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X-RAY DIFFRACTION STUDY OF POLY(*P*-PHENYLENE TEREPHTHALAMIDE) FIBRES

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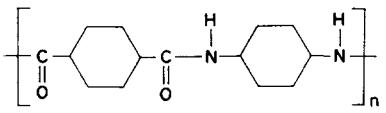
Abstract—On the basis of an X-ray diffraction study, a model is proposed for the crystal and molecular structure of poly(*p*-phenylene terephthalamide). The monoclinic (pseudo-orthorhombic) unit cell [a = 7·87 Å, b = 5·18 Å, c (fibre axis) = 12·9 Å and γ = 90°] possesses Pn or $P2_1/n$ space-group symmetry. Two molecular chains pass through the cell, one through the centre and the other through a corner. Approximate values for the orientation angles between the phenylene planes and the amide planes are 38° for the *p*-phenylene diamine segment and −30° for the terephthalic segment. Hydrogen bonds are formed between adjacent chains lying in the (100) plane. The conformation of the chain is primarily governed by competitive intramolecular interactions between the conjugated groups.

INTRODUCTION

Many X-ray diffraction studies have been made on the crystalline structure of aliphatic polyamides, of which the two well-known examples are nylon 6 [1] and nylon 66 [2]. To the author's knowledge no detailed diffraction study has been published yet of one of the aromatic polyamides. Members of this group of polymers have good thermal stability and their mechanical properties, e.g. high elasticity modulus and low elongation at breakage, are quite remarkable when compared with those of other polyamides [3,4]. In solution some of the aromatic polyamides show liquid-crystalline behaviour [5,6]. In order to gain an insight into the nature of these interesting physical properties, an X-ray diffraction study was made of poly(*p*-phenylene terephthalamide) fibres. Part of the results have been published earlier in a preliminary form [6]. This paper gives a detailed description of the analysis and the arguments which led to the proposed structure.

EXPERIMENTAL

For the purpose of this investigation, the polymer poly(*p*-phenylene terephthalamide)



was prepared by mixing terephthaloylchloride in a solution of *p*-phenylenediamine in N-methyl-pyrrolidone and hexamethylphosphorictriamide. After washing successively in water, ethanol and acetone, the polymer was isolated by filtration. For the wet spinning of the fibres, a sulphuric acid solution was selected. After washing and drying, the filament was led through an oven heated up to 500°.

X-Ray diffraction photographs of the fibres were taken in a cylindrical camera with a diameter of 114·6 mm using CuKα radiation. During the exposure the camera was evacuated. A total number of 44 reflections were classified as being above background and their intensities could be estimated visually. For 14 reflections, the intensity was measured with a Philips vertical diffractometer using a xenon filled proportional counter and a pulse-height discriminator. In order to apply the transmission geometry for these measurements, the fibres were wound parallel around a frame. The procedure for the determination of integrated intensities from the radial and azimuthal scans has been described elsewhere [7]. The results are given in Table 1.

ANALYSIS AND RESULTS

Well-oriented fibres of poly(*p*-phenylene terephthalamide) give a diffraction pattern as shown in Fig. 1a. All the reflections observed could be satisfactorily indexed by assuming a monoclinic (pseudo-orthorhombic) unit cell with dimensions a = 7·87 Å, b = 5·18 Å and c (fibre axis) = 12·9 Å, γ being approximately 90°. The observed extinctions are (hko) with (h + k) odd and (hol) with l odd. As will be discussed later, it has appeared in the course of the analysis that the extinction (hol) with l odd is explained by pseudo-symmetry. Hence, a choice had to be made between three possible space-groups, viz Pn, P2/n and $P2_1/n$. For two monomeric units per cell, the crystallographic density is 1·48 g/cm^3 which is slightly higher than the measured value of 1·43 g/cm^3.

The X-ray diffraction pattern of poly(*p*-phenylene terephthalamide) abbreviated as PT, resembles the patterns of poly(*p*-phenylene oxide) (PO) and of poly(*p*-phenylene sulphide) (PS), the structure of which were determined in this laboratory by Boon *et al.* [8,9]. Tables 2 and 3 present the unit cell dimensions and the observed intensities of the (hko) and (hkl) reflections of the three compounds. This analogy provided a general idea of the packing of the chains in the structure of oriented crystalline PT. The translation period along the fibre axis in PT contains one monomeric unit,

Table 1. List of observed and calculated intensities

hkl*	I_{obs} (a)	I_{obs} (b)	I_{cal} (c)	hkl	I_{obs} (a)	I_{obs} (b)	I_{cal} (c)	hkl	I_{obs} (a)	I_{obs} (b)	I_{cal} (c)	hkl	I_{obs} (a)	I_{obs} (b)	I_{cal} (c)
001	—		0	112	w		1	021	w		1	321	w–m	4	2
002	m	7	9	113	w–m		3	022	m	4	1	411			
003	—		<	114	w		2	023	w		<	322	—		<
004	s	30	32	115	—		1	024	w		<	412			
005	vw		1	116	vw	1	1	025	vw		<				
006	s	35	22									031	—		0
007	—		0	200	vs	100	100	121	w		1	032	—		<
008	—		0	201	—		0	122	—		<				
				202	w		3	123	—		<	130	—		0
101	—		0	203	—		<	124	—		<	131	—		0
102	—		<	204	—		1					132	w		<
103	—		<	205	—		<	310	m	4	4				
104	w		2					311	vw		1	231	—		<
105	—		<	211	s	14	17	312	—		<	232	—		<
106	s	11	7	212	—		1	313	—		<				
				213	w		2					420	w–m	1	1
011	vw		0	214	—		1	220	w		<	421	—		0
012	vw		1					221	w		<	422	—		<
013	w		1	301	—		0	222	w		<				
014	w		1	302	—		<	223	vw		<	510	vw		<
015	w		1	303	—		<	224	vw		<	330	vw		<
016	w		1	304	—		<					600	—		0
				305	—		0	400	w	1	1	040	—		0
110	vs	81	72					401	—		0	240	—		0
111	s	8	8	020	vw		<	402	w		2	620	w		<

* $I(hkl)$ and $I(\bar{h}kl)$ are taken together.

(a) Visually estimated intensities: vs = very strong; s = strong; m = medium; w = weak; vw = very weak; (—) = not above background.

(b) Integrated intensities taken from azimuthal and radial diffractometer scans.

(c) Calculated intensities, when $I_{calc.} < 0{\cdot}1$ indicated by 0 and when $0{\cdot}1 \leqslant I_{calc.} \leqslant 0{\cdot}5$ by <.

whereas in PO and PS this period is formed by two monomeric units. For the packing of the chains in the latter two structures, this results in the symmetry elements of the *b* glide plane parallel (100) and the *c* glide plane parallel (010). If one of these symmetry elements is left out from the group of symmetry elements belonging to the space group Pbcn, the space-group symmetry is reduced to $P2_1/n$. This argument leads to the adoption of $P2_1/n$ as the probable space group for the crystal structure of PT and it was used in the setting up of the initial model.

Table 2. Comparison of the unit cell dimensions of poly(*p*-phenylene terephthalamide), poly(*p*-phenylene oxide) and poly(*p*-phenylene sulphide)

Cell-data	PT	PO	PS
a	7·87 Å	8·07 Å	8·67 Å
b	5·18 Å	5·54 Å	5·61 Å
c (fibre axis)	12·9 Å	9·72 Å	10·26 Å
γ	~ 90°	90°	90°
Number of chains in the cell	2	2	2
Space-group	Pn or $P2_1/n$	Pbcn	Pbcn

Information on the conformation of the monomeric unit was mainly derived from the crystal structure determinations of benzamide [10,11] and acetanilide [12] from which it was found that, due to steric hindrance, coplanarity of the planes through the centres of the atoms of the amide groups and through

Table 3. Comparison of the intensities of poly(*p*-phenylene terephthalamide), poly(*p*-phenylene oxide) and poly(*p*-phenylene sulphide)

hkl	PT	PO	PS
110	vs	vs	s
200	vs	vs	vs
020	vw	m	w
310	m	w	—
220	w	w	vw
011	vw	—	—
111	m–s	s	vs
201	—	—	—
211	s	s	m
301	—	—	—
021	w	—	vw
121	ww	w	—
311	vw	m	w

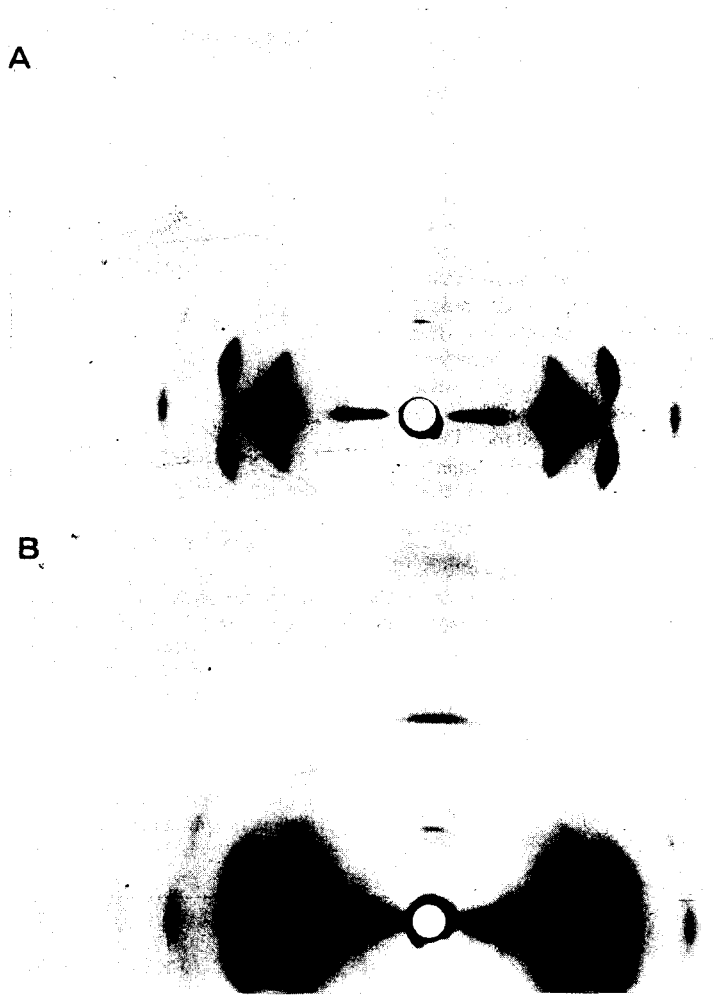


Fig. 1. (a) X-Ray diffraction pattern of poly(*p*-phenylene terephthalamide) fibre heat-treated at 500°, (b) heat-treated at 400°. Fibre axis vertical.

the centres of the atoms of the phenylene groups had to be excluded. A similar interaction, repulsion between an amide hydrogen and an *ortho* hydrogen within a molecule, is found in terephthalamide [13].*

The orientation angles of the axes, defined by the carbon atoms in the one and four positions of both phenylene groups, with the *c* axis were derived from the molecular dimensions of the benzamide and the acetanilide molecules together with the restriction that the length of the monomeric unit should equal the length of the *c* axis of 12·9 Å. These angles are approximately 6° for the *para*-phenylenediamine segment and approximately 14° for the terephthalic segment, which implies that the tilt with respect to the *c* axis is different for each of the segments.

The molecular chains, running parallel to the *c* axis, were placed at (0,0) and $(\frac{1}{2},\frac{1}{2})$. The centres of gravity of the phenylene groups were located at the symmetry centres thereby introducing a parallel orientation of the amide groups. At this stage in the analysis, three parameters of the model structure still had to be determined. They are the rotation angles of the phenylene groups around their axes, defined by the carbon atoms in the one and four positions, with respect to the plane through the amide atoms, and the rotation angle of the chain around the *c* axis. Approximate values for these angles were derived from a comparison of the diffracted intensities, calculated for a series of these rotation angles applying steps of 4°, with the observed intensities.

The expressions for the diffracted intensity and

* The author is indebted to the referee for calling his attention to the redetermination of the benzamide structure and the crystal structure determination of terephthalamide.

the correction factors used in these calculations are given in ref. [7]. The scattering factors for the atoms were calculated from analytical expressions [14] and the thermal parameter, assumed to be equal for all the atoms, was taken to be 5×10^{-16} cm^2. Good agreement between observed and calculated intensities was obtained at an angle of $-30°$ between the amide plane and the terephthalic segment, and at an angle of 38° between the amide plane and the phenylene plane of the *p*-phenylenediamine segment. These values correspond with similar interplanar angles found in the benzamide and acetanilide molecules, where they are 25° and 38°, respectively. For the orientation of the chain defined by the angle between the amide plane and the (100) plane a value of 4° was calculated, such that the phenylene planes make approximately equal angles with the (100) plane. This orientation of the chain resulted in acceptable dimensions for the hydrogen bonds formed between the chains, viz. a distance N...0 of 3·04 Å and angle N.H---0 of 160°.

Diffraction patterns taken with the fibre axis tilted relative to the rotation axis of the camera showed the presence of a strong reflection (106), a weak reflection (104) which was not well resolved from (004), and a very weak (005) reflection. From the model, the first reflection was calculated to be very weak, the second was calculated zero and the presence of the third was not in agreement with the adopted space group symmetry. It was impossible to improve the fit of the (104) and (106) reflections, either by introducing small alterations in the chain conformation or by changing the

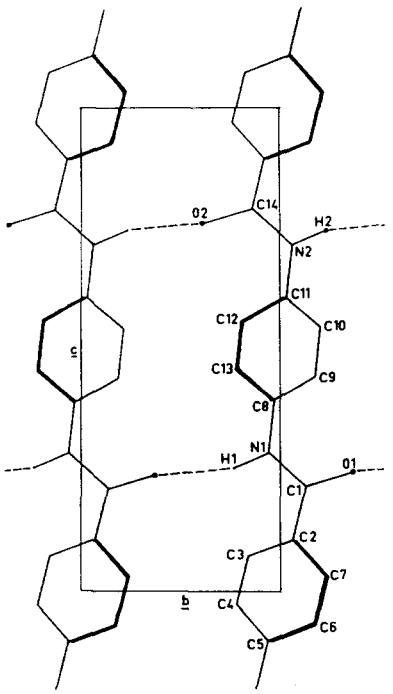


Fig. 2a.

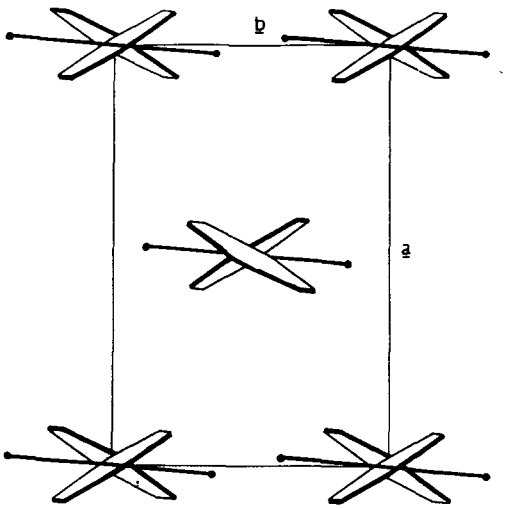


Fig. 2b.

Fig. 2. (a) A layer of hydrogen-bonded chains. Projection parallel to the *a* axis. Glide planes *n* with orientation (001) are located halfway between the centres of the phenylene groups. (b) Packing of the chains in the unit cell. Projection parallel to the *c* axis.

Table 4. Fractional positions of the atoms of poly(*p*-phenylene terephthalamide) in the unit cell

Atom	*x*	*y*	*z*
O(1)	−0·021	−0·367	0·015
O(2)	0·021	0·367	0·535
N(1)	0·003	0·056	0·058
N(2)	−0·003	−0·056	0·492
C(1)	−0·008	−0·138	−0·010
C(2)	−0·004	−0·067	−0·121
C(3)	0·085	0·150	−0·153
C(4)	0·089	0·217	−0·257
C(5)	0·004	0·067	−0·329
C(6)	−0·085	−0·150	−0·297
C(7)	−0·089	−0·217	−0·193
C(8)	0·002	0·028	0·168
C(9)	0·084	−0·179	0·214
C(10)	0·082	−0·207	0·321
C(11)	−0·002	−0·028	0·382
C(12)	−0·084	0·179	0·336
C(13)	−0·082	0·207	0·229
C(14)	0·008	0·138	0·560
H(1)	0·013	0·232	0·027
H(2)	−0·013	−0·232	0·523
Phenylene	0·148	0·260	−0·100
Hydrogens	0·154	0·376	−0·280
	−0·148	−0·260	−0·350
	−0·154	−0·376	−0·170
	0·145	−0·311	0·169
	0·143	−0·359	0·354
	−0·145	0·311	0·381
	−0·143	0·359	0·196

Table 5. Bond distances in Å, used in the calculations

Bond	Distance
C(1)—C(2)	1·47
C(2)—C(3)	1·39
C(3)—C(4)	1·39
C(1)—O(1)	1·24
C(1)—N(1)	1·34
N(1)—H(1)	1·00
N(1)—C(8)	1·42
C(8)—C(9)	1·39
C(9)—C(10)	1·39
C—H(phenyl)	1·00

orientation of the chain around *c* axis. However, it was found that an appreciably better fit for these reflections, and at the same time for the (004) and (006) reflections, was obtained by introducing a small displacement parallel to the *c*-axis between the hydrogen-bonded planes of 0·32 Å. Consequently, this alteration lowers the space group symmetry from $P2_1/n$ to Pn.

Figures 2a and 2b show the projections along *a* and *c*, respectively, of a layer of hydrogen-bonded chains and of the cell content. Table 4 lists the final atomic positions as used in the calculation of the intensities (Table 1) for the space group Pn. Tables 5 and 6 give the intramolecular dimensions.

Table 6. Bond angles in degrees, used in calculations

Bond angle	
C(4)—C(3)—C(2)	120
C(3)—C(2)—C(7)	120
C(3)—C(2)—C(1)	120
C(7)—C(2)—C(1)	120
C(2)—C(1)—N(1)	117
C(2)—C(1)—O(1)	120
N(1)—C(1)—O(1)	123
C(1)—N(1)—C(8)	125
C(1)—N(1)—H(1)	115
C(8)—N(1)—H(1)	120
N(1)—C(8)—C(9)	120
N(1)—C(8)—C(13)	120
C(9)—C(8)—C(13)	120
C(8)—C(9)—C(10)	120

The similarity of the segments in the monomeric unit causes pseudo-symmetry in the structure, like a *c* glide plane parallel to (010) for the segments in the chain and, disregarding the shift, an *n* glide plane also parallel to (010) between segments in adjacent hydrogen-bonded planes.

DISCUSSION

The conformation of the polymer chain is primarily governed by competitive intramolecular interactions between the conjugated groups in the chain as was also found for the conformation of the benzamide, acetanilide and terephthalamide molecules. These interactions are (1) the resonance effect trying to stabilize coplanarity of the amide groups and the phenylene groups, (2) the counteracting steric hindrance found between the oxygen and an *ortho*-hydrogen of the *p*-phenylene diamine segment, and between the amide hydrogen and an *ortho*-hydrogen of the terephthalic segment.

With respect to the uncertainty in the space-group determination, the following observation should be mentioned. X-ray diffraction patterns of fibres of poly(*p*-phenylene terephthalamide) heat-treated at a lower temperature indicate that other packing modes of the chains with a lower symmetry do occur. Figure 1b for instance shows the pattern of a fibre heat-treated at 400°. No change in lattice dimensions was observed, but the pattern clearly shows the presence of the reflections (hko) with (h + k) odd and a change in the relative intensities for most of the reflections. Although this study seems to indicate that, for fibres heat-treated at 500°, the probable space group is Pn, the low precision of the intensity data does not permit a final conclusion. Moreover, the presence of segments, which in themselves are stereochemically centrosymmetric, together with the fact that in the presented structure it is possible for the amide group to form centrosymmetric pairs of hydrogen bonds, suggest that the most favourable symmetry may indeed be $P2_1/n$.

Note—At a meeting of the Soc. Cryst. Japan, December 8, 1973, Prof. H. Tadokoro presented the results of an investigation of poly(*p*-phenylene terephthalamide) fibres which show substantially the same crystal structure as described in this paper.

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Résumé—On propose un modèle pour le cristal et la structure moléculaire du poly(*p*-phénylène-terephtalamide) à partir des études de diffraction des rayons X. La maille élémentaire monoclinique (pseudo-orthorhombique) [a = 7,87 Å, b = 5,18 Å, c (axe de la fibre) = 12,9 Å et γ = 90°] possède une symétrie de groupe spatial Pn ou $P2_1/n$. Deux chaînes moléculaires traversent la maille, une par le centre et l'autre par un coin. Les valeurs approchées des angles d'orientation entre les plans phénylène et les plans amide sont de 38° pour le segment *p*-phénylène diamine et −30° pour le segment téréphtalique. Des liaisons hydrogène sont formées entre deux chaînes adjacentes situées dans le plan (100). La conformation de la chaîne est essentiellement gouvernée par les interactions intramoléculaires compétitives entre les groupes conjugués.

Sommario—Basandosi su di uno studio di diffrazzione di raggi ×, si propone un modello per la struttura cristallina e molecolare del poli(*p*-fenileneteftalamide). La cella monoclina(pseudo-ortorombica) (a = 7,87 Å, b = 5,18 Å, c (asse della fibra) = 12,9 Å e γ = 90°) possiede una simmetria di gruppo spaziale Pn oppure $P2_1/n$. Due catene molecolari passano atraverso la cella, una attraverso il centro e l'altra attraverso un angolo. I valori approssimati per gli angoli di orientamento tra i piani del fenilene e quelli dell'amide sono di 38° per il segmento di *p*-fenilenediamina e −30° per il segmento tereftalico. I legami dell'idrogeno sono formati tra catene adiacenti giacenti nel piano (100). La conformazione della catena è governata principalmente da competitive interazioni intermolecolari tra i gruppi coniugati.

Zusammenfassung—Auf der Grundlage von Röntgenuntersuchungen wird ein Modell der Kristall- und molekularen Struktur für Poly-*p*-phenylenterephthalamid vorgeschlagen. Die monokline (pseudo-orthorhombische) Elementarzelle [a = 7,87 Å, b = 5,18 Å, c (Faserachse) = 12,9 Å und γ = 90°] hat eine Pn oder $P2_1/n$ Raumgruppensymmetrie. Zwei molekulare Ketten laufen durch die Elementarzelle: eine durch das Zentrum und eine durch eine Ecke der Zelle. Ungefähre Werte für die Orientierungswinkel zwischen den Phenylen-Ebenen und den Amid-Ebenen betragen 38° für die *p*-Phenylendiamin-Segmente und −30° für die Terephthalsäure-Segmente. Zwischen benachbarten Ketten, die in der 100-Ebene liegen, bilden sich Wasserstoffbrücken aus. Die Konformation der Kette wird in erster Linie durch competitive intramolekulare Wechselwirkungen zwischen konjugierten Gruppen bestimmt.