polymer papers

Morphology and structure of poly(*p*-phenylene terephthalamide) crystallized from dilute organic solution*

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The high-temperature crystallization of poly(*p*-phenylene terephthalamide) (PPTA) from dilute organic solutions was achieved through the introduction of a non-solvent, or precipitating agent, at the desired crystallization temperature. The morphology and crystal structure were examined for crystals produced from PPTA polymer with two different molecular weights ($M_w = 46\,000$ and $3430\,\mathrm{g\,mol^{-1}}$), using transmission electron microscopy. For the high-molecular-weight polymer, ribbon-like crystals were produced, while the low-molecular-weight polymer yielded small needles or platelets. In both cases, electron diffraction showed that the Northolt allomorph was obtained. For the high-molecular-weight polymer, the molecular axes were parallel to the ribbon axes in a chain-extended type structure. A hypothesis for the orientation of the low-molecular-weight PPTA in the small platelets, is also given.

(**Keywords: poly(*p*-phenylene terephthalamide); solution crystallization; morphology**)

INTRODUCTION

The transformation of liquid crystalline polymer (LCP) solutions into oriented, solid-state materials is an important technological and scientific field of study. Technologically, many high performance polymers are produced from LCP solutions in fibre spinning operations. One example of this is KEVLAR® aramid fibres, marketed by E. I. Du Pont de Nemours and Company. Scientifically, the phase behaviour of LCP solutions is known to be extremely complex, with thermoreversible gel formation and crystal solvate complexes frequently reported. The thermodynamics and kinetics of these LCP systems is only just beginning to be understood by experimental and theoretical scientists in any great detail. In this work, we will focus on the morphology of poly(*p*-phenylene terephthalamide) (PPTA) crystallized from dilute organic solutions.

A discussion of previous work on the crystal structure and morphology of PPTA fibres, determined using X-ray diffraction[1,2], transmisson electron microscopy (TEM)[3,4] and optical microscopy[5] is relevant for this study. The crystal structure is a pseudo-orthorhombic type, with the unit cell parameters shown in *Figure 1a*. The polymer crystallization under fibre processing conditions is extremely complex and difficult to study *in situ*. Typically, fibres are spun from concentrated sulfuric acid solution in the nematic liquid crystal state, followed by a quench and solvent exchange into cold water. The formation of polymer crystal solvates with the acid, due to the strong hydrogen bonding which occurs, have been reported[6,7]. A minor degree of sulfonation of the aromatic rings, which can have an effect on the solubility of the fibres, is also reported[8].

Another crystalline polymorph of PPTA has been prepared by dilute solution precipitation of the polymer[9]. This form is called the Modification II or Haraguchi allomorph and is identified by the unit cell shown in *Figure 1b*. The Modification II polymorph is formed by coagulation of a PPTA solution (3 wt%) in sulfuric acid using water as the coagulating solvent. Conversion from Modification II to Modification I is possible by boiling in methanol or acetone. Unquestionably, solution studies of PPTA have been limited by the poor solubility of this polymer in more common organic solvents. A small number of other studies, in addition to the work of Haraguchi *et al.*[9,10], have been carried out in sulfuric acid using 3–15 wt% of PPTA[11–13]. Some early work was also done by dissolving low-molecular-weight PPTA ($M_w = 6500$) in hexamethylphosphoric triamide/1-methyl-2-pyrrolidone/lithium chloride solutions, a polymerization cosolvent system[14]. Both sets of experiments produced

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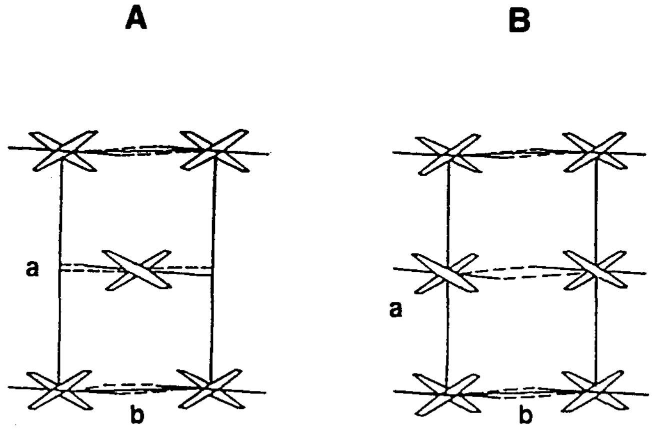

Figure 1 Crystalline polymorphs reported for PPTA: a, Modification I or Northolt allomorph[1] and; b, Modification II or Haraguchi allomorph[9]

primarily spherulitic crystals consisting of 'fibrous' lamellae, several hundred angstroms in width, where the chain axis is perpendicular to the long axis of the lamellae. For the high-molecular-weight polymer, hydrolysis occurred during crystallization and the width of the 'fibrous' lamella depended on the degree of degradation. In one case, fibrillar crystals, where the molecular axes were parallel to the fibre axis, were produced by precipitating, with stirring, the polymer into a non-solvent[11].

The ultimate goal of this work was to prepare single crystals of PPTA. To achieve this, dilute solutions of PPTA in a novel organic solvent system were prepared using polymers with two different molecular weights. We hoped to determine if lamellar crystals of PPTA would form with low-molecular-weight polymer, rather than the fibrillar, chain-extended structures often seen with high-molecular-weight rigid-rod polymers[15]. The polymer was precipitated from solution with a non-solvent at various temperatures. The effect of these variables on the morphology and the crystal structure was investigated using transmission electron microscopy (TEM) techniques.

EXPERIMENTAL

Materials and solution preparation

The PPTA used in this study was the 'as polymerized' polymer, rather than polymer which had been previously spun into fibre form from a sulfuric acid solution. Two different molecular-weight extremes were investigated, namely a low-molecular-weight (*MW*) PPTA with inherent viscosity, $\eta_{inh}=0.2$, and a high-*MW* PPTA with $\eta_{inh}=6.0$, with these viscosities determined in sulfuric acid. The molecular weights as determined by size exclusion chromatography (s.e.c.)[16] in dimethylpropyleneurea (DMPU)/LiCl solution are given along with approximate molecular characteristics in *Table 1*.

The polymer solutions, containing 0.05 wt% PPTA, were prepared in a mixture of freshly distilled DMPU (plus 3% LiCl) under dry box conditions. The solutions were heated at 110°C for 8–16 h to dissolve the polymer, and subsequently stored in a desiccator at room temperature.

Polymer crystallization

High temperature crystallization of the polymer was successfully carried out over the temperature range from 150–200°C in a stainless steel autoclave. The method used[17] allows the precipitation of polymer from DMPU/LiCl solution by the addition of non-solvent at the crystallization temperature. Non-solvents (precipitating agents) that were used included water, methanol and glycerin, mixed in various proportions with the original PPTA solution.

Table 1 Molecular characteristics of PPTA of different molecular weights

η_{inh} in sulfuric acid	M_w[a] ($g\,mol^{-1}$)	x[b]	L[c] (nm)
0.2	3430	14.4	18
6.0	46 000	193	240

[a] M_w determined by size exclusion chromatography in DMPU/LiCl at 80°C[16]

[b] Calculated using $x=M_w/M_0$, where $M_0=238\,g\,mol^{-1}$ for PPTA

[c] Calculated using an estimated monomer length, l_0, of 1.25 nm[14], using the equation $L=l_0x$

The crystallization was conducted in the following way. A measured quantity of PPTA solution was sealed in a glass ampoule with a breakseal, containing a small stainless steel 'hammer'. The ampoule was placed inside the autoclave and a measured quantity of non-solvent was added. The autoclave was then sealed and equilibrated at the desired temperature for 1 h, and after this time the autoclave was shaken in order to puncture the breakseal and produce a mixing of the PPTA solution and the precipitating agent. Crystallization was then allowed to proceed at the chosen temperature for ~0.5 h, and the mixture was cooled to room temperature. The precipitate or 'polymer crystals' were then collected and washed by successive centrifugation in methanol.

Electron microscopy

The crystal suspensions were deposited on carbon-coated copper mesh grids. The crystals were imaged using a JEOL 2000 FX microscope operating at 200 kV, and electron diffraction measurements were made using either the selected area diffraction method of Le Poole[18] or the microdiffraction technique of Riecke and Ruska[19]. Low-dose TEM principles were applied in order to obtain the diffraction patterns and dark-field images, including use of a small condenser aperture, small spot size, reduced beam current and a beam blanker to preserve specimen integrity. Electron diffraction diagrams were calibrated with gold. Some imaging was also done at 80 kV on preparations shadowed with W/Ta alloy on a Philips 400 T instrument.

RESULTS AND DISCUSSION

The high temperature crystallization of PPTA from organic solutions was easily achieved by using water or methanol as the precipitating agents. Different morphologies were obtained for the high- and low-*MW* polymer, which will be described in detail below. In general, the morphologies observed were very different from previously published reports of higher concentration solution crystallization of PPTA, which are generally described as spherulitic crystals[9–13]. It is noteworthy that attempts to crystallize the PPTA by slow adsorption of water at room temperature were also made but these most often produced weak gels from which crystals could not be isolated for further study.

The high-*MW* crystals of PPTA consisted of twisted ribbons with widths of 50–100 nm and thicknesses of the order of 5–10 nm. A typical batch of crystals prepared at 200°C is shown in *Figure 2* in an image shadowed with W/Ta alloy. The long ribbons are interconnected in a 'network' with a random overall orientation, and the ribbons are often twisted.

A bundle of ribbons, such as that shown in *Figure 2*, analysed by the selected area electron diffraction method, gives the fibre pattern shown in *Figure 3a*. This pattern consists of three arcs: along the meridian there is an arc at a spacing of 0.22 nm, and along the equator there are two closely spaced arcs at 0.43 (strong) and 0.40 nm (weak). This diagram resembles the essential features of the fibre diagram of PPTA recorded from an ultrathin section of a commercial KEVLAR-49® fibre sectioned longitudinally (see *Figure 3b*), and allows the identification of the form shown in *Figure 3a* as the Northolt allomorph. The meridional diffraction can be identified as the 006 reflection, whereas those along the equator correspond to the 110 and 200 reflections. The measured *d* spacings are given in *Table 2*, along with the literature values. Thus, in the corresponding crystals, the chain axes are along the long axis of the ribbon, in contrast to other polyamides, where the chain axis is perpendicular to the ribbon axis and chain-folding is found to occur. It is most likely that there is no chain folding in these crystals, as the stiffness of the molecules and their liquid crystalline properties are well known.

In *Figure 4*, the microdiffraction technique is used to record a microdiffraction diagram on one of the ribbons. In this experiment, a microdiffraction probe of 50 nm was used and appears as the bright white spot in the centre of the figure. The corresponding fibre pattern, shown in the inset of *Figure 4*, no longer consists of arcs but of sharp dots, especially on the equator, where two spots indexed along the 200 diffraction line can be observed. This indicates that within the size of the diffraction probe, there are two crystalline blocks which are slightly rotated with respect to one another. The image shown in *Figure 4* is a low-dose image on the unstained and unshadowed specimen.

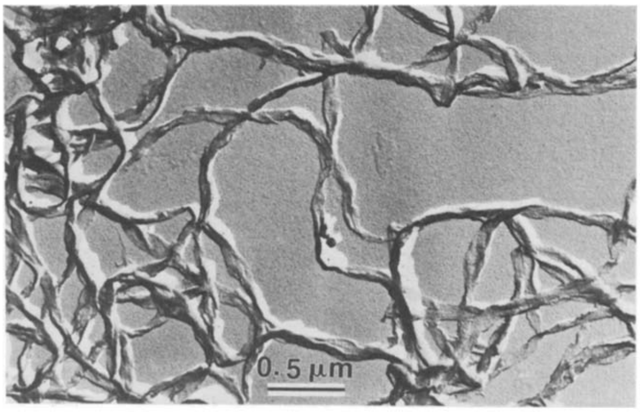

Figure 2 Crystals of high-*MW* PPTA grown from 0.05 wt% PPTA in DMPU/LiCl solution with water as the non-solvent. The W/Ta shadowed bright-field image shows the twisted ribbon-like morphology

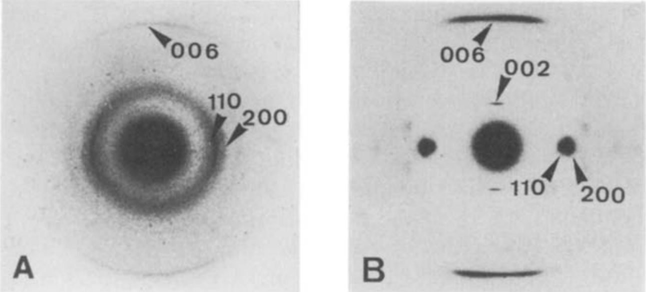

Figure 3 Crystals of high-*MW* PPTA: A, fibre diffraction pattern from a bundle of ribbons with vertical axis showing the 110, 200 and 006 reflections typical of the Northolt allomorph and; B, fibre diffraction pattern from a longitudinal section of PPTA commercial fibre (KEVLAR®), also as the Northolt allomorph, shown for comparison

Table 2 Experimental and literature *d* spacings for PPTA

	d spacing (nm)			
	Literature values		This work	
hkl	I^a	II^b	Low *MW*	High *MW*
002	0.64	–^{c}	–	0.64
010	Absent	0.51	Absent	Absent
110	0.43	Absent	0.43	0.43
200	0.39	0.40	0.39	0.40
004	0.32	0.32	0.32	0.31
006	0.22	0.22	0.21	0.22

[a] Data from ref. 1
[b] Data from ref. 10
[c] Not reported

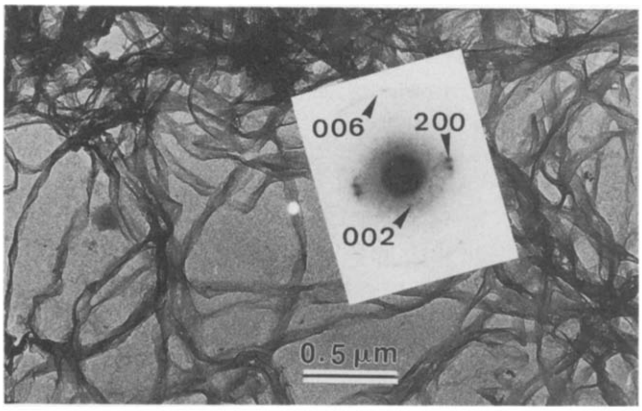

Figure 4 Crystals of high-*MW* PPTA, bright-field image, unshadowed and unstained, with bright white spot indicating the region from which electron microdiffraction (in inset) of a ribbon is obtained, showing a fibre pattern with the 200, 002 and 006 reflections

The observation of the Modification I type of crystal structure was not expected at the onset of this work, since previous attempts to crystallize PPTA from very dilute solutions by using water as the precipitating agent have produced only the Modification II type of crystals[9]. However, Modification II crystals that were formed at room temperature were fairly easily converted to the Modification I type by heating, indicating that temperature, not solvent, is the controlling factor. We note that a similar morphology and crystal structure were obtained for the high-molecular-weight polymer at 160°C.

Dark-field images of the high-*MW* PPTA crystals were obtained by the high resolution beam tilting method for the combined 110 and 200 equatorial reflections, and are shown in *Figure 5*. The dark-field technique allows a visualization of the crystallites within the fibrillar

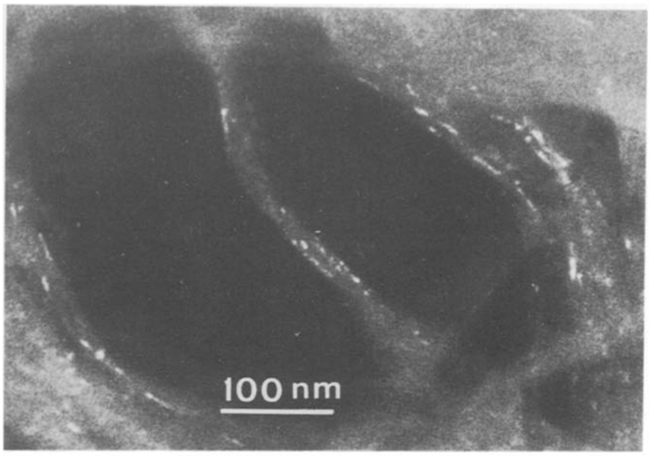

Figure 5 Crystals of high-*MW* PPTA, dark-field image of the combined 110 and 200 reflections, showing orientation of small crystals along the ribbon axis

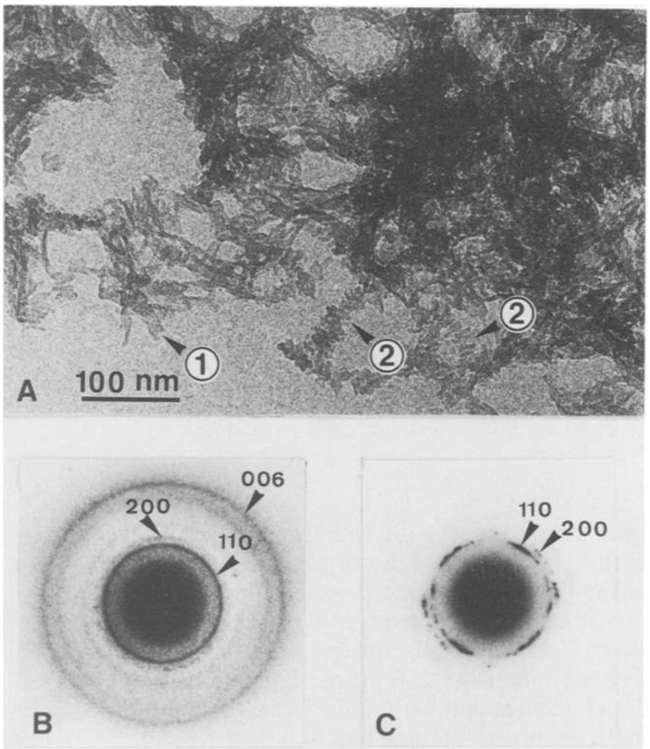

Figure 6 Crystals of low-*MW* PPTA grown from 0.05 wt% PPTA in DMPU/LiCl solution with water as the non-solvent: A, bright-field image, unshadowed and unstained; B, electron diffraction of a group of crystals, showing the 110, 200 and 006 reflections typical of the Northolt allomorph and; C, microdiffraction showing the dotted patterns of the 110 and 200 reflections

structure, and can also give an idea of the size and orientation of the crystallites. In *Figure 5*, they consist of white elongated areas within the ribbons that are quite small; typically their dimensions are on the order of 5–10 nm. The overall orientation of the crystallites is along the axis of the fibrils. Attempts to image the 006 reflection in the dark-field mode were unsuccessful, due to the very weak intensity of this reflection.

The low-*MW* crystals of PPTA showed a very different morphology, as given in the low-dose image in *Figure 6a* for a typical batch of crystals grown at 160°C, (unshadowed and unstained). This image shows an agglomeration of small crystals which resemble platelets or needles. The size of the crystals ranges from 20–50 nm in length and are ~10 nm in width. In some cases, the platelets are lying flat (labelled 1), while in other areas shish-kebab structures are seen (labelled 2). The structures are not perfectly regular, so it is difficult to specify an exact size. The uniformity of these crystals might be improved if a careful fractionation of the sample were made prior to crystallization, so that the molecular lengths were more monodisperse.

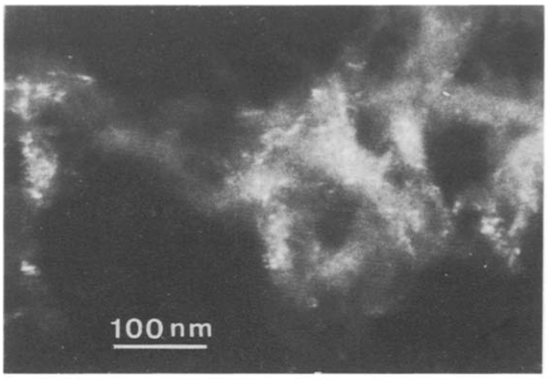

Figure 7 Crystals of low-*MW* PPTA as the dark-field image of the combined 110 and 200 reflections

Selected area electron diffraction of a group of crystals contained in approximately one square micrometre of the specimen is shown in *Figure 6b*. The diagram shows a powder pattern that also corresponds to the Northolt type (Modification I) of PPTA. In particular, one can identify the rings corresponding to the 110 (strong), 200 (weak) and 006 (weak) reflections. The measured *d*-spacings are given in *Table 2*. The rings observed for the 110, 200 and 006 reflections indicate that many small crystals in different orientations are present in the selected area chosen.

Attempts were made to gain information about molecular orientation within the small crystals of the low-molecular-weight PPTA, using microdiffraction and dark-field techniques. In *Figure 6c*, a microdiffraction pattern is shown, with the area of the specimen sampled in this case ~100 nm^2. Only two dotted arcs are observed in this mode, and they correspond to the diffraction of the (110) and (200) planes. In *Figure 7*, a dark-field image of the combined 110 and 200 reflections is given and shows bright white streaks. These are likely to correspond to crystals laying edge on, as in the region labelled 2 in *Figure 6a*, in a shish-kebab type of structure. The dimensions in this case are 4–6 nm. An interpretation of the low-molecular-weight PPTA is much less straightforward than in the case of the fibrils of the high-molecular-weight polymer, since the morphological features are much smaller and less distinct.

Although the experimental data are limited, we believe that the chain axes may be oriented parallel to the long axis of the platelet, similar to that of a short fibre, since the 'lamellar' thickness is too small to accommodate the calculated length of the molecule, i.e. 18 nm, as given in *Table 1*. In rigid-rod polymers such as PPTA, chain folding is not observed except for LCP copolymers with flexible spacers[20], and we do not consider this to be a possibility. Alternatively, the molecular axes may be normal to the substrate, but this is difficult to determine since the thickness of the crystals is not known. It remains to be explained why the width of the platelets is fairly uniform, i.e. ~10 nm, if the width is not controlled by the molecular length. We propose that this may be related to the kinetics of crystallization of the PPTA. For example, in PPTA fibres, the lateral crystallite size (perpendicular to the fibre axis) is known to be very small, in the range of 5–10 nm[21,22], when compared to the length of the crystal along the *c*-axis (fibre axis)[21].

SUMMARY

Two different morphologies of PPTA were produced by solution crystallization at high temperature, depending on the molecular weight of the polymer. In both cases, the crystal structure was the Northolt allomorph, also called Modification I crystals. For the high-molecular-weight PPTA, highly interconnected ribbon-like morphologies were observed, with ribbon widths in the range of 50–100 nm. For the low-molecular-weight PPTA, very small platelets were obtained with lengths of 20–50 nm and widths of ~10 nm. This is the first report of such morphologies for crystals of PPTA and may be a promising route for preparing single crystal structures from more carefully fractionated samples.

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