

## Notes

## New Insights into the Structure of Poly(*p*-phenylene terephthalamide) from Neutron Fiber Diffraction Studies

K. H. Gardner,<sup>†</sup> A. D. English,<sup>†,||</sup> and V. T. Forsyth<sup>\*,‡,§</sup>

DuPont Central Research and Development, Experimental Station, Wilmington, Delaware 19880; Department of Materials Science and Engineering, University of Delaware, Newark, Delaware 19716; Institut Laue Langevin, 6 Rue Jules Horowitz, 38042 Grenoble Cedex 9, France; and Lennard Jones Laboratory, School of Chemistry and Physics, Keele University, Staffordshire ST5 5BG, UK

Received July 28, 2004

Revised Manuscript Received September 25, 2004

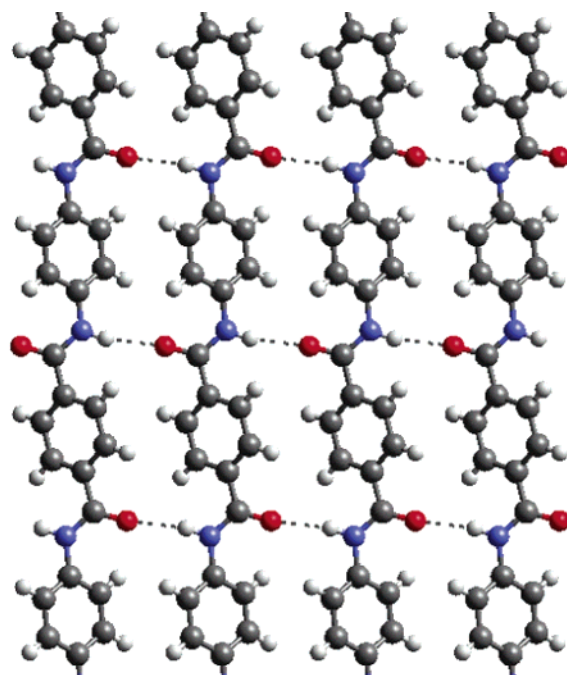
### Introduction

Poly(*p*-phenylene terephthalamide), PPTA, is a highly crystalline polymer that can be spun into fibers that exhibit exceptional thermal and mechanical properties.<sup>1</sup> It has numerous commercial applications and is sold under the trade names of Kevlar and Twaron. In some respects the structure of PPTA is well-known—the unit cell parameters, chain conformation, and the hydrogen bonding of neighboring chains (between amide groups) to form sheets are all well established (Figure 1). However, the relative displacement of the chains and the nature of the intersheet interactions are still in question.

In 1973, very similar structures for PPTA were independently proposed by Northolt<sup>2,3</sup> and Tadokoro and co-workers<sup>4,5</sup> based on X-ray fiber diffraction studies. The structure described by Northolt has *Pn* space group symmetry while that proposed by Tadokoro has *P2<sub>1</sub>/n* symmetry. The proposed space groups require a relative translation of  $0.5c$  between the two chains (between sheets), placing a terephthaloyl group in one chain at the same height as a phenylene diamine group in the second chain (in the adjacent sheet). A schematic representation of the chain packing in these structures is shown in Figure 2a.

More recently Liu and co-workers,<sup>6</sup> using electron diffraction data from single crystals, concluded that the true structure belongs to space group *Pa*. This space group places the chains at the same height, with the terephthaloyl groups in one chain at the same height as terephthaloyl groups in the second chain in the adjacent sheet (see Figure 2b).

The aim of the current study is to resolve the issue of the structure of PPTA in a way that is compatible with the available neutron fiber diffraction data. It is clear



**Figure 1.** PPTA structure showing the hydrogen bonding of neighboring chains to form a characteristic sheet.

**Table 1.** Table Showing Crystal Structure Data for the Three Published Models for PPTA

	Northolt <sup>2,3</sup>	Tadokoro <sup>4,5</sup>	Liu <sup>6</sup>
<i>a</i> (Å)	7.87	7.80	7.88
<i>b</i> (Å)	5.18	5.19	5.22
<i>c</i> (Å)	12.9	12.9	12.9
$\alpha, \beta, \gamma$	90, 90, 90	90, 90, 90	90, 90, 90
space group	<i>Pn</i>	<i>P2<sub>1</sub>/n</i>	<i>Pa</i>
chain location ( <i>a</i> × <i>b</i> )	[0,0], [ $1/2, 1/2$ ]	[0,0], [ $1/2, 1/2$ ]	[ $1/4, 1/4$ ], [ $3/4, 3/4$ ]
<i>Z</i>	2	2	2
<i>c</i> translation between terephthaloyl groups in the two chains I	~0.5	0.5	0.0

that previous X-ray fiber diffraction work has suffered from the fact that the terephthaloyl and diamine groups differ only slightly in their overall scattering of X-rays. As a result, it has proved difficult to distinguish between a number of competing models. A key aspect of this study has been the use of selectively deuterated PPTA fibers in which the terephthaloyl residues were selectively deuterated, so that the terephthaloyl and diamine groups make markedly different contributions to the observed neutron diffraction patterns.

### Experimental Methods

**Material Synthesis.** The selectively deuterated PPTA polymer [PPTA-*T*(*d*<sub>4</sub>)] (see Figure 3) was produced by the polymerization of *p*-phenylenediamine with >99% isotopically

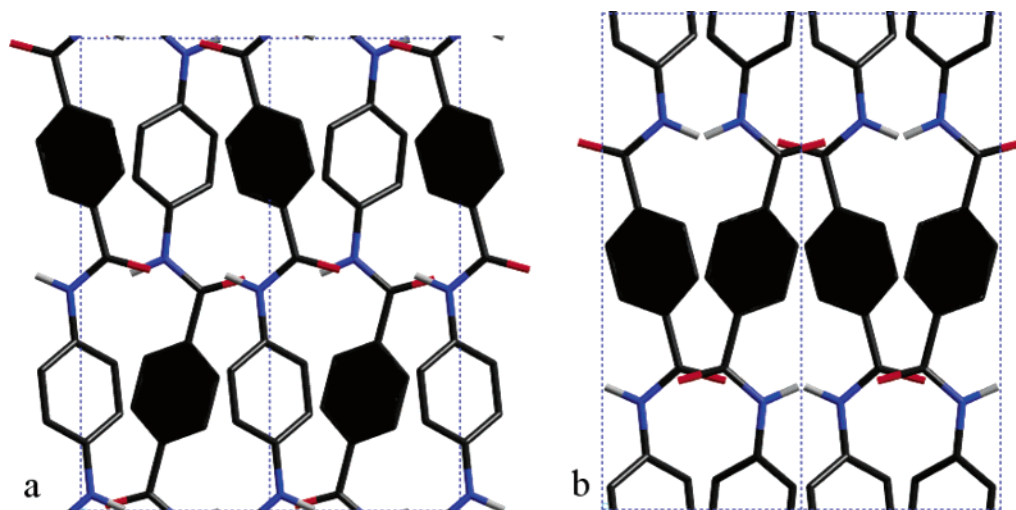
\* Corresponding author. Email: tforsyth@ill.fr.

<sup>†</sup> DuPont Central Research and Development.

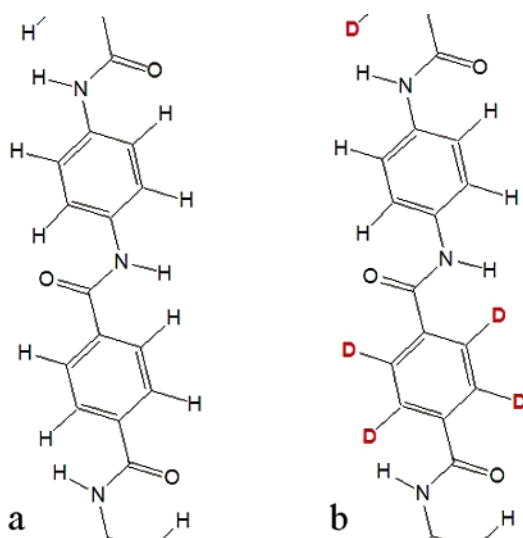
<sup>‡</sup> Institut Laue Langevin.

<sup>§</sup> Keele University.

<sup>||</sup> University of Delaware.



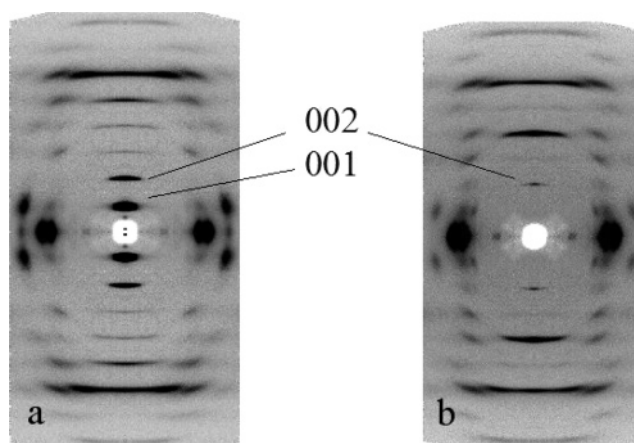
**Figure 2.** Projections of the PPTA unit cell (in the  $bc$  plane). The terephthaloyl residues are shown in black. (a) shows the Northolt/Tadokoro-type structure and (b) the structure due to Liu et al.<sup>6</sup>



**Figure 3.** Diagrams showing (a) the nondeuterated PPTA polymer and (b) the selective deuteration of the terephthaloyl residues used in this study.

pure terephthaloyl- $d_4$  chloride in an 8% solution of  $\text{CaCl}_2$  in  $N$ -methylpyrrolidone followed by precipitation in water. The nondeuterated PPTA polymer was prepared using the same procedure. In both cases the fibers were air gap spun from a 20% solution of polymer in 100%  $\text{H}_2\text{SO}_4$  at 80 °C, through a 10-hole 3 mm diameter spinneret (aspect ratio of 3) with an air gap of 0.5 cm, solution jet velocity of 20 m/min, and a spin stretch factor of 6, into a 35 cm long 3 °C water bath. Further details are given in ref 7, which describes the procedures as part of a previous NMR study of selectively deuterated PPTA fiber.

**D19 Diffractometer at the ILL.** The D19 diffractometer at the Institut Laue Langevin (ILL) and its application for high-angle neutron fiber diffraction has been described previously.<sup>8–13</sup> In the current work this instrument was used with a monochromatic beam of neutrons of wavelength 1.542 Å, produced by Bragg reflection from the (220) plane of a focusing copper monochromator, which was curved about its vertical axis. The wavelength spread  $\Delta\lambda/\lambda$  was  $\sim 1\%$ . The beam size was limited by adjustable rectangular lithium fluoride slits. The detector was a “banana”-shaped multiwire gas-filled position-sensitive device with a vertical aperture of 64° and a horizontal aperture of 4°. The long axis of the detector had a radius of curvature of 1.164 m and was symmetrically located about the equatorial plane with its long axis vertical. The detector had 16 cathodes parallel to its long axis with a 5.0



**Figure 4.** Neutron fiber diffraction patterns recorded from (a) selectively deuterated and (b) nondeuterated fibers of PPTA.

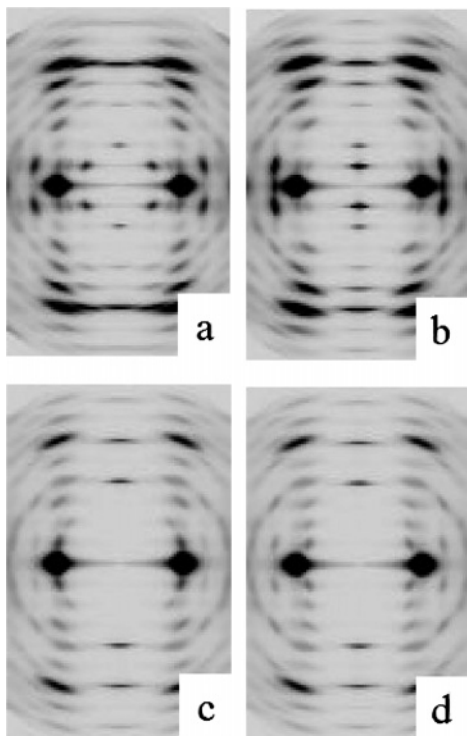
mm wire spacing and 512 anodes parallel to its short axis with a spacing of 2.54 mm, giving an angular resolution of  $0.25^\circ \times 0.125^\circ$ . The sample was positioned at the center of curvature of the detector. The detector was calibrated for nonuniformity of response by recording the diffuse scattering from a 1 cm solid cylindrical rod of vanadium. An online data acquisition system (MAD) enabled diffractometer movements and data collection to proceed according to a preselected set of instructions. Data processing occurred through a purpose-designed software package designed for compliance with the CCP13 data processing suite.<sup>14</sup>

**Simulation of Neutron Fiber Diffraction Patterns.** Simulations of fiber diffraction patterns were carried out using the Cerius2 (4.2) (Molecular Simulations, Inc.) software. Neutron fiber diffraction patterns were calculated using the following parameters:  $\lambda = 1.5$  Å; crystallite sizes in the  $a$ ,  $b$ , and  $c$  direction were 6, 6, and 10 nm, respectively. The misorientation factor was  $5^\circ$  (fwhm).

## Results

**Neutron Diffraction.** Figure 4 shows the corrected neutron diffraction patterns for PPTA-T( $d_4$ ) (left) and the nondeuterated PPTA control (right). Clear differences in the observed intensities are apparent throughout the range of diffraction covered.

The diffraction pattern recorded from the control (hydrogenated) sample has strong meridional reflections of even order while those of odd order are very weak.



**Figure 5.** Neutron fiber diffraction patterns simulated from PPTA model structures: (a) and (b) show respectively the patterns simulated from the Northolt and Liu models with selectively deuterated terephthaloyl residues; (c) and (d) show the patterns simulated from the same models, with no deuteration.

In this respect the data are similar to those recorded by X-ray fiber diffraction and could be thought of as consistent with all of the previously summarized models as summarized in the Introduction, i.e., consistent with a structure having a  $2_1$  screw along the  $c$ -axis or a relative shift of the two molecules by  $c/2$ .

The diffraction pattern recorded from the selectively deuterated analogue (Figure 4, left) shows strong meridional reflections on all layer lines. It is evident that these data are not consistent with models for this polymer of the Northolt/Tadokoro type since there are strong meridional reflections on layer lines of odd order.

**Comparison of Observed Meridional Diffraction with Data Simulated from Model Structures.** Figure 5 shows the neutron fiber diffraction patterns simulated from the Northolt and Liu models for PPTA, both with and without deuteration. The chain conformation was taken from the relevant model and then, with the appropriate space group symmetry, used to generate the second chain in the unit cell.

## Discussion

On the basis of the meridional data observed for the selectively deuterated PPTA fiber, it is evident that the observed neutron data are not consistent with models for this polymer of the Northolt/Tadokoro type (compare Figure 4a with Figure 5a), while they are consistent with the model proposed by Liu (compare Figure 4a with Figure 5b). It should be noted however that there remain discrepancies between the observed data and that predicted by the Liu model. Our samples diffract well beyond the resolution range we have so far covered, and we are currently planning a higher resolution neutron study of this polymer. We then intend to

undertake a definitive structural analysis against both neutron and X-ray fiber diffraction data.

This study highlights a number of issues relating to the use of neutron fiber diffraction for the study of polymer conformation and the complementarity of such work with X-ray diffraction studies. First, hydrogen atoms scatter neutrons much more strongly than they do X-rays and are usually far more visible in neutron structure determination than they are in comparable X-ray studies. Hence, given sufficient resolution, neutron fiber diffraction data can be used to distinguish between terephthaloyl and diamine residues. In the current work our data are limited in resolution, particularly in the equatorial direction, and it can be seen from a comparison of the observed data for the completely hydrogenated PPTA (Figure 4b) with the simulations shown in Figure 5c,d that the results do not provide a strong basis for distinguishing between candidate models. For the data recorded from the selectively deuterated PPTA fiber sample, the opposite is true—the deuteration has introduced clear contrast between the two residue types and enabled a high degree of certainty in determining the relative intersheet chain translations in the PPTA unit cell. It can be expected that this type of approach may become of more general use in fiber diffraction studies where information on subtle aspects of structure in an otherwise regular polymer system may be of functional importance. Major developments are in progress for the development of facilities for neutron diffraction and are likely to be of importance for future neutron fiber diffraction work.<sup>15</sup>

**Acknowledgment.** We gratefully acknowledge Sax Mason and John Archer for advice with the preparation of the neutron diffraction experiments.

## References and Notes

- (1) Yang, H. H. *Kevlar Aramid Fiber*; Wiley: New York, 1993.
- (2) Northolt, M. G.; van Aartsen, J. J. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 333.
- (3) Northolt, M. G. *Eur. Polym. J.* **1974**, *10*, 799.
- (4) Hasagawa, R. K.; Chatani, Y.; Tadokoro, H. In *Proceedings of the Meeting of the Crystallographic Society of Japan*, Osaka, Japan, 1973; p 21.
- (5) Tashiro, K.; Kobayashi, M.; Tadokoro, H. *Macromolecules* **1977**, *10*, 413.
- (6) Liu, J.; Cheng, S. Z. D.; Geil, P. H. *Polymer* **1996**, *37*, 1413.
- (7) Schaefer, D. J.; Schadt, R. J.; Gardner, K. H.; Gabara, V.; Allen, S. R.; English, A. D. *Macromolecules* **1995**, *28*, 1152.
- (8) Forsyth, V. T.; Shotton, M. W.; Ye, H.; Pope, L. H.; Boote, C.; Langan, P.; Denny, R. C. *Fibre Diffraction Rev.* **1998**, *7*, 17.
- (9) Forsyth, V. T.; Mahendrasingam, A.; Pigram, W. J.; Greenall, R. J.; Bellamy, K. A.; Fuller, W.; Mason, S. A. *Int. J. Biol. Macromol.* **1989**, *11*, 236.
- (10) Langan, P.; Forsyth, V. T.; Mahendrasingam, A.; Pigram, W. J.; Fuller, W.; Mason, S. A. *J. Biomol. Struct. Dyn.* **1992**, *10*, 489.
- (11) Shotton, M. W.; Pope, L. H.; Forsyth, V. T.; Langan, P.; Denny, R. C.; Giesen, U.; Dauvergne, M.-T.; Fuller, W. *Biophys. Chem.* **1997**, *69*, 85.
- (12) Shotton, M. W.; Pope, L. H.; Forsyth, V. T.; Denny, R. C.; Archer, J.; Langan, P.; Ye, H.; Boote, C. *J. Appl. Crystallogr.* **1998**, *31*, 758.
- (13) Nishiyama, Y.; Langan, P.; Chanzy, H. *J. Am. Chem. Soc.* **2002**, *124*, 9074.
- (14) Squire, J.; Al-Khayat, H.; Arnott, S.; Crawshaw, J.; Diakun, G.; Denny, R.; Dover, D.; Forsyth, V. T.; He, A.; Knupp, C.; Mant, G.; Rajkumar, G.; Rodman, M.; Shotton, M.; Windle, A. *Fibre Diffraction Rev.* **2003**, *11*, 7.
- (15) Forsyth, V. T.; Mason, S. A.; Howard, J. A. K.; Davidson, M. G.; Fuller, W.; Myles, D. A. A. *Neutron News* **2001**, *12*, 20.