

# Structural order in alkali-degraded PAN as seen in studies of low-temperature thermal conductivity

N. S. Batty, A. J. Gradwell and J. T. Guthrie

*Department of Colour Chemistry and Dyeing, University of Leeds, Leeds LS2 9JT, West Yorkshire, UK*

D. Greig, N. D. Hardy, R. Jakeways and M. Sahota

*Department of Physics, University of Leeds, Leeds LS2 9JT, West Yorkshire, UK*  
(Received 8 March 1982)

The thermal conductivity,  $\kappa$ , of polyacrylonitrile (PAN), subjected to varying degrees of degradation, has been measured in the temperature range 2–100 K as a means of studying the structural order of the samples. Although, at higher temperatures, the variation in  $\kappa$  throughout the range of specimens is only ~30%, at 2 K there is an order of magnitude increase in conductivity between the undegraded and most highly degraded samples. Such a change is indicative of a pronounced decrease in crystallinity, and this interpretation is supported by estimates of crystallinity as seen through X-ray analysis.

**Keywords** Polyacrylonitrile; low temperature; thermal conductivity; crystallinity morphology

## INTRODUCTION

There has recently been some considerable interest in the alkali induced degradation of polyacrylonitrile (PAN) with particular emphasis on chain scission, thermal stability and other physical characteristics. For example, possible structural changes on degradation have been investigated<sup>1</sup>. In this paper we are concerned with the changes that take place on degradation, in the level and type of structural order within samples of PAN, using the temperature dependence of thermal conductivity in the temperature range 2–100 K as a probe. Recent measurements of this parameter in other polymers have shown that while its value at a given temperature is largely independent of the type of polymer, it is dependent on structure and the degree of crystallinity present<sup>2</sup>. In the experimental section we discuss sample preparation in detail and some of the more important points in measuring thermal conductivity. The details of this technique have been published elsewhere<sup>3</sup>.

## EXPERIMENTAL

A sample (25 g) of polyacrylonitrile (PAN) was prepared by solution polymerization of acrylonitrile using a 2:1 molar mixture of dimethylformamide and acrylonitrile. Initiation was radiation induced by exposure to  $4 \times 10^5$  rads using a 10 000 Curie <sup>60</sup>Co source. Degassed solutions were prepared by evacuating and sealing at  $1.33 \times 10^{-2}$  N m<sup>-2</sup>. Four freeze-thaw cycles were applied in the range 77–293 K in the normal manner. After irradiation, the polymer solution was diluted four fold with dimethylformamide before precipitation in a 10 times excess of rapidly stirred water. The suspension was filtered on number 4 porosity sintered crucibles, thoroughly washed

with water and then methanol before drying to constant mass at 313 K and  $1 \times 10^2$  N m<sup>-2</sup>.

## DEGRADATION PROCEDURES

The PAN was dissolved in DMF (17.4 g dm<sup>-3</sup>, density,  $\rho = 0.9518$  kg dm<sup>-3</sup>) so that there was 1 mole of acrylonitrile residue to 39 moles of DMF. 75 cm<sup>3</sup> of this solution was transferred to a tightly stoppered flask which was immersed in a water-bath for 10 min at 303 K. The flask was then stirred with a magnetic stirrer while 0.50 cm<sup>3</sup> of aqueous potassium hydroxide solution was added carefully. The flask was immediately stoppered and returned to the water bath where it was gently agitated. The concentration of the potassium hydroxide solution was 18% (w/v). This addition of alkali corresponds to 1.2 g of solid alkali per dm<sup>3</sup> of polymer solution. The time for degradation was varied between  $1.1 \times 10^4$  and  $1.3 \times 10^5$  s. After degradation, the polymer was precipitated by discharging the solution into a mixture of methanol and diethyl ether (90:10), containing 0.03 cm<sup>3</sup> of hydrochloric acid. The non-solvent provided a means of obtaining a suitable sample form while neutralizing excess alkali in the system. After considerable preliminary experimentation, it was realized that this was the suitable composition for the non-solvent mixture. The degraded polymer was isolated on a number 4 porosity, sintered crucible, washed with distilled water and dried as described previously. In this way, samples were obtained which had been subjected to various levels of alkali induced degradation.

To assess the degree of apparent 'recovery' from degradation a representative sample of the most highly degraded sample was treated with hydrochloric acid (4.0 g

per dm<sup>3</sup> of solution) after solution in dimethylformamide at a concentration which was in excess of that needed for neutralization. The treatment led to a pronounced reduction in colour of the polymer solution. The polymer was then isolated from the solution by precipitation and after-treatment as described above.

Samples of undegraded, degraded and 'recovered' PAN were then prepared for assessment of their thermal conductivity characteristics. Using a specially designed disc-press, each polymer was compressed into a disc (2.5 cm in diameter, 0.3 cm thickness) by subjection of the die and sample to a force of  $5 \times 10^4$  N m<sup>-2</sup> for 120 s in a hydraulic press at room temperature. The discs were of sufficient strength to withstand subsequent handling and machining.

### THERMAL CONDUCTIVITY

The thermal conductivity measurements were made between 2 and 100 K using a steady heat-flow method in a cryostat immersed in liquid helium. As full details have appeared elsewhere<sup>3</sup>, only a brief description of the technique will be given here.

The principle of the method is to measure the inward radial flow of heat generated in a heater wound on the rim of the sample. For poor thermal conductors such a geometry lends itself to a much shorter equilibrium time than would be found in the more familiar method of measuring the temperature gradient along a rod. Other advantages of the method include smaller heat losses along the leads and a more uniform flow of heat.

In this particular experiment, the distance between the thermocouple thermometers, mounted radially on the discs, was of the order of 5 mm. For each disc, thermal contact to the cryostat was provided by a 10BA screw threaded into its central axis, while the heater wound on the rim was about 200Ω.

The temperature gradient along the direction of heat flow and the absolute temperature of one point on the sample were measured by Au-Fe/chromel thermocouples, with the temperature of the helium bath used as a reference in the latter case. The lengths of the thermocouple wires were chosen to ensure negligible heat loss by conduction. During the experimental runs, the sample chamber was evacuated to less than 10<sup>-5</sup> Torr. The absolute accuracy was largely determined by the geometrical factors and was estimated to be 5 per cent.

### RESULTS AND DISCUSSION

#### Alkali induced degradation

On treatment of the PAN solutions with alkali, the solutions became yellow almost immediately and, with the higher concentrations of alkali, the colour deepened, through orange to deep brownish red. Selected samples of the degraded polymer were compared with each other, the undegraded sample and the 'recovered' samples using a number of techniques. On 'recovery' the deep brownish-red colouration was rapidly discharged, leaving a pale yellow solution. Without exception, precipitation from solution produced a polymer, having the same colour as its solution. The residual liquid phase was colourless. The techniques used in evaluation included ultra violet, visible and infra-red spectroscopy, viscometry, osmometry and thermal analysis. Our observations on viscometric factors

have been reported earlier<sup>4</sup>. Here we shall consider observations concerned with the low temperature thermal conductivity of the samples and possible interpretations based on changes in bulk structure.

#### X-ray measurements: crystallinity

An estimation of the crystalline fraction of each sample was made using standard X-ray techniques. The basis of the method is that the ratio of the intensity of coherent scattering (from ordered material) to the intensity of incoherent scattering (from disordered material) is equal to the mass ratio of ordered to disordered material.

A diffractometer was used to record the X-ray scattering from the samples using CuKα radiation over a range of 2θ from 10° to 100°. Broad peaks were observed superimposed on a considerable incoherent background. The spectra were corrected for polarization and the geometrical (Lorentz) factor and the areas under the curve corresponding to the peaks and to the background were estimated. The ratio of the two areas is then equal to *X*, the ratio of the fractions of crystalline and non-crystalline material as given in Table 1.

Owing to the low crystallinity and to the fact that (1) the crystal structure of PAN is not well defined and (2) the peaks were very broad, there is considerable uncertainty in the absolute values of crystallinity but the relative crystallinities of the samples are well represented by the data.

#### X-ray measurements: morphology

Precise details of the morphology of these materials are not easy to obtain but some useful information can be gleaned from X-ray studies. Small angle photographs using CuKα radiation and a Frank's camera capable of revealing structure up to about 300 Å show very strong scattering but not discrete peaks. There is thus no unique lamellar spacing of less than about 300 Å. This is in accord with studies on fibres (e.g. ref 5) where no permanent peak is seen in the SAXS pattern.

Wide angle diffractograms yield more definite information in that the breadth of discrete lines can be used to estimate a dimension of the crystalline entity, giving rise to the reflection. For these samples only one line at 2θ = 16.7° (CuKα) is sufficiently well separated to be used in this way. The assignment of this reflection is dubious but it is known to be of type (hk0) from fibre studies<sup>5</sup>. Early work<sup>6</sup> suggested it to be a (200) reflection from an orthorhombic structure but there is actually considerable uncertainty in the structure of PAN. Therefore we can deduce only a rough figure for the mean 'crystalline dimension' normal to the chain axis. The full width at half height of the peaks Δ(2θ) was measured after subtracting the continuum radiation and these are shown

Table 1 Crystallinity, *X*, crystalline size,  $\bar{L}$ , and crystallite separation, *D*, as deduced from X-ray data

Sample	<i>X</i>	Δ(2θ)°	$\bar{L}$ (Å)	$D = \bar{L}X^{-1/3}$ (Å)
P1 Undegraded	0.12	1.7	47	95
P2 Slightly degraded	0.11	1.7	47	98
P3 Moderately degraded	0.095	2.6	31	68
P4 Highly degraded (with acid treatment) (partly recovered)	0.079	2.3	35	82
P5 Highly degraded	0.039	2.9	28	82

in Table 1. The instrumental line width is so small (a fraction of a degree) that no correction is necessary and so a mean crystalline size  $\bar{L}_{hkl}$  can be deduced from the usual relationship.

$$\bar{L}_{hkl} = \frac{C\lambda}{\cos \theta_{hkl} \Delta(2\theta)} \quad (1)$$

where  $\Delta(2\theta)$  is measured in radians and  $C$  is a constant generally taken to be 0.9. The figures in the Table are comparable with those in fibres<sup>5</sup>.

The simplest model of the material is to consider that the crystalline elements are all identical cubes of side  $\bar{L}$  as in the Table, spaced a distance apart,  $D$ , equal to  $\bar{L}X^{-1/3}$ . Degradation would reduce  $\bar{L}$  but leave  $D$  unchanged. The final column in Table 1 shows values of  $\bar{L}X^{-1/3}$  which indeed remain reasonably constant at around  $85 \pm 15 \text{ \AA}$ .

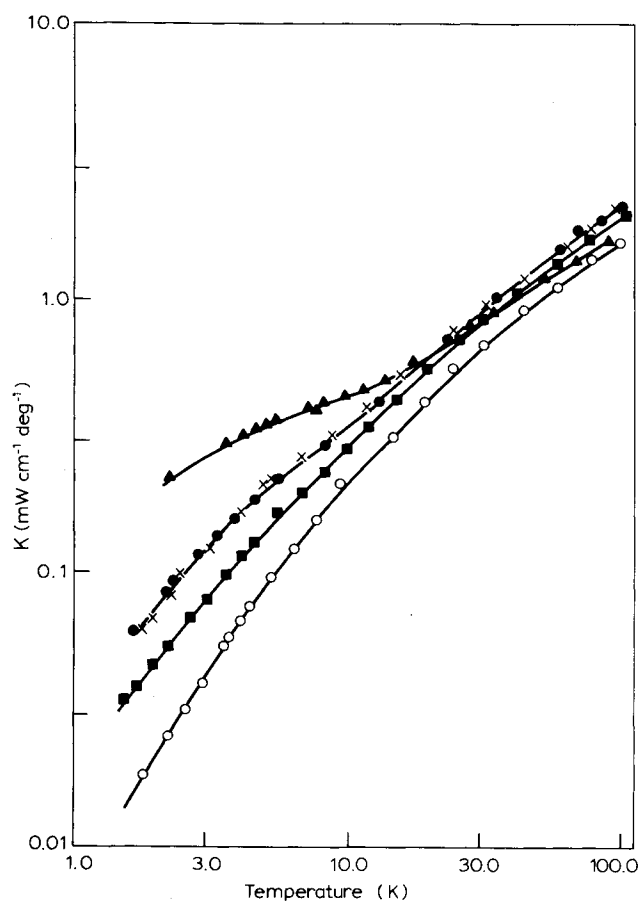


Figure 1 Temperature dependence of thermal conductivity,  $\kappa$ . The symbols represent: (▲) highly degraded; (+) moderately degraded; (■) slightly degraded; (●) highly degraded with acid treatment; (○) undegraded

Although these figures have large uncertainties, we should bear in mind that they are based on a fairly crude model, since the small angle measurements indicate a wide distribution of spacings between diffracting elements. The calculated values of  $D$  give a guide, however, to the general morphology of the samples in which we visualize an array of crystalline blocks of 'dimension'  $L$  in a matrix on non-crystalline material whose volume we know relative to the total volume of the ordered polymer.

#### Thermal conductivity

The temperature dependence of thermal conductivity,  $\kappa$ , is shown in Figure 1 with values at selected temperatures given in Table 2. It is clear that, although above about 20 K there is only a relatively narrow spread in the values, at the lowest temperatures there is an order of magnitude difference across the range. This general trend has been reported in a number of previous papers<sup>7,8</sup> in which it has been correlated with a change in the size and concentration of the scattering centres. We note that this effect is seen, not only in polymers with varying crystallinity, but also in all composite solids<sup>9,10</sup> of which semicrystalline polymers are only a sub-group.

The characteristic features of a composite system consisting of an amorphous matrix with a filler of high bulk conductivity are shown in Figure 2. Starting from the 'Universal' temperature dependence of completely amorphous solids<sup>11</sup> we find that increasing the fractional volume of filler (the crystallinity in the case of a polymer) results in an overall increase in conductivity at high temperatures but a large decrease below about 25 K. This latter feature is attributed to boundary effects limiting the conductivity of the filler and blocking the heat flow through the matrix when the mean free path of the conducting phonons becomes relatively large.

There is also the possibility of a change in conductivity due to altering the size of the filler particles or crystallites. This effect, brought about by a change in the number of particles in a given volume, is observed almost entirely at the lower end of the temperature range where an increase in particle size leads to an overall enhancement of  $\kappa$ . However, for the present samples, the variation of crystallite size is relatively low so the effect on  $\kappa$  is likely to be small.

Comparing Figure 2 with Figure 1 it is clear that the overall features are present in our results. At one extreme in the highly degraded sample, there is evidence of a plateau between 3 and 20 K with a strong implication that the sample is largely amorphous. On the other hand, the conductivity of the undegraded sample at the lowest temperatures is more than an order of magnitude smaller, and, taking account of the X-ray data, we postulate that the extra resistance is caused by the presence of small crystallites.

Table 2 Measured thermal conductivities ( $\text{mW cm}^{-1} \text{ deg}^{-1}$ ) at selected temperatures

Sample	Temperature								
	2	3	5	10	20	40	60	80	100
P1	0.022	0.040	0.089	0.22	0.44	0.84	1.16	1.42	1.60
P2	0.045	0.076	0.145	0.28	0.56	1.02	1.40	1.70	1.95
P3	0.072	0.120	0.21	0.34	0.65	1.12	1.50	1.85	2.20
P4	0.072	0.120	0.21	0.34	0.65	1.12	1.50	1.85	2.20
P5	0.20	0.265	0.35	0.44	0.65	1.02	1.30	1.50	1.70

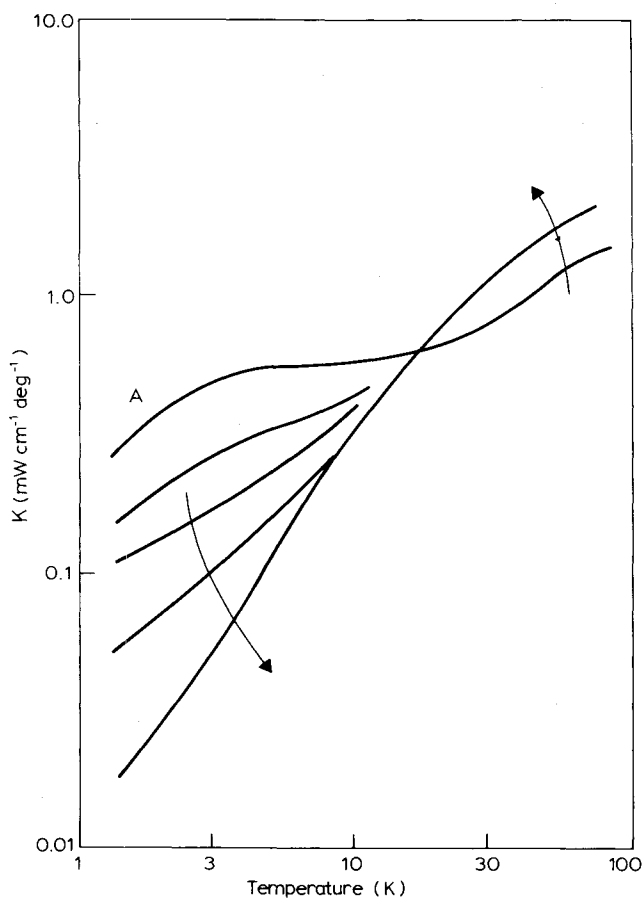


Figure 2 Schematic variation of the temperature dependence of thermal conductivity with crystallinity in semicrystalline polymers. Curve A is characteristic of amorphous materials with a plateau region from about 4 to 15 K. The arrows show the direction of change with increasing crystallinity and are seen to be in opposite directions at high and low temperatures (see references 7 and 8)

There are various models for the conductivity (thermal and electrical) of a composite system, all of which depend on (i) the separate conductivities of the matrix and filler and (ii) the geometrical arrangement of the filler particles<sup>12</sup>. As a simple approximation to the present system of a dilute homogeneous assembly of crystallites, we have chosen the model that gives the overall  $\kappa$  for a dilute random array of discs. For a volume fraction  $X$  (in our case  $X$  is the fractional crystallinity) the appropriate expression is:

$$X = \frac{3\kappa_C(\kappa - \kappa_A)}{(\kappa_C - \kappa_A)(\kappa_A + 2\kappa_C)} \quad (2)$$

where  $\kappa_A$  is the thermal conductivity of the amorphous matrix and  $\kappa_C$  that of the crystalline discs. If we assume that for any particular polymer system the values of  $\kappa_A$  and  $\kappa_C$  are constant, we see that  $X$  should be proportional to  $(\kappa - \kappa_A)$  and that  $\kappa$  is a unique function of  $X$ .

We must emphasize that equations such as this are only approximations with the conductivity given in terms of the volume fraction of the crystalline phase, with no allowance for details of the crystallite dimensions. (The only limitation of the model is that the dimensions of the 'filler' phase are small compared to the size of the specimen.) In practice, changes in the dimensions of the crystallites could manifest themselves both as size-dependent  $\kappa_C$  and as an additional mismatch between the

two phases. In using expressions such as (2) we are therefore assuming that size-dependent effects are small, and, for the PAN samples, this is supported by the X-ray data in Table 1.

As a test of the relationship, we show in Figure 3 the variation of  $(\kappa_A - \kappa)$  at 1.5 K with the known crystallinities of several samples of poly(ethylene terephthalate) (PET). The data were obtained from reference 7 with  $\kappa_A = 0.268 \text{ mW cm}^{-1} \text{ deg}^{-1}$  as found in a specimen that is virtually amorphous. We have chosen the values at the lowest temperature at which measurements are available, as we see in Figure 2 that the differences between the measured  $\kappa$  are then at their greatest. It is clear from Figure 3 that the

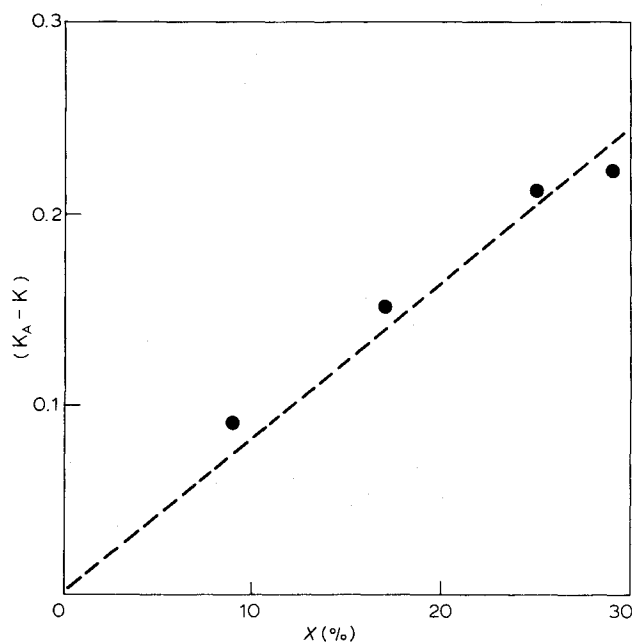


Figure 3 Variation of  $(\kappa_A - \kappa)$  for PET at 1.5 K with crystallinity,  $X$ , where  $X$  was obtained from density measurements. The value of  $\kappa_A$  is  $0.268 \text{ mW cm}^{-1} \text{ deg}^{-1}$  (all data from reference 7)

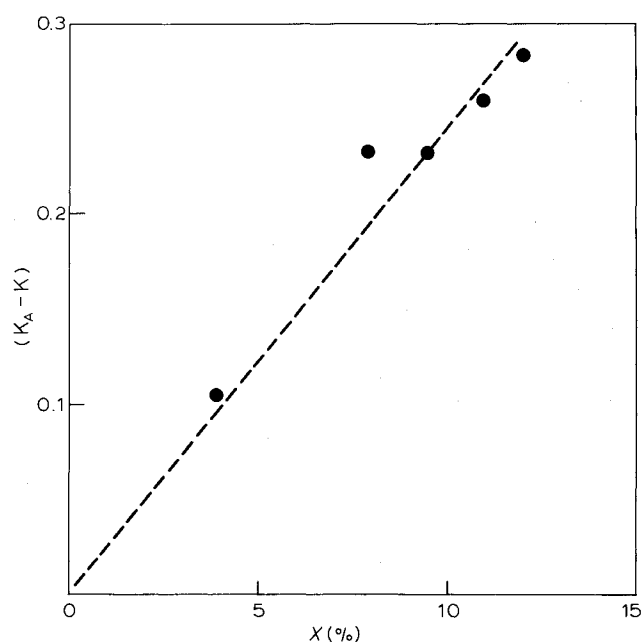


Figure 4 Variation of  $(\kappa_A - \kappa)$  with PAN at 2 K with crystallinity,  $X$ , as given in Table 1. The value of  $\kappa_A$  is  $0.305 \text{ mW cm}^{-1} \text{ deg}^{-1}$

linear relationship between  $(\kappa_A - \kappa)$  and  $X$  is amply confirmed.

Returning, therefore, to the results on PAN we are faced with the problem that we do not have a sample that is truly amorphous from which to obtain  $\kappa_A$ . However, as the  $\kappa$  versus  $T$  curve for amorphous solids is essentially 'universal', we can adopt the value measured in nearly amorphous PET. The variation of  $(\kappa_A - \kappa)$  at the lowest temperature measured (in this case 2 K) with the crystallinity deduced from X-ray data (Table 1) is then shown in Figure 4. We see that apart from one anomalous point that relates to the specimen that has been treated with acid the others all lie on a straight line. This impressive correlation with the X-ray measurements shows both the self-consistency of the argument and the value of low temperature thermal conductivity measurements in estimating the crystallinity of polymers.

## CONCLUSIONS

Correlation of X-ray data with those provided by thermal conductivity measurements indicates that a significant decrease in physical order occurs in PAN with increase in the level of degradation, induced by alkali when in solution in DMF. These physical changes are observed to be a consequence of changes in the structural nature of the PAN arising from degradation. This is especially so when possible hydrolysis reactions and scission events are taken into account. Treatment of highly degraded PAN with controlled amounts of HCl solution provides an apparent

increase in ordering, as shown by the estimates of crystallinity shown in Table 1. The information provided by this study supports observations of recovery phenomena occurring in PAN solutions after alkali induced degradation, upon treatment with an acidic medium as seen in changes in the viscometric properties<sup>4</sup> and spectroscopic properties<sup>13</sup> of such solutions.

## ACKNOWLEDGEMENTS

We acknowledge the financial support given by the International Atomic Energy Agency, Vienna (J.T.G. and N.S.B.) and by the S.E.R.C. (D.G., N.D.H., R.J. and M.S.) towards this work.

## REFERENCES

- 1 Batty, N. S. and Guthrie, J. T. *J. Appl. Polym. Sci.* 1980, **25**, 2539
- 2 Choy, C. L. *Polymer* 1977, **18**, 984
- 3 Burgess, S. and Greig, D. *J. Phys., (D)* 1974, **7**, 2051
- 4 Batty, N. S. and Guthrie, J. T. *Polymer* 1978, **19**, 1145
- 5 Warner, S. B., Uhlmann, D. R. and Peebles, L. H. *J. Math. Sci.* 1979, **14**, 1893
- 6 Stefani, R., Chevreton, M., Garnier, M. and Eyraud, C. *Compt. Rend. Acad. Sci. Paris* 1960, **251**, 2174
- 7 Choy, C. L. and Greig, D. *J. Phys., (C)* 1975, **8**, 3121
- 8 Assfalg, A. *J. Phys. Chem. Solids* 1975, **36**, 1389
- 9 Garrett, K. W. and Rosenberg, H. M. *J. Phys., (D)* 1974, **7**, 1247
- 10 Schmidt, C. *Cryogenics* 1975, **15**, 17
- 11 Stephens, R. B. *Phys. Rev., (B)* 1973, **8**, 2896
- 12 Hale, D. K. *J. Math. Sci.* 1976, **11**, 2105
- 13 Batty, N. S. and Guthrie, J. T. *Makromol. Chem.* 1981, **182**, 71