* **1960**, *XLIII*, 467.
- [27] J. Runt, I.R. Harrison in *"Methods of Experimental Physics"*, pp. 287, vol. 16, part B (Academic Press, New York 1980).
- [28] C.L. Angell, *Trans. Faraday Soc.* **1956**, *52*, 1178.

Received May 17, 1993