polymer papers

The variation of the *d*-spacings with stress in the hexagonal polymorph of polyacrylonitrile

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(Received 12 November 1993; revised 21 March 1994)

The normal X-ray fibre pattern of polyacrylonitrile (PAN) consists of just two sharp equatorial peaks ($d_1 \sim 0.53$ nm and $d_2 \sim 0.30$ nm), and very diffuse meridional and off-axis scattering. This has been attributed to a hexagonal packing of chains, with no periodicity along the chain axis. In this work, we have investigated the effect of a tensile stress on this fibre pattern. It was found that both d_1 and d_2 decreased with increasing stress, but the ratio d_1/d_2 remained constant within experimental error at $\sqrt{3}/1$. This indicated that the 'molecular rods' decreased in diameter on application of the stress, but their packing remained essentially hexagonal. The normal meridional scattering from PAN shows a two-component broad peak; when stress was applied, there was no shift in the positions of either component, but there was a transfer of intensity from high to low 2θ values. This was also consistent with a slight extension of the rod. By adopting a simple model of extending rods, it was possible to compute an X-ray stress–strain curve and a modulus from the change in the two equatorial peaks.

(Keywords: polyacrylonitrile; hexagonal polymorph; X-ray diffraction)

INTRODUCTION

The diffraction patterns of polyacrylonitrile (PAN) appear to be of two types. The most common pattern[1–11], attributed to a hexagonal polymorph, contains just two sharp equatorial peaks, $d_1 \sim 0.525$ nm and $d_2 \sim 0.305$ nm, whose ratio d_1/d_2 is $\sqrt{3}/1$. This is shown schematically in *Figure 1*. We shall refer to this as the 'standard' fibre pattern of PAN, as it is always observed in highly drawn fibres and films[1,2,11]. Unlike more common semicrystalline polymers such as polyethylene and cellulose, it can be seen that there are no sharp non-equatorial peaks in *Figure 1*; there is some meridional and off-axis scattering, but it is so diffuse that Bohn *et al.*[2], Lindenmeyer and Hosemann[12] and others have concluded that it cannot be regarded as crystalline in origin. This kind of diffraction pattern has led Bohn *et al.* to suggest that PAN is a 'laterally ordered' polymer[2,3].

Diffraction patterns of PAN different from the one shown in *Figure 1* have been reported by some workers, though these appear to be less common[13–18]. These are usually characterized by two intense, close spacings (0.53 and 0.51 nm). However, in these 'non-standard' patterns, there appear to be significant variations between different authors in terms of the peak positions and their number[13–18]; for instance, one set of authors report 13 peaks[16], while another set quotes as many as 19 peaks[17]. These diffraction patterns have been associated with an orthorhombic form[13–18]. The conditions under which the hexagonal or orthorhombic forms appear are often not discussed, and some authors appear to think that the orthorhombic form is the definitive structure of PAN principally because more peaks have been obtained[14–19]. However, recently it has been suggested that the hexagonal form always appears in dry polymer[20], whereas the orthorhombic form tends to appear in solvent-containing samples such as gels[20,21], or single crystals obtained from solutions[13,22,23]. It has also been suggested that the non-standard patterns may arise from the formation of solvated crystallites[20,21,24–29].

In a previous work, we attempted to measure an 'X-ray crystal modulus' for PAN[7]. This was based on the technique of measuring the displacement of a meridional crystalline peak on the application of a tensile stress. This method has been successfully applied to several semicrystalline polymers such as polyethylene, cellulose and poly(vinyl alcohol)[30,31]. Such experiments showed that the modulus attained normally in macroscopic fibres was very much lower than the maximum attainable tensile modulus, and such information provided some of the spur for obtaining high-modulus fibres from several polymers in recent times. In the case of PAN, there appeared to be no such estimates of the maximum attainable modulus.

We had hoped that the X-ray technique would be applicable to PAN, as a few workers such as Colvin and Storr[18] had shown diffraction patterns with sharp meridional spacings. However, in our last investigation, we invariably obtained the 'standard' diffraction pattern of PAN, of the type shown in *Figure 1*; further, since our specimen was biaxially oriented, it was possible to show directly the existence of hexagonal symmetry by

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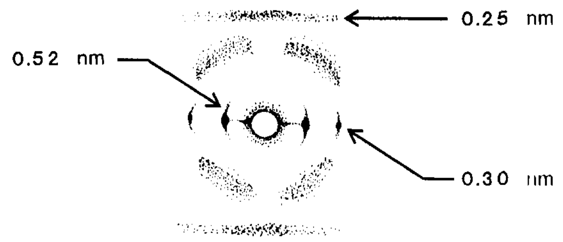

Figure 1 A sketch of the standard fibre pattern of oriented polyacrylonitrile (hexagonal polymorph) with fibre axis vertical. There are two equatorial peaks ($d_1 \sim 0.52$ nm and $d_2 \sim 0.30$ nm) and diffuse meridional and off-axis scattering. The meridional scattering is much weaker than suggested here

obtaining a diffraction pattern with the X-ray beam passed down the fibre axis[7]. As a result, we were forced to come to the view that the normal diffraction pattern of highly drawn PAN is *always* of the type shown in *Figure 1*, and all other patterns arise for other reasons[13–20]. Owing to the absence of sharp meridional peaks in *Figure 1*, it was not possible to measure directly a crystal modulus by the above-cited method[7]. However, by comparing the conformations adopted by the atactic PAN chains with polymers that adopt a helical conformation, the maximum tensile modulus of PAN was estimated[7] to be about 55 GPa.

Though we were thwarted in our attempts to reproduce the diffraction patterns of those who claimed meridional peaks in PAN[16–18], we have nevertheless gone ahead and investigated the effect that tensile stress has on the equatorial peaks of *Figure 1*. This is reported here. here.

EXPERIMENTAL

Sample preparation

The sample used was a biaxially oriented strand (typically 50 mm long, 2 mm wide and 0.2 mm thick) produced by a method we previously[7] called 'compression–elongation'. Briefly, this consists of compression moulding a plaque from PAN powder and then deforming this in a mould between two backing sheets of poly(methyl methacrylate). More details of sample preparation can be found in the previous work[7]. With this sample, when the X-ray beam was passed in a direction perpendicular to the long axis of the strand, the conventional fibre pattern of the hexagonal polymorph (*Figure 1*) was obtained. Passing the beam down the fibre axis gave a six-arc pattern revealing the hexagonal symmetry[7].

Application of stress and X-ray measurements

As polymer samples can show viscoelastic behaviour on application of a stress, so that the 'equilibrium strain' is not attained instantly, the change in the diffraction pattern on imposition of a constant tensile stress was probed as a function of time. The time evolution of the strong equatorial reflections in *Figure 1* with the applied stress was examined using a position-sensitive detector (PSD) and a conventional X-ray source working at 40 kV and 30 mA. The time evolution of the weak meridional scattering in *Figure 1* on application of a stress was followed by using X-rays from a synchrotron source (Daresbury, UK).

The variation of the diffraction pattern of a sample under a series of constant stress levels was observed using the conventional X-ray source. A tensile stress was applied to the sample in incremental steps until it broke. At each new level of stress, the sample was held for 5 min so that the 'equilibrium strain' was achieved before its diffraction pattern was recorded. The pattern was acquired in 1 min. Equatorial diffractograms were acquired with the beam perpendicular to the strand (fibre) axis, using the PSD. The change in the meridional scattering on application of a progressive stress was acquired with the sample tilted at 19° to the beam and the PSD centred at $2\theta = 38°$. The acquisition time for this was 30 min.

RESULTS AND DISCUSSION

The effect of stress on the equatorial peaks

The change in the two equatorial d-spacings (d_1 and d_2) as a function of time on application of a constant stress was initially examined. *Figures 2a* and *2b* show a rapid response to a stress of 2.16×10^8 N m^{-2}. The first point at $t = 0$ in *Figure 2* gives the d-spacings of the unstressed sample; the ratio of d_1/d_2 for the unstressed sample is $0.5246/0.3032 \simeq \sqrt{3}/1$, which is characteristic of hexagonal packing. After 5 min, it can be seen that an equilibrium d-spacing, which is lower than the unstressed value, has effectively been established. Similarly, the real-time response of the meridional scattering about $2\theta = 38°$, which was investigated using the synchrotron source, revealed that there was no detectable change 1 min after application of the stress (not shown).

Based on the preceding experiment, an equilibration time of 5 min at each stress level was therefore considered sufficient in the next experiment, where the change in the two equatorial spacings, d_1 and d_2, as a function of stress was probed. *Figures 3a* and *3b* show that both d_1 and

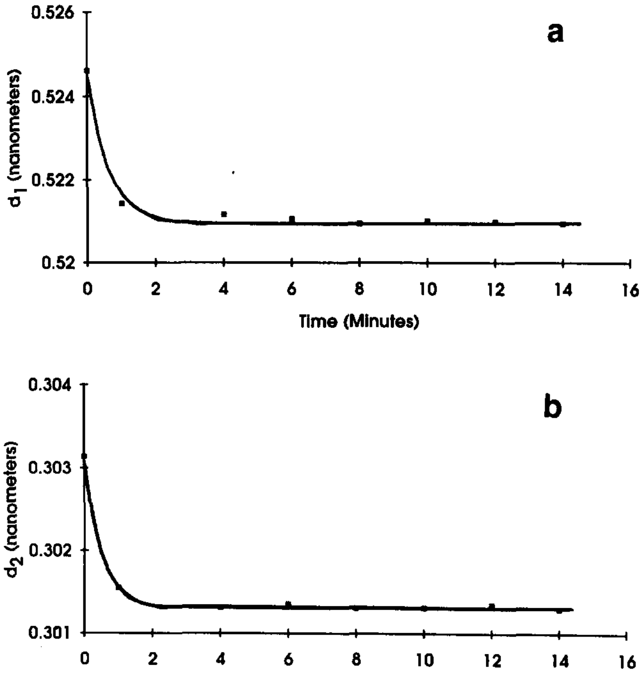

Figure 2 The variation of (a) the d_1-spacing and (b) the d_2-spacing with time after application of a constant stress of 0.216 GPa

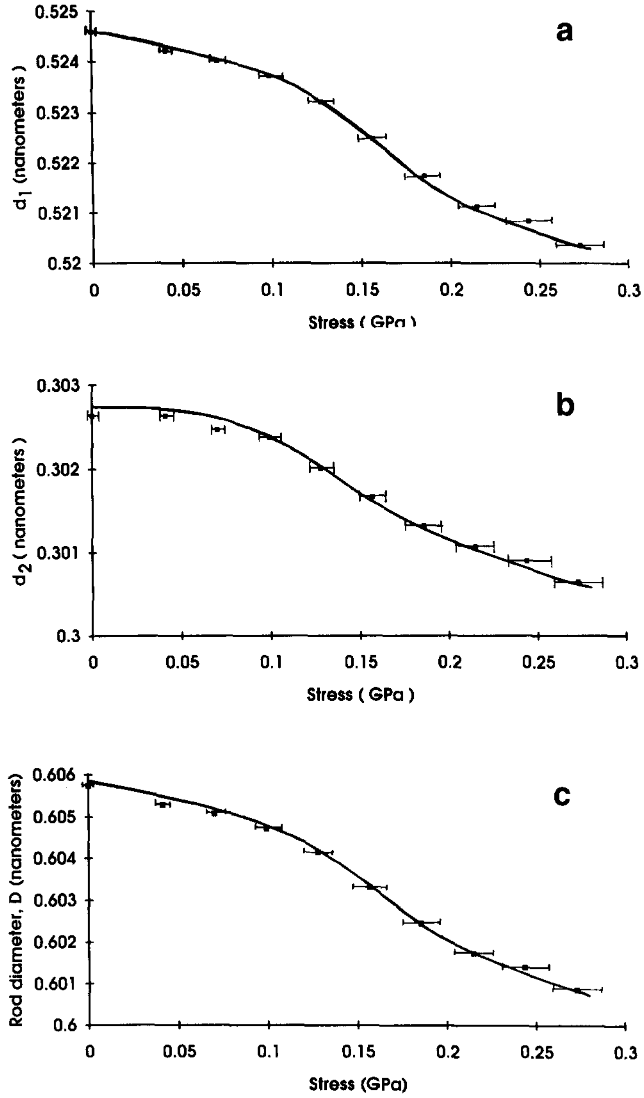

Figure 3 The variation of (a) the d_1-spacing and (b) the d_2-spacing with stress; and (c) a plot of molecular rod diameter $D = 2d_1/\sqrt{3}$ *versus* stress

d_2 decreased with increasing stress. Within experimetal error, the ratio d_1/d_2 remained close to $\sqrt{3}/1$ throughout the range of stresses applied to the sample, as can be seen in *Figure 4*. Note that a different sample was used for the experiment shown in *Figure 3* compared with that in *Figure 2*, so that the initial values of d_1 and d_2 were slightly different. For the sample in *Figures 3a* and *3b*, at zero stress, $d_1/d_2 = 0.5246/0.3027$, which approximates $\sqrt{3}/1$.

In order to understand the above results, it is necessary to consider models used to explain the diffraction pattern of the hexagonal polymorph. The earliest description or model of the hexagonal polymorph of PAN appears to be that of Bohn *et al.*[2]. They proposed that the atactic PAN chain adopts a stiff rod-like conformation due to the intramolecular nitrile-dipole repulsions. That is, the molecule adopts a 'helical' type of structure, though one must emphasize that there is no pitch or handedness as associated with a proper helix. These molecular rods have a diameter of about 0.6 nm and they pack together in a hexagonal fashion with no periodicity along the chain axis[20,32,33]. Liu and Ruland[34] have recently provided a more refined picture, based on computer simulations of the standard fibre pattern of PAN, which essentially tallies with the picture proposed by Bohn *et al.* These authors propose that the PAN chain consists of planar zig-zag syndiotactic units interrupted at irregular intervals by kinks arising from isotactic units. They indicated that a kink of the type tg^+tg^-t does not change the general orientation of the chain but leads to an increase of the number of monomer units per chain length in the projection onto the chain axis. That is, the molecules adopt a randomly kinked yet rod-like structure. By assuming a hexagonal packing of such chains, Liu and Ruland were able to simulate the standard two-peak diffractogram of PAN.

The above picture of the chain packing in the hexagonal polymorph can be used to understand the changes that occur on application of a stress. Tensile stress can have two effects: orientation of the molecular rods and extension of the molecules that form the rods. The orientating effect of stress is chiefly felt during the sample preparation stage. Thereafter, one may anticipate that application of a stress to the oriented sample causes the chains to extend slightly and kinks to be straightened out, thus reducing the rod diameter. The interchain spacing (i.e. the rod diameter D) is not directly given by the d_1-spacing[33], but is related to it by $D = 2d_1/\sqrt{3}$ (ref. 20). *Figure 3c*, which displays a plot of D *versus* stress, shows the small decrease of the rod diameter as the sample is loaded. The results of *Figure 4* suggest that the hexagonal packing of chains is retained, even though the rod diameter decreases.

Estimate of the X-ray modulus from the shift in the equatorial peaks

If the model of hexagonally packed rods with an initial diameter of ~0.6 nm deforming to thinner hexagonally packed rods is valid, it may be thought that it would be possible to estimate the crystal modulus by converting the reduction in rod diameter ΔD to a longitudinal tensile strain. Working on the assumption that there is no volume change (i.e. Poisson's ratio $v = 0.5$) as the sample is strained, then the tensile strain can be calculated from the rod diameters D and D' in the unstressed and stressed states, respectively. Since D and D' are related to d_1 and d'_1, the values of the unstressed and stressed d_1-spacings, the lateral strain $\varepsilon_{\mathrm{lat}}$ is given by $\varepsilon_{\mathrm{lat}} = -(d_1 - d'_1)/d_1$ and the longitudinal strain is given by $\varepsilon_{\mathrm{long}} = \varepsilon_{\mathrm{lat}}/v$. *Figure 5* shows a plot of stress *versus* $\varepsilon_{\mathrm{long}}$. From the slope of the line connecting the first two data points, an initial modulus of 28 GPa is obtained.

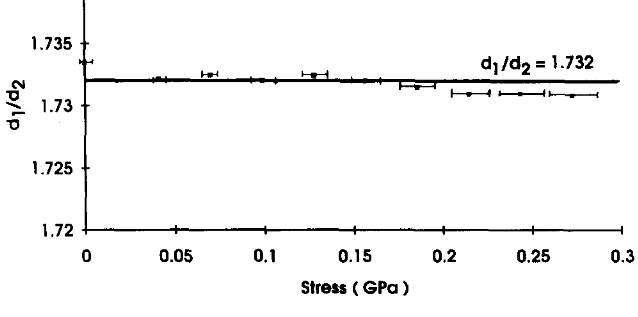

Figure 4 A plot of d_1/d_2 *versus* stress; the horizontal line represents $d_1/d_2 = \sqrt{3}/1 = 1.732\ldots$

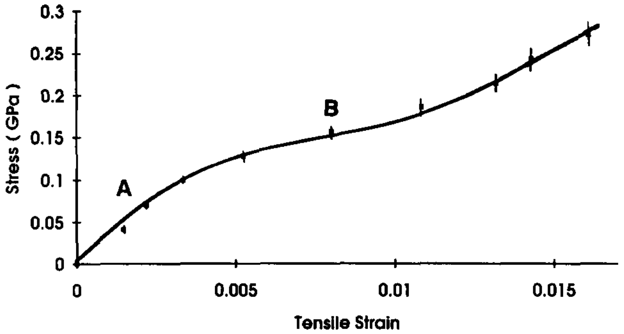

Figure 5 Stress–strain curve calculated from the X-ray data in *Figure 3a*

Rosenbaum[35] has shown that the normal stress–strain curve of oriented PAN fibres manifests three zones: an initially linear region A up to the yield point (0–2% strain); followed by a knee or plateau region B (about 2–2%); and a region C at even higher extensions occurs at temperatures above T_g. In *Figure 5* here, the same initially linear region A, followed by the knee and a plateau region B, is observed.

It should be noted that the points separating the regions A and B in *Figure 5* occur at relatively low strains of 0.003–0.004 compared with the mechanical stress–strain curves of acrylic fibres reported by Rosenbaum[35]. Apart from the fact that mechanical stress–strain curves are testing-rate dependent, the other difference appears to be that Rosenbaum may have used fibres with a lower degree of orientation (the azimuthal arc width of the d_1-spacing is quoted somewhat ambiguously[35] as being less than 30° whereas for the strands here it is about 12°). Thus, we think that the X-ray stress–strain curve in *Figure 5* mimics the general mechanical stress–strain curve of acrylic fibres[35].

In the unstressed state, one may envisage *intramolecular* nitrile repulsions forcing the individual chains into a kinked yet rigid structure, but the hexagonal packing of the chains would lead to *intermolecular* pairing of nitrile dipoles between adjacent chains. Rosenbaum states that the initial resistance to axial deformation (corresponding to region A) would arise from the stretching and breaking of the intermolecular dipole bonds and that the subsequent main extension in region B is made possible by the short-range straightening of individual molecules, untwisting from a kinked conformation, rather than being due to rubber-like deformation, or due to alignment of fibre elements such as misoriented fibrils or crystallites[35].

Dart has found that, for PAN fibres, the resistance to tensile deformation is due almost entirely to an increase in internal energy[36]. If the effect of the external stress is to counteract the repulsive resistance of the nitrile dipoles so that the molecule straightens out by rotation of bonds in the chain backbone, the result would be an increase in internal energy, in accordance with Dart's findings[36]. Thus, Dart's results also support the view that the response to stress in oriented PAN is not a rubber-like (entropy-dominated) deformation. Our present X-ray results in *Figures 3* and *4* provide direct evidence for the view that the primary effect of a tensile stress on a highly oriented PAN specimen is to unkink the chain.

X-ray versus *mechanical modulus*

It is necessary now to consider whether the value of 28 GPa obtained from X-rays is a reliable estimate of the maximum value of the chain modulus of PAN. The nature of and the difference between the X-ray and mechanical moduli needs to be discussed. Though PAN fibres normally have mechanical moduli in the range of 10–20 GPa, values of about 30–33 GPa have been quoted for the mechanical moduli of drawn fibres and films prepared from very high-molecular-weight polyacrylonitrile[37–39].

In the previous work[7], from force constants obtained by Sakurada and Kaji[39] for polymers that adopt a similar conformation and that have comparable cross-sectional areas as PAN, we estimated that the maximum modulus would be 55 GPa. The fact that the X-ray modulus is about 28 GPa suggests that the previous guess may be an overestimate. This is because Sakurada and Kaji's[40] force constants were obtained for polymers that have a regular, helical conformation; choosing a value for the force constant for PAN is problematic because this polymer does not adopt a regular conformation[7]. The fact that the mechanical moduli of the best PAN fibres are comparable or slightly exceed the X-ray modulus estimated from the equatorial data here suggests that the highest attainable mechanical properties from atactic PAN may have already been achieved with high-molecular-weight polymer[37–39].

However, the possibility also remains that the X-ray modulus estimated here is slightly on the low side. It is worth seeing what factors could affect the value of the initial modulus obtained from the shift in the equatorial peaks, using the simple model of elongation of rods. First, the conversion of the lateral strain measured in the X-ray experiment to a tensile strain depended on the adoption of a Poisson's ratio of 0.5. This is questionable as the typical values of Poisson's ratio for most polymers lie in the range 0.3–0.45 (ref. 41). However, if the lower limit of 0.3 is chosen for Poisson's ratio, it in fact decreases the X-ray modulus from 28 GPa (the value obtained with the upper limit of Poisson's ratio) to 17 GPa.

Another factor to consider in explaining the fact that the X-ray modulus is apparently only comparable to (28 GPa, Poisson's ratio 0.5) or even lower than (17 GPa, Poisson's ratio 0.3) the maximum mechanical moduli of 30–33 GPa reported in the literature[37–39] is that the X-ray experiment here is essentially a zero-deformation-rate experiment, whereas the moduli obtained in mechanical tests are from high-deformation-rate experiments. Owing to the viscoelastic response of polymers, the 'equilibrium strain' is not attained at each stress level and hence the mechanical modulus is strain-rate-dependent, with higher testing rates giving higher moduli.

Further, unlike the drawn polyethylene studied by Sakurada, which had a crystalline–amorphous (i.e. two-phase) morphology, in the case of highly oriented PAN, we have a substance that behaves like a single-phase material[2]. (In fact, the nature of the order in PAN is reminiscent of a mesophase, with an array of hexagonally packed chains in a nematic-like structure with some network links.) With polyethylene, the crystal strain would be much lower than the macroscopic strain and the X-ray modulus would be much higher than the mechanical modulus (240 GPa *versus* 0.65–15 GPa, ref. 40). In the case of a single-phase material, the X-ray strain will be the same as the macroscopic strain. Thus, for oriented PAN, it may be expected that the difference between the X-ray modulus and the maximum mechanical modulus will not be great in any case; it can even lead

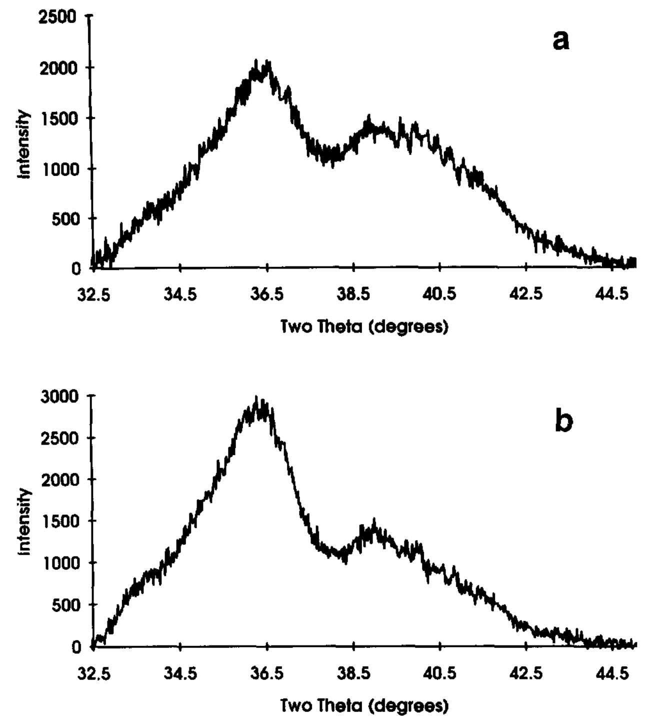

Figure 6 Meridional diffractograms of the oriented strand showing the two-component peak and the transfer of intensity between the peaks on application of a tensile stress: (a) unstressed sample; (b) after application of a stress of 0.198 GPa

to an apparent inversion where the X-ray modulus appears to be lower than the highest mechanical moduli reported for oriented fibres because the latter are measured at relatively high testing rates. With polyethylene, on the other hand, even with the best drawn fibres currently available and the high deformation rates used in mechanical testing, the X-ray modulus is so much higher that the mechanical moduli appear to be always lower.

Effect of stress on the meridional scattering

Finally, it is worth commenting on the behaviour of the meridional scattering of the hexagonal polymorph (*Figure 1*) after the application of a tensile stress. *Figure 6a* shows a meridional diffractogram from the oriented strand in the unstressed state. It can be seen that there is a weak, broad, two-component peak centred about $2\theta = 38°$. When a stress is applied, neither peak shifts in 2θ space. However, there is a change in the intensity profile of the meridional scattering on application of the stress (*Figure 6b*). It appears that intensity diminishes between $2\theta = 38°$ and 44° and simultaneously increases between 34° and 38°. This can be seen by comparing *Figure 6b* with *Figure 6a*.

The transfer of meridional intensity between the two peaks suggests a rapid change from a conformation with a short to a long 'repeat' distance. With increasing stress, X-ray intensity progressively diminished over a broad range of 2θ values centred about 41°, which corresponds to a repeat distance of about 0.220 nm, while it increased in intensity for the peak centred about $2\theta = 36.13°$, corresponding to 0.248 nm. This is a little less than the value of 0.254 nm expected for all-*trans* polyethylene. It seems likely that this transfer of intensity from high to low 2θ values represents an unravelling of a contracted conformation of a rod-like chain. This complements the picture deduced from the effect of stress on the equatorial peaks, where the decrease in the spacings was explained in terms of a decrease of the rod diameter due to unkinking and chain extension.

It may be thought that it would be possible to estimate the longitudinal strain by examining the shift of the centre of gravity of the intensity profile with applied stress. However, when the scattering profile consists of two overlapped components, such a shift does not give the true strain.

In any case, while the shifts in the centre of gravity of the meridional diffractograms acquired at each stress level showed reproducibility at higher stresses, there was a great deal of scatter in the data at low stress levels where the changes in the intensity profile were small and were comparable to the noise, so that no estimates of strain at low stresses could be obtained.

CONCLUSIONS

The main points covered here are summarized as follows.

The two equatorial spacings d_1 and d_2 of the hexagonal polymorph of PAN decrease with increasing stress. The ratio of d_1/d_2 appears within experimental error to remain constant at $\sqrt{3}/1$. The above two experimental findings indicate that the diameter of the molecular rod decreases due to slight chain extension, but the packing remains hexagonal or close to it.

The meridional scattering showed a broad, two-component peak. On application of a stress, there was no shift in the peak positions, but there was a transfer of intensity from high to low 2θ values. This also fits the picture of the molecular rod extending on application of stress.

A stress–strain curve calculated from the change in the equatorial spacings using a simple model of extending rods gave a curve that reproduced the features of the mechanical stress–strain curve of acrylic fibres[35]. This suggests that the interpretation of the experimentally observed shift in the *d*-spacings on application of stress is essentially correct.

From the stress–strain curve obtained from the equatorial data, an initial modulus of 28 GPa was calculated.

Despite the possibility that the X-ray modulus may be an underestimate of the chain modulus, the conformation adopted by *atactic* PAN is such that the latter cannot be expected to be much greater than the X-ray modulus[7].The highest reported moduli for acrylic fibres[37–39] is about 30–33 GPa and it would appear that the limit to what can be reasonably attained with atactic PAN has already been reached.

Thus, the production of ultra-stiff fibres with mechanical moduli of 100–200 GPa, which is possible with fibres of polymers that adopt an all-*trans* form such as polyethylene or poly(vinyl alcohol), cannot be expected from this polymer even with high-molecular-weight atactic PAN processed from dilute solutions[37–39]. True high-modulus fibres can only be expected from syndiotactic or possibly isotactic PAN.

ACKNOWLEDGEMENTS

R. A. Allen wishes to thank Courtaulds for funding this work. We also wish to thank Dr G. Mitchell, Mr J. Pople and Mr P. Keates, Polymer Science Centre, University of Reading, for provision of time and assistance at the Daresbury synchrotron source.

REFERENCES

1 Houtz, R. C. *Textile Res. J.* 1950, **20**, 786
2 Bohn, C. R., Schaefgen, J. R. and Statton, W. O. *J. Polym. Sci.* 1961, **55**, 531
3 Statton, W. O. *Ann. NY Acad. Sci.* 1959, **83**, 27
4 Joh, Y. *J. Polym. Sci., Polym. Chem. Edn* 1979, **17**, 4051
5 Grove, D., Desai, P. and Abhiraman, A. S. *Carbon* 1988, **26**, 403
6 Gupta, A. K. and Chand, N. *Eur. Polym. J.* 1979, **15**, 899
7 Allen, R., Ward, I. M. and Bashir, Z. *Polymer* 1994, **35**, 2063
8 Urbanczyk, G. W. *Zeszyty Nauk, Politech. Lodz Wlokiennictwo* 1962, **9**, 79; *Chem. Abstr.* 1964, **61**, 5836(b)
9 Natta, G., Mazzanti, G. and Corradini, P. *Rend. Acad. Naz. Lincei* 1958, **XXV**, 3
10 Rein, H., cited by Kast, in *Landolt-Bornstein Tabellen,* 6th Edn., Part 3, Springer-Verlag, Berlin, 1957, Vol. 4
11 Mathur, R. B., Bahl, O. P. and Kundra, K. D. *J. Mater. Sci. Lett*, 1986, **5**, 757
12 Lindenmeyer, P. H. and Hosemann, R. *J. Appl. Phys.* 1963, **34**, 42
13 Holland, V. F., Mitchell, S. B., Hunter, W. L. and Lindenmeyer, P. H. *J. Polym. Sci.* 1962, **62**, 145
14 Stefani, R., Chevreton, M., Garnier, M. and Eyraud, C. *C. R. Acad. Sci. Paris* 1960, **251**, 2174
15 Menčik, Z. *Vysokomol. Soyed.* 1960, **2**, 1635
16 Hinrichsen, G. and Orth, H. *Kolloid Z. Z. Polym.* 1971, **247**, 844
17 Kumamaru, F., Kajiyama, T. and Takayanagi, M. *J. Cryst. Growth* 1980, **48**, 202
18 Colvin, B. G. and Storr, P. *Eur. Polym. J.* 1974, **10**, 337
19 Baltá-Calleja, F. J. and Vonk, C. G. 'X-Ray Scattering of Synthetic Polymers', Elsevier, Amsterdam, 1989, Ch. 3, pp. 102–3
20 Bashir, Z. *J. Polym. Sci., Polym. Phys. Edn* 1994, **32**, 1115
21 Bashir, Z. *J. Polym. Sci., Polym. Phys. Edn* 1992, **30**, 1299
22 Klement, J. J. and Geil, P. H. *J. Polym. Sci.* (*A2*) 1968, **6**, 1381
23 Yamazaki, H., Kajita, S. and Kamide, K. *Polym. J.* 1987, **19**, 995
24 Bashir, Z. *Polymer* 1992, **33**, 4304
25 Bashir, Z., Atureliya, S. K. and Church, S. P. *J. Mater. Sci.* 1993, **28**, 2721
26 Herbert, I. R., Tipping, A. and Bashir, Z. *J. Polym. Sci., Polym. Phys. Edn* 1993, **31**, 1459
27 Bashir, Z. *J. Mater. Sci. Lett.* 1993, **12**, 1526
28 Bashir, Z., Church, S. P. and Price, D. M. *Acta Polym.* 1993, **44**, 211
29 Atureliya, S. K. and Bashir, Z. *Polymer* 1993, **34**, 5116
30 Sakurada, I., Nukushina, Y. and Ito, T. *J. Polym. Sci.* 1962, **57**, 651
31 Sakurada, I., Ito, T. and Nakamae, K. *Makromol. Chem.* 1964, **75**, 1
32 Olivé, G. H. and Olivé, S. *Adv. Polym. Sci.* 1979, **32**, 123
33 Warner, S. B., Uhlmann, D. R. and Peebles, L. H., Jr *J. Mater. Sci.* 1979, **14**, 1893
34 Liu, X. D. and Ruland, W. *Macromolecules* 1993, **26**, 3030
35 Rosenbaum, S. *J. Appl. Polym. Sci.* 1965, **9**, 2071
36 Dart, S. L. *Textile Res. J.* 1960, **30**, 372
37 Dobretsov, S. L., Lomonosova, N. V., Stelmakh, V. P. and Frenkel, S. Ya. *Vysokomol. Soyed. SSR* (*A*) 1972, **14**(5), 1143
38 Maslowski, E. and Urbanska, A. *America's Textile International, Fibre World,* FW2, Sept. 1989
39 Kamada, T. and Kanamoto, T. *Nihon Reoroji Gakkaishi* (*J. Soc. Rheol. Jpn*) 1993, **21**, 156
40 Sakurada, I. and Kaji, K. *J. Polym. Sci.* (*C*) 1970, **31**, 57
41 Brandrup, J. and Immergut, E. H. (Eds) 'Polymer Handbook', 3rd Edn., Wiley-Interscience, New York, 1989, pp. V/83–84, V/103, V/113