

Surface microstructure of a Kevlar* aramid fibre studied by direct atomic force microscopy

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(Received 29 January 1996; revised 8 May 1996)

The surface morphology and molecular arrangement of a Kevlar[®] aramid fibre (coded Fibre A, from E. I. DuPont de Nemours and Co.) were studied by atomic force microscopy (AFM). Pleats parallel to the fibre axis have been observed. At nanometre scale, the polymer chains display several different arrangements from the reported crystalline structures for the bulk polymer especially in the polymer chain direction. The benzene rings at the surface seem to have a co-planar like rotation instead of an opposite one as proposed for bulk crystalline structure according to X-ray diffraction results. The factors inducing the less perfect surface crystalline structure are discussed. © 1997 Elsevier Science Ltd.

(Keywords: Kevlar[®] aramid fibre; surface structure; atomic force microscopy)

INTRODUCTION

The structures of poly(*p*-phenylene terephthalamide) (PPTA) fibres, such as DuPont's Kevlar* aramid fibres with high strength and high modulus, have been already studied by scanning probe microscopy (SPM) including scanning tunnelling microscopy (STM)^{1,2} and atomic force microscopy (AFM)^{3–5}. Being a good insulator, the fibre is not suitable to be observed by STM unless the surface is coated by a conducting layer like in the classical scanning electronic microscopy. Thus it is difficult to achieve the high resolution at the molecular scale because the surface is screened by the deposited layer. AFM, which is based directly upon the force interaction between the probe tip and the sample surface, seems more interesting for this purpose. Theoretically it can reach the same resolution as STM for conducting samples. In reality the force interaction in AFM is more complex than the tunnelling current in STM and the achievement of true molecular resolution is more difficult. In case of aramid fibre, few results of structural study by AFM have been reported³. To our knowledge, only one paper by Snétivy *et al.*³ concerns the crystalline structure of PPTA fibre. The sample was specially treated and the inner structure was observed by AFM.

The aramid fibre can be used as an important component of composite materials and the surface structure is a key parameter for good adhesion between the fibre and other components. In this paper, we present

some AFM results of surface microstructure, obtained directly on a finish-free commercial grade PPTA fibre without any pre-treatment and special sample preparation.

EXPERIMENTAL

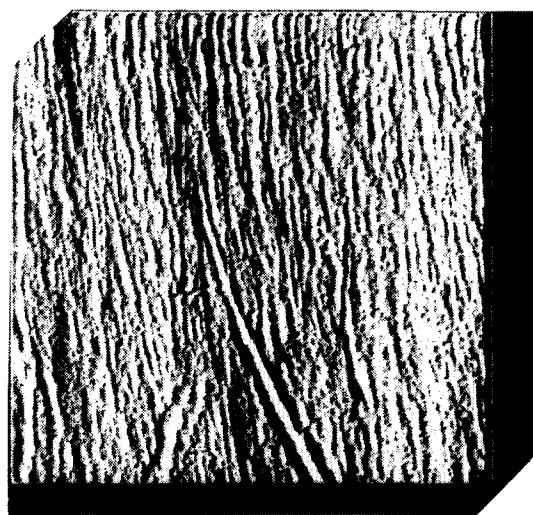
The fibre sample (named Fibre A) is a Kevlar[®] 29 product from E. I. DuPont de Nemours and Co.

The yarn sample is made of 1000 filaments of an average diameter of 12 μm . The sample has a light yellow colour and presents a strong electrostatic effect since no processing aid (called finish in the textile industry's jargon) has been applied for this sample on the surface at the end of the process. A small segment of the sample was carefully fixed on the support without any surface pre-treatment.

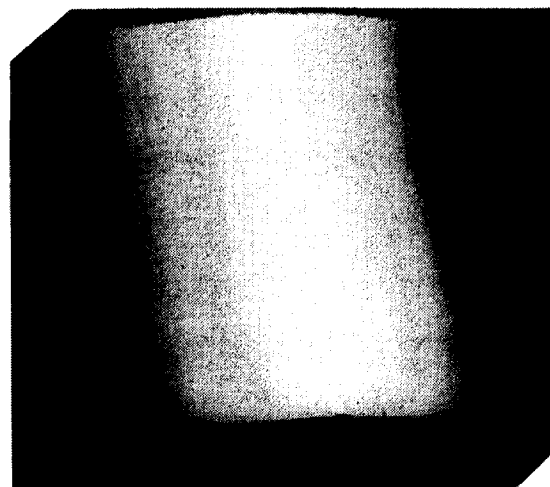
The observation was made on a commercial AFM instrument (Nanoscope II, Digital Co., Santa Barbara, USA) in air and at room temperature. We used two AFM heads ('A' and 'D') in this work: 'D' head for lower magnification (image size > 500 nm) and 'A' head for molecular resolution. The 'D' head was calibrated with a 1000 lines/micrometre standard, no correction is needed for our topological results. The 'A' head was calibrated by mica and highly oriented pyrolytic graphite (HOPG) with an error less than 10%. We tested the effect of the tip nature with different chemical compositions: one is the 100 μm triangular Si₃N₄ cantilever (spring constant 0.58 N m⁻¹) with pyramidal tip form, the other is a bar-shaped cantilever (spring constant < 0.7 N m⁻¹) with etched single crystal silicon tip. It seems that the former tip can give stable AFM images at a scale larger than 100 nm while the last one gives better results at

* DuPont's registered trademark for its high strength para-aramid fibres

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a

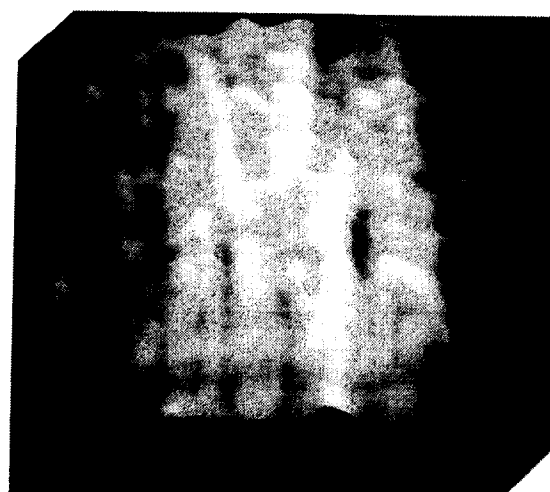


b

Figure 1 Morphological image of Fibre A observed by AFM, $2000 \times 2000 \text{ nm}^2$: (a) 'constant height mode', 2D presentation; (b) 'constant force mode', 3D presentation



a



b

Figure 2 Morphological image of Fibre A observed by AFM, $500 \times 500 \text{ nm}^2$: (a) 'constant height mode', 2D presentation; (b) 'constant force mode', 3D presentation

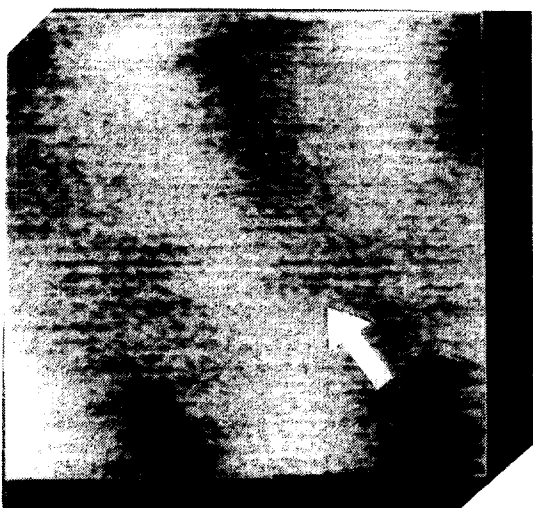


Figure 3 Surface microfibrillar structure of Fibre A, $18 \times 18 \text{ nm}^2$: 'constant force mode', low pass filtered. The arrow indicates the fibre direction

nanometre scale. Therefore the two tips were used respectively at the two different scales. Even with the monocrystal silicon tip, the images at molecular resolution were not easily obtainable because of the strong interaction between the tip and the aramid fibre surface which has a highly polar character.

RESULTS AND DISCUSSION

The curved cylindrical fibre surface was visualized at $5 \mu\text{m}$ scale and the filament radius is calculated to be $5.7 \mu\text{m}$, another image at $2 \mu\text{m}$ scale gives the same result. Starting from the $2 \mu\text{m}$ magnification (*Figure 1*), the non-smooth character of the fibre surface appears, with many pleats parallel to the fibre axis direction. The planar details (x - y plane) of the pleats are better presented by the 'force mode' images (*Figure 1a*) and the real morphological dimension (z direction) is better observed with the 'height mode' (*Figure 1b*). The pleats have a distance of 30 – 80 nm and a height of 2 – 15 nm . In *Figure 2*, the pleat feature is enlarged and clearly shown. This feature may be the memory effect of the fibre spinning

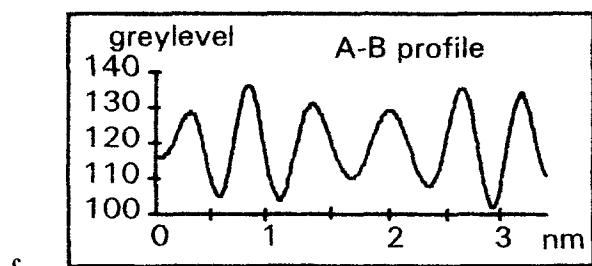
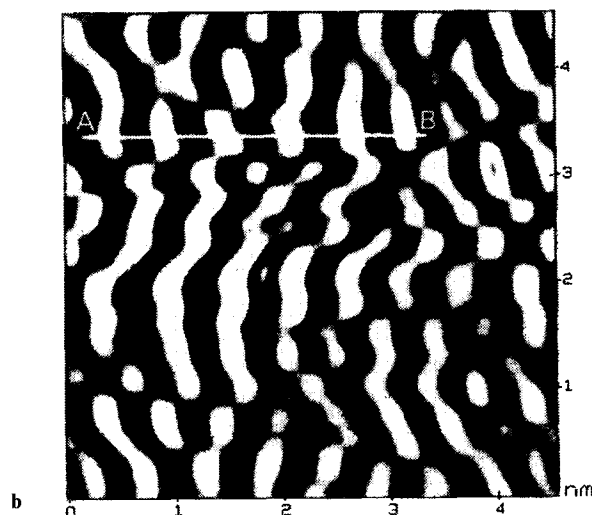
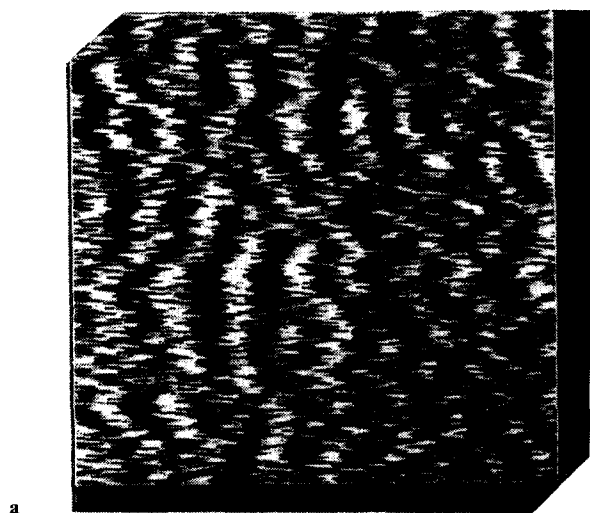


Figure 4 High resolution AFM image of Fibre A, $4.5 \times 4.5 \text{ nm}^2$: 'constant height mode': (a) raw image; (b) 2D Fourier reconstructed image; (c) height profile in A-B direction

process and similar to the surface memory effect observed on carbon fibres⁶. With a high draw ratio during spinning process, apparently the fibre we studied has a surface smoother than the reported one with larger diameter and low draw ratio³.

As we have mentioned before, the surface structure of the aramid fibre is difficult to be observed directly by AFM at molecular resolution. *Figures 3–7* present some images at this scale obtained after a long effort.

Figure 3 shows a surface molecular arrangement of a filament of Fibre A, observed with the 'constant force mode' in a surface area of $18 \times 18 \text{ nm}^2$. Apart from the horizontal stripes which are formed during the tip scanning and are considered as a noise, the molecular orientation is clearly visible. The polymer chains are

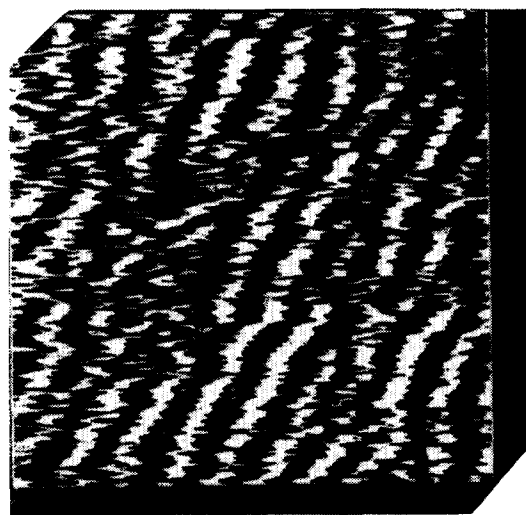


Figure 5 Raw AFM image of Fibre A at high resolution, $4.5 \times 4.5 \text{ nm}^2$: 'constant height mode'

arranged in the nearly vertical direction in the image with an average inter-chains distance of 0.65 nm. The fibre axis direction is indicated by the arrow and the microfibrillar structure, appearing as bright ribbons of about 8–10 nm apart and parallel to the fibre direction, is also observed. However the polymer chains seem to follow not exactly in the fibre axis direction as described by a pleat structure model of Kevlar[®] aramid fibre⁷ in which the polymer chain orientation and the fibre axis form an angle of about 10° . The structure of *Figure 3* occurs perhaps within the surface ordered lamella area.

By increasing the enlargement, the surface crystalline structures can be seen more clearly as presented in *Figures 4–7* where the fibre axis direction remains the same as in *Figure 3*.

Figure 4 presents a raw AFM image and its 2D Fourier reconstructed one to show the crystalline structure. Some arrangement order is observed but it is difficult to fit it to a well-organized crystalline structure, revealing a less perfectly crystalline area. Nevertheless a preferential order in nearly horizontal direction is evident with a periodicity of 0.63 nm. The distance is larger than the reported lateral unit cell parameter b (0.45–0.52 nm) of bulk PPTA fibre observed by wide-angle X-ray diffraction⁸ and AFM³, but is smaller than the parameter a (0.79 nm)⁸. The raw image shown in *Figure 5* has a better structure regularity which is seen as parallel lines with an average line distance of 0.45 nm, near to the above-mentioned b value.

In another image (*Figure 6*), a locally well ordered structure is observed. Crystalline polymer chains can be fit at least partially to the 2D Fourier treated image. From this fitting, the two-dimensional unit cell parameters are calculated as: lateral periodicity 0.50 nm and chain periodicity 1.28 nm. These parameters are nearly the same as one reported bulk structure (called structure modification III to distinguish the structure I and II obtained by WAXD study¹⁰ for an as-spun PPTA fibre³ but the registration angle is smaller (72° instead of reported 80°). It is worthy to notice that the molecular fitting in *Figure 6* puts the chain in one side of the observed light spot lines. This means that the benzene rings have the like orientation, i.e. all the benzene rings in the polymer chains have the same side

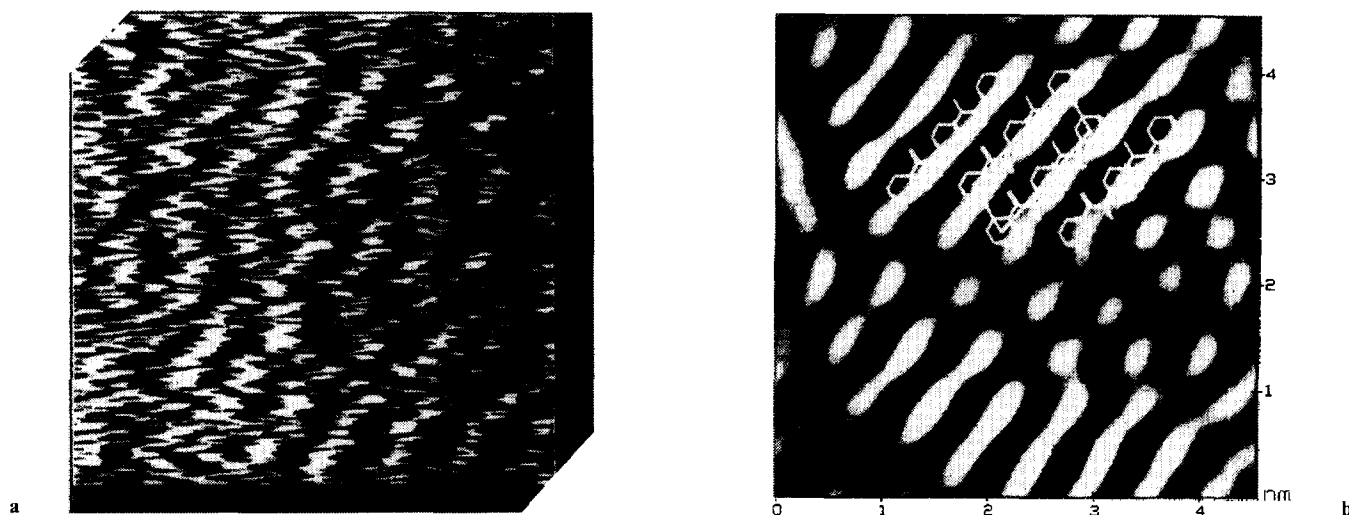


Figure 6 AFM image of Fibre A at high resolution, $4.5 \times 4.5 \text{ nm}^2$: (a) raw image; (b) 2D Fourier reconstructed image, molecular arrangement is suggested

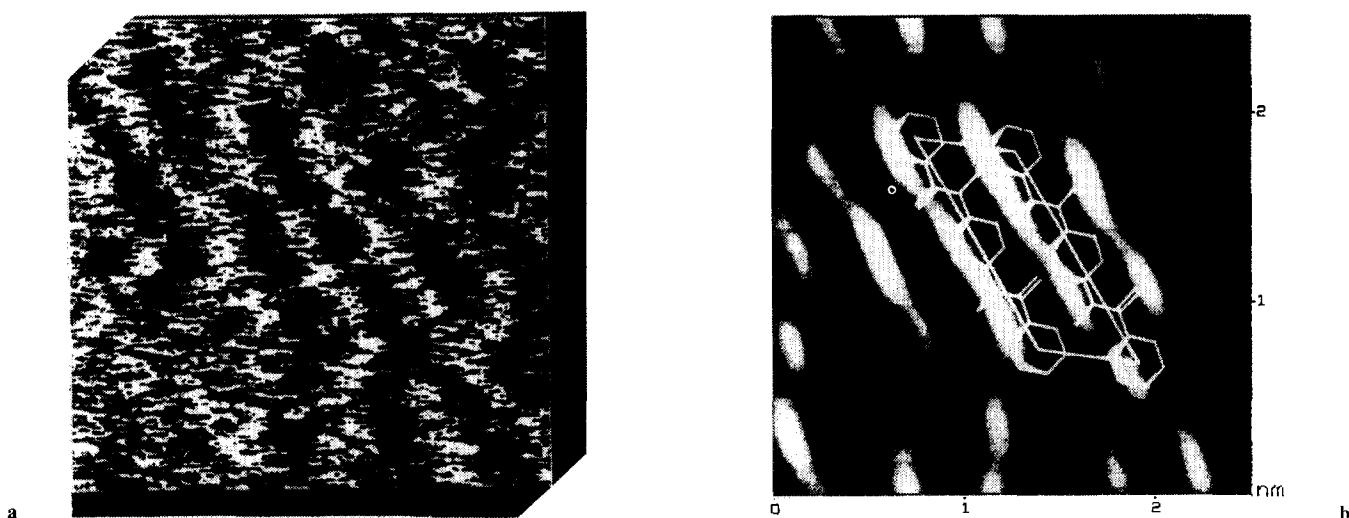


Figure 7 AFM image of Fibre A at high resolution, $2.5 \times 2.5 \text{ nm}^2$: (a) raw image; (b) 2D Fourier reconstructed image, molecular arrangement is suggested

'protruding' outside the surface and thus give a linear bright AFM pattern where the AFM tip has a higher deflection. In case of the opposite rotation of benzene rings the AFM patterns appear as alternated spot arrangement³. The co-planar successive benzene ring configuration has been proposed in Snétivy's work³ and is confirmed by our observation.

A similar structure is also presented in *Figure 7* where there are several common aspects with *Figure 6* which are worth being pointed out: (1) the fitting polymer chains have the same benzene ring orientation (like rotation) as the structure in *Figure 6*; (2) the two-dimensional unit cell parameters are 0.52 nm in lateral periodicity and 1.29 in chain periodicity; (3) the registration angle is even smaller (52°).

The images presented in *Figures 4–7* reveal interesting crystalline structure information which can be compared to the reported results³. In ref. 3, the conditions of fibre preparation are very different: (1) the fibre was dissolved in solution and re-spun with low draw ratio, resulting in fibres having larger diameters; (2) subsequently one of the fibres was annealed at 450°C twice to promote the crystallite size; (3) for AFM observation the fibre was

embedded in epoxy resin and cleaved with ultramicrotoming, therefore the observed structure is the internal part of the fibre instead of the fibre surface as we observe in the present work. Although the inner phase can become new surface after the microtoming and eventually this part of new surface structure will undergo a rearrangement, we have no idea concerning the kinetics of this possible structure change. For crystalline polymer, there are sometimes few or no energy barriers for different chain packing. Generally the surface microstructure of material may be quite different from the bulk structure. This structure evolution after a new surface is formed may be a factor to take into consideration if the surface and bulk crystalline structures are compared.

In the case of commercial aramid fibre with high draw ratio, skin-core structure is often observed with variable skin thickness^{10,11}. X-ray diffraction results encompass the average contribution of the structures in the two different regions. AFM is a surface structure analysis method which can probe only the first skin layer if the fibre is not microtomed. This explains probably the structure differences observed by WAXD, AFM with microtomed and bare finish-free fibre as in this work.

The different experimental observations underline similar unit cell parameters b and c , but the registration angles are variable especially for the AFM results. This means that at the surface the polymer molecules are arranged less strictly in the chain direction than in perfect bulk crystallite¹¹. The surface polymer chains have more freedom to move than in bulk and the crystalline structure tend to be less perfect especially for the as-spun fibre. The different polymer chain orientation angles in Figures 4–7 is also an indication of the polymorphism at the fibre surface, the fibre axis direction being as in Figure 3. The heat-treatment by annealing will have the effect of increasing the regularity of the chain arrangement and transform the crystalline structure into more stable states as indicated in ref. 3.

Another effect should also be taken into account, i.e. water molecules at fibre surface. The aramid fibre has a polar surface and the observation by AFM is done in air containing a certain level of moisture. As we know, hydrogen bonding occurs between the aramid polymer chains. Washing by water can change the crystalline form⁹. Adsorption of water molecules, which are also able to form hydrogen bond, could disturb surface polymer arrangement. In case of AFM measurement, the presence of adsorbed water and the AFM tip scanning action could promote, at least locally, this influence on the original surface crystalline regularity. The present work aims mainly at the fibre structure in its original state. The AFM measurement under a dry atmosphere and the eventual treatment to desorb the water molecules at the aramid fibre surface could help to overcome these difficulties but care should be taken to avoid the likely structural changes during these treatments¹².

CONCLUSION

The surface microstructure of an aramid fibre was observed directly by atomic force microscopy. The unit cell parameters b and c of the crystalline structures and the co-planar like rotation of benzene rings are similar to the reported results but the registration angle is not constant. This discrepancy is explained as the difference between surface and bulk crystalline structure. At the surface of the polymer chains tend to be arranged less perfectly and the surface crystalline structure can be influenced by several parameters such as the fibre manufacturing conditions and post treatment, adsorbed water, and even the possible AFM tip friction.

REFERENCES

- 1 Binnig, G., Quate, C. F. and Gerber, Ch. *Phys. Rev. Lett.* 1982, **56**, 930
- 2 Sawyer, L. G., Chen, R. T., Jamieson, M. G., Musselman, I. H. and Russell, P. E. *J. Mater. Sci. Lett.* 1992, **11**, 69
- 3 Snétivy, D., Vancso, G. J. and Rutledge, G. C. *Macromolecules* 1992, **25**, 7037
- 4 Li, S. F. Y., McGhie, A. J. and Tang, S. L. *Polymer* 1993, **34**, 4573
- 5 Li, S. F. Y., McGhie, A. J. and Tang, S. L. *J. Vac. Sci. Technol. A* 1994, **12**, 1891
- 6 Donnet, J. B. and Qin, R. Y. *Carbon* 1993, **31**, 7
- 7 Dobb, M. G., Johnson, D. J. and Saville, B. P. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 2201
- 8 Northold, M. G. *Eur. Polym. J.* 1974, **10**, 799
- 9 Haraguchi, K., Kajiyama, T. and Takayanagi, M. *J. Appl. Polym. Sci.* 1979, **23**, 915
- 10 Yang, H. H. 'Kevlar[®] Aramid Fibre', Wiley, Chichester, 1992, p. 88
- 11 Rebouillat, S., Escoubes, M., Gauthier, R. and Vigier, A. *J. Appl. Polym. Sci.* 1995, **58**, 1305
- 12 Rebouillat, S., Escoubes, M., Gauthier, R. and Vigier, A. *Polymer* 1995, **36**, 4521