

References

- [1] Pinnock, P.R. and Ward, I.M., *Trans. Faraday Soc.* (1966) **62**, 1308.
- [2] Long, S.D. and Ward, I.M., *J. Polym. Sci. Polym. Phys. Ed.* (1991) **42**, 1921.
- [3] Bunn, C.W., Daubeny, R. de P. and Brown, C.J., *Proc. Roy. Soc. A* (1954) **10**, 275.
- [4] Nobbs, J.H., Bower, D.I. and Ward, I.M., *J. Polym. Sci. Polym. Phys. Edn* (1979) **17**, 259.
- [5] Mahendrasingam, A., MacKerron, D.H., Fuller, W., Forsyth, V.T., Oldman, R.J. and Blundell, D.J., *Rev. Sci. Instrum.* (1992) **63**, 1097.
- [6] Blundell, D.J., Mahendrasingam, A., MacKerron, D.H., Turner, A., Rule, R., Oldman, R.J. and Fuller, W., *Polymer* (1994) **35**, 3875.
- [7] Blundell, D.J., MacKerron, D.H., Fuller, W., Mahendrasingam, A., Martin, C., Oldman, R.J., Rule, R. and Riekel, C., *Polymer* (1996) **37**, 3303.
- [8] Salem, D.R., *Polymer* (1992) **33**, 3189.
- [9] Salem, D.R., *Polymer* (1992) **33**, 3182.

8th Annual Workshop Prize-Winning Posters

An XRD Study of the Rigid-Rod Polymer Fibre M5 (PIPD)

E.A. Klop and M. Lammers

Akzo Nobel Central Research, P.O.Box 9300, 6800 SB Arnhem, Netherlands.

Introduction

The spinning of rod-like polymer molecules from liquid crystalline solutions has proven to be an effective way of preparing fibres that exhibit high stiffness and tenacity. The high level of molecular orientation already present in the as-spun state can be further increased by heat treatment resulting in materials suitable for high-performance structural applications. This spinning and heat treatment process is used in the production of the rigid-rod polymer fibre poly (*p*-phenylene benzobisoxazole) (PBO). The performance of this fibre (and related fibres) in compression, however, is disappointing, due to the absence of strong interchain bonding. In recent years much effort has been spent on increasing

the lateral strength of rigid rod polymer fibres, often by crosslinking after fibre formation. These efforts were not very successful.

Figure 1 shows the structural formula of the rigid-rod polymer M5, which was discovered in our laboratory [1]. The design of this polymer, with chemical name poly {2,6-diimidazo[4,5-b:4'5'-e]pyridinylene-1,4(2,5-dihydroxy) phenylene}, abbreviated as "PIPD", was motivated by its ability to form intermolecular hydrogen bonds. Fibres spun from a nematic solution of the polymer in polyphosphoric acid not only exhibit a high stiffness and tenacity (330 and 5 GPa respectively), but also a compression strength (1.7 GPa) which exceeds that of any other polymer fibre. Compared with carbon fibre, the material has the advantage of having a very high damage tolerance; moreover, it is an electrical insulator. While the heat-treated material has attractive properties, the as-spun material is interesting as well, as it is highly fire-resistant. The work reported here concerns the structural order both in heat-treated and as-spun M5 fibre.

Heat-treated M5 fibre

The diffraction pattern of heat-treated M5 fibre (Figure 2(a)) shows several reflections on the first three layer-lines, indicating three-dimensional crystalline order. Despite the small number of reflections, it was possible to determine the unit cell parameters and the packing of the polymer molecules, using a diffraction modelling approach. Based on the flat plate diffraction pattern, two models are proposed which have the same lattice (with parameters 12.60 Å, 3.48 Å, 12.01 Å, 90.0°, 108.6°, 90.0°) but different symmetry, viz. a triclinic

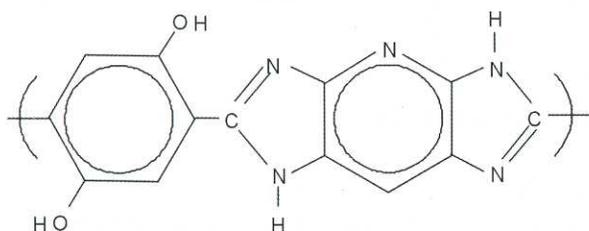


Figure 1: Chemical structure of M5.

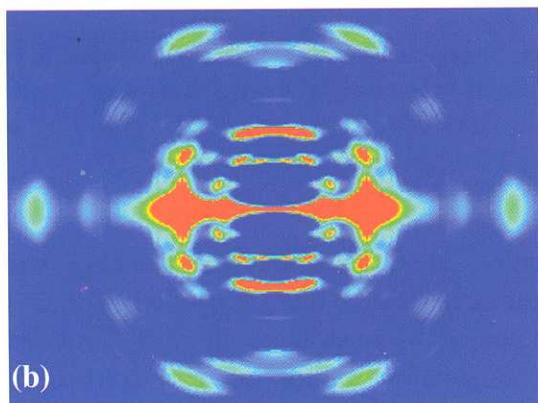
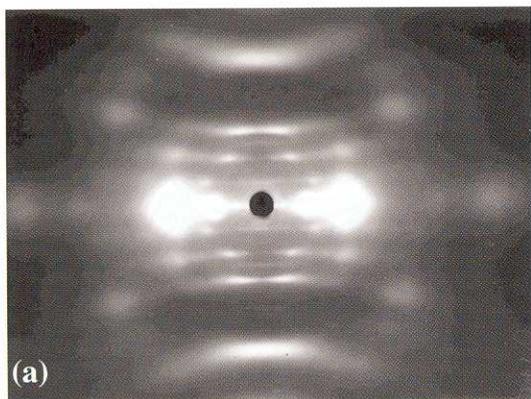


Figure 2: Flat plate diffraction pattern of heat-treated M5 fibre, (a) observed, (b) calculated (based on the monoclinic model).

model (described for obvious reasons in a c -centred unit cell, see Figure 3) and a monoclinic model with Pa symmetry (pseudo $P2_1/a$) (Figure 4). The key interchain interaction in these models is N-H—O hydrogen bonding. The only difference between the models is that in the monoclinic model the heterocyclic fragment of the centre chain is rotated in the opposite direction compared to that of the corner chain, unlike in the triclinic model. This influences the hydrogen bonding scheme drastically: the triclinic model exhibits a sheet-like hydrogen bonding scheme, whereas in the monoclinic model the intermolecular hydrogen bonds form a bi-directional hydrogen bonding network. Figure 2(b) shows the diffraction pattern calculated on the basis of the monoclinic model. Due to the limited crystalline perfection it is impossible to discriminate between the two models on the basis of the flat plate diffraction pattern. However, as the two models differ in the intermolecular interactions along the diagonals of the unit cell, useful information can be obtained from thermal expansion data as provided by high-temperature XRD. For the sheet-like model one would expect different coefficients of thermal expansion for the $(1\ 1\ 0)$ and $(1\ -1\ 0)$ planes, *i.e.* a

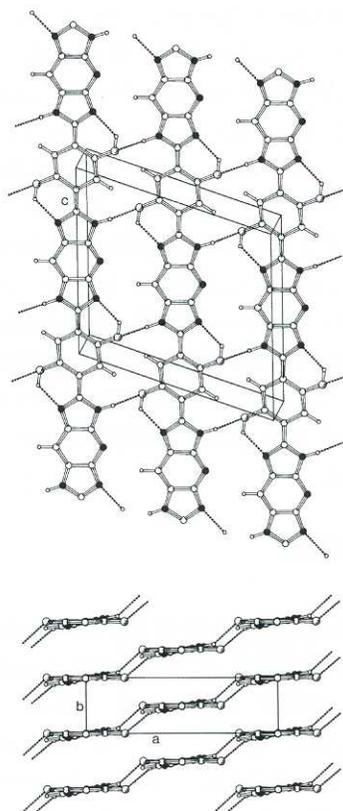


Figure 3: Triclinic model of heat-treated M5 fibre with sheet-like hydrogen bonding scheme. The upper picture shows the polymer chains at the (x, y) positions $(0, 0)$, $(1/2, 1/2)$ and $(1, 1)$. Nitrogen atoms are coloured black, oxygen atoms are drawn somewhat larger to discriminate them from carbon atoms.

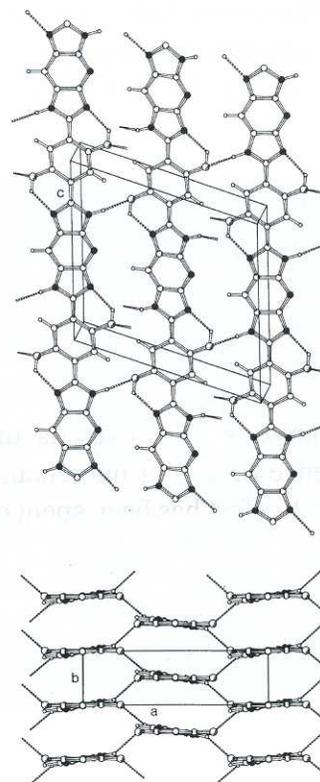


Figure 4: Monoclinic model of heat-treated M5 fibre with bi-directional hydrogen bonding network. The only difference with the model in Figure 3 is that the c -centering is replaced by a -glide symmetry.

splitting up of the corresponding 3.34 Å peak ($2\theta = 26.7^\circ$) in the equatorial diffraction pattern with temperature. As such splitting up is not observed, it can be concluded that the coefficients of thermal expansion for the two planes are equal, which is consistent with the monoclinic model. We therefore conclude that the crystal structure of heat-treated M5 fibre is monoclinic, although it may exhibit sheet-like distortions. The bi-directional hydrogen bonding scheme implied by the monoclinic symmetry leads to a honeycomb structure which provides a satisfactory explanation for the good compression performance of the material.

As-spun M5 fibre

Surprisingly, the structure of the as-spun fibre differs completely from that of the heat-treated material, quite unlike other rigid-rod fibres where heat treatment merely leads to increased crystalline perfection. The material lacks three-dimensional crystalline order due to translational disorder of the polymer molecules in the direction of the fibre axis. The polymer chains pack in a two-dimensional lattice described by a non-primitive rectangular unit cell with parameters $a = 16.85$ Å, $b = 3.38$ Å. The a -axis is much larger than that in the heat-treated material, which is due to the presence of water molecules in the crystal lattice: the as-spun material is a hydrate in which stacks of polymer molecules are separated by sheets of hydrogen bonded water

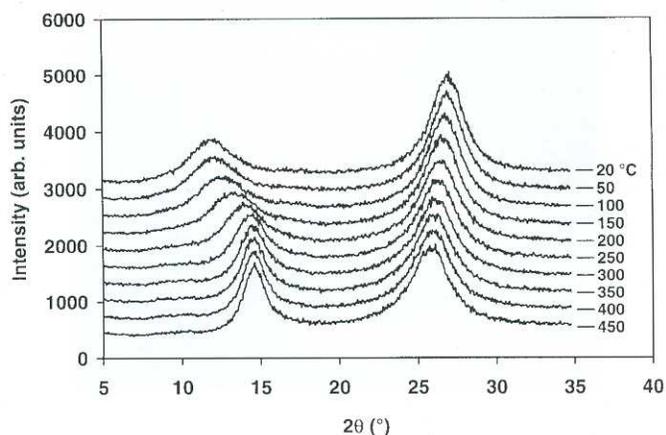


Figure 5: Equatorial X-ray scattering of as-spun M5 fibre as function of temperature in a nitrogen atmosphere. The first peak is the 2 0 0 peak, the second peak is indexed as 1 1 0 and 1 -1 0.

molecules. Heat treatment (or flushing with dry nitrogen) causes dehydration of the material. This is accompanied by a shift of the 2 0 0 reflection to larger diffraction angles, as can be observed in Figure 5 which shows the changes in the equatorial X-ray scattering of as-spun M5 upon heating. The *continuous* shift of this reflection indicates that in partly dehydrated material the two-dimensional lattice is disordered in the direction of the a -axis. This disorder can be described by a model assuming a random distribution of two repeat units in the a direction [4], as is shown schematically in Figure 6. Hence we propose that partly dehydrated M5

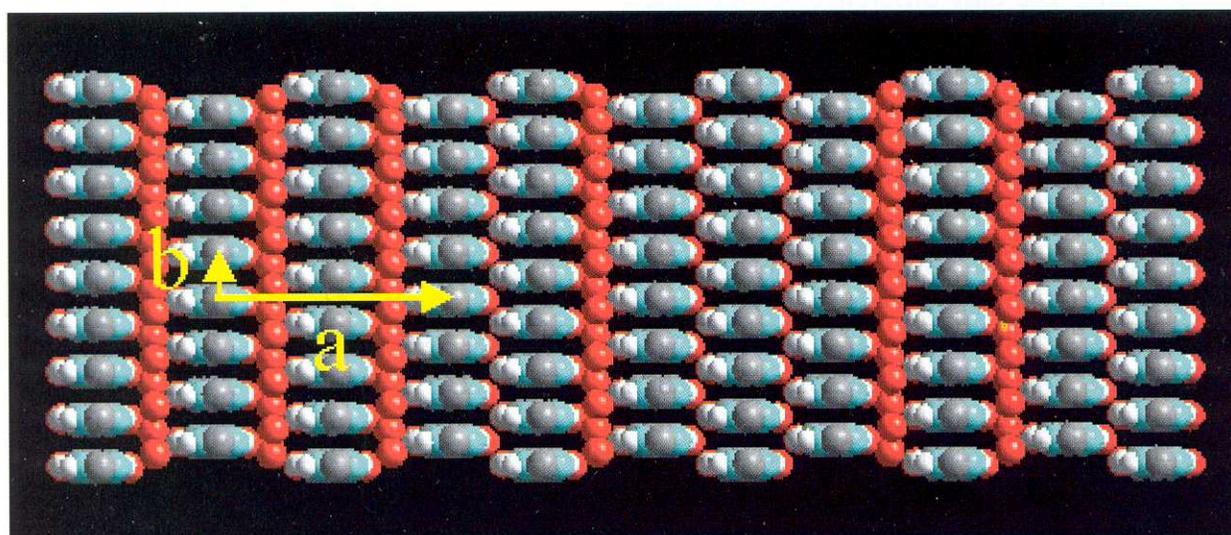


Figure 6: Schematic model of partially (de)hydrated M5 fibre showing lattice disorder in the a direction. The a and b -axes of as-spun M5 fibre are indicated in yellow. Oxygen, nitrogen and carbon atoms are coloured red, blue and grey respectively. The hydrogen atoms of the water molecules have been omitted. Note that in the illustration neighbouring stacks of polymer molecules are assumed to be correlated in the b direction. However, the stacks of polymer molecules which are separated by a sheet of water molecules may show translational disorder in the b direction. Such disorder may also exist in as-spun M5 fibre (*i.e.* in completely hydrated material).

consists of crystallites in which stacks of polymer molecules and sheets of water molecules form a non-periodic sequence. A related type of disorder is found in completely different material, *viz.* in random copolymers of two types of monomers that differ in molecular length [5, 6]. Crystallites based on identical but non-periodic sequences within neighbouring copolymer molecules were designated NPL (non-periodic layer) crystallites by Windle *et al.* [6]. Generalizing the concept of NPL crystallites somewhat, the crystallites in partly dehydrated M5 can also be referred to as NPL crystallites. Clearly, the hydrogen bonded water molecules in as-spun M5 contribute to the high fire resistance of the material. The model in Figure 6 suggests that dehydration proceeds via a "zipper" mechanism, so that removal of water molecules from a sheet that has already lost some water molecules has a higher probability than removal of water molecules from an entirely intact sheet of water molecules.

Acknowledgements

This work would have been impossible without the unflagging zeal of Dr Doetze Sikkema in making the M5 project successful. The authors also wish to acknowledge the stimulating interest of Dr. Maurits Northolt and a helpful discussion with Prof. Alan Windle.

References

- [1] Sikkema, D.J., *Polymer* (1998) **39**, 5981-5986.
- [2] Klop, E.A. and Lammers, M., *Polymer* (1998) **39**, 5987-5998.
- [3] Lammers, M., Klop, E.A., Northolt, M.G. and Sikkema, D.J., *Polymer* (1998) **39**, 5999-6005.
- [4] "b direction" should be replaced by "a direction" in ref. [2], p. 5996.
- [5] Blackwell, J., Biswas, A. and Bonart, C., *Macromolecules* (1985) **18**, 2126-2130.
- [6] Windle, A.H., Viney, C., Golombok, R., Donald, A.M. and Mitchell, G.R., *Faraday Disc. Chem. Soc.* (1985) **79**, 55.

X-Ray Analysis of the Network-Forming Collagen in the Dogfish *Scyliorhinus Canicula* Egg Case

C. Knupp and J.M. Squire

Biological Structure and Function Section, Biomedical Sciences Division, Imperial College School of Medicine, London SW7 2AZ.

Introduction

Network-forming collagens are essential to life for most multicellular organisms. In basal membranes, which are the part of the extracellular matrix that remain in direct contact with their formative cells, they accomplish supportive, protective and filtering roles, and they help cellular attachment, differentiation, migration and growth [1]. In human eyes, the building of abnormal collagen-like networks is related to serious sight threatening diseases that are poorly understood. Of these, age related macular disease alone is responsible for about 50% of the cases of legal blindness in the western world [2]. Structural studies of these molecular organisations are the first step towards understanding their function in the structures that they form or in the pathologies with which they are associated. Unfortunately, in most cases, network-forming collagens assemble into structures that are poorly ordered, making structural investigations particularly difficult. One way round this problem is to find and study in detail a network-forming collagen that assembles naturally in a regular way, in the hope that it can give general insights into the way network-forming collagens behave. The egg case of the dogfish *Scyliorhinus canicula* appears to be a very appropriate candidate for this task. It is formed by a collagen network that naturally possesses a high degree of order. Like the basal membrane it fulfils a supportive, protective and filtering role, being the only medium between the embryo and the sea. Furthermore, its molecular arrangement is strikingly similar to that found in the ocular assemblies associated with age related macular disease.

Dogfish Egg Case

With the naked eye, the capsule containing the dogfish egg appears as a small convex rectangular-shaped container, 50 by 20 mm on average (Figure 1). The two anterior and the two posterior corners are elongated to form horn-like structures that continue their extension as four long, coiled, thread-like