Structural analysis of β-form poly(*p*-xylylene) starting from a high-resolution image

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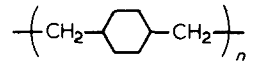
The crystal structure of β-form poly(*p*-xylylene) is analysed starting from a high-resolution image of a single crystal of this polymer. The high-resolution image corresponding to the projection of molecules onto the *ab*-plane along the chain axis shows clearly the mutual position of each molecule in a unit cell. The molecules are aligned wavily in the direction along the *a*-axis and the rough positions of their centres in a unit cell can be determined from the image. The refinement of the structure is carried out by the usual least-squares method using the intensities of electron and X-ray diffractions. The space group of the β-form is trigonal, P3, and the lattice dimensions are $a=2.052$ nm, $c=0.655$ nm and $\gamma=120°$. The unit cell contains 16 molecules and one of them is considered to occupy statistically one of three equivalent orientations so as to satisfy the P3 symmetry.

Keywords Poly(*p*-xylylene); crystal structure; high-resolution image

INTRODUCTION

Structural analysis is usually carried out by means of X-ray, electron or neutron diffraction. Recently the high-resolution electron microscope has been considered to be a powerful tool to analyse crystal structures. The resolution of modern electron microscopes is high enough to enable us to analyse directly the crystal structure on the atomic level[1]. High-resolution images are utilized to minimize the variety of structural models at the early stage of structural analysis. Of course, one must be careful in interpreting a high-resolution image, since the image varies largely with the conditions of the electron microscope, especially with the defocus value. For radiation-sensitive materials, such as polymers, the radiation damage prevents us from getting a high-resolution image, because high electron dosage would be required to take a high-resolution image. However, poly(*p*-xylylene)



(abbreviated to PPX) was found to be relatively strong against electron radiation and, fortunately, easy to crystallize in the form of single crystals from solution. A high-resolution image of the β-form PPX single crystal was obtained with a high-resolution electron microscope (JEM-500)[2]. It was the first success in direct imaging of each molecule comprising a polymer crystal. This image corresponds to the projection of molecules onto the plane normal to the incident direction of the electron beam and shows clearly the mutual arrangement of each molecule in a crystal.

In PPX single crystals, two crystalline modifications (the α- and β-forms) are known. The crystal structure of the α-form has already been analysed by Iwamoto and Wunderlich[3], but for the β-form only the unit cell dimensions were known (hexagonal or trigonal, $a=2.052$ nm, $c=$ fibre axis $=0.685$ nm)[4,5]. This is mainly due to the difficulty of construction of a molecular packing model in the very large unit cell. The purpose of this paper is to determine the crystal structure of the β-form starting from the high-resolution image of this crystal. It is found that high-resolution electron microscopy is of major value for the structural analysis in the present case.

EXPERIMENTAL

Electron microscopy

PPX single crystals of the β-form were crystallized for 10 h at 210°C from a dilute α-chloronaphthalene solution (0.1 wt%). A hexagonal shaped single crystal of β-form PPX is shown in *Figure 1*. The chain axis (*c*-axis) is perpendicular to the basal plane of the crystal and parallel to the incident electron beam. On the evaluation from the crystal thickness and the *c*-axis dimension, each high-resolution molecular image corresponds to the projection of about 12 monomer units on the basal plane along the *c*-axis. Reflection spots up to 440 were observed on the optical transform of the image. Image processing was carried out by an optical filtering method in order to reduce film graininess and to enhance the regularity of the image. Details of the methods for taking the high-resolution image of PPX and for image processing were presented in the previous article[2].

Electron diffraction patterns (*hk0* reflections) were taken to determine the two-dimensional symmetry of β-form PPX crystal and their diffraction intensities were measured to refine the crystal structure. The optical density of diffraction spots was measured with a Joyce–Loebl densitometer and transformed to diffraction in

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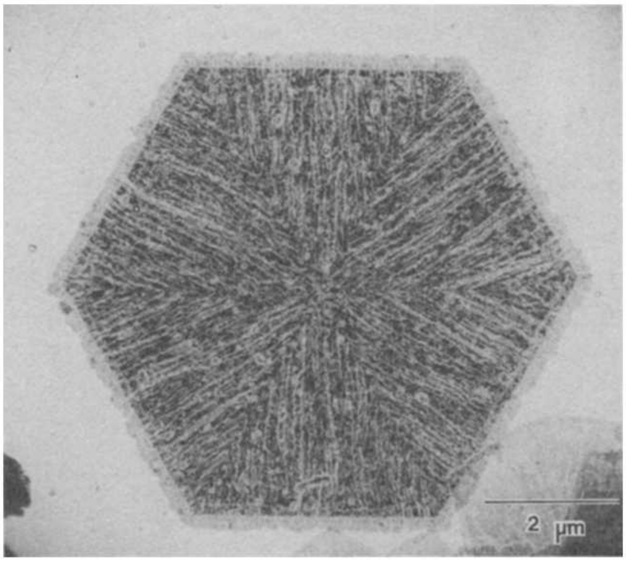


Figure 1 A hexagonal shaped single crystal of β-form PPX grown from α-chloronaphthalene solution (0.1 wt%) at 210°C. The thickness of the single crystal is about 8.0 nm. Radial striations are due to diffraction contrast and six sectors indicate the tent-like structure in a solution prior to deposition on the electron microscope grid

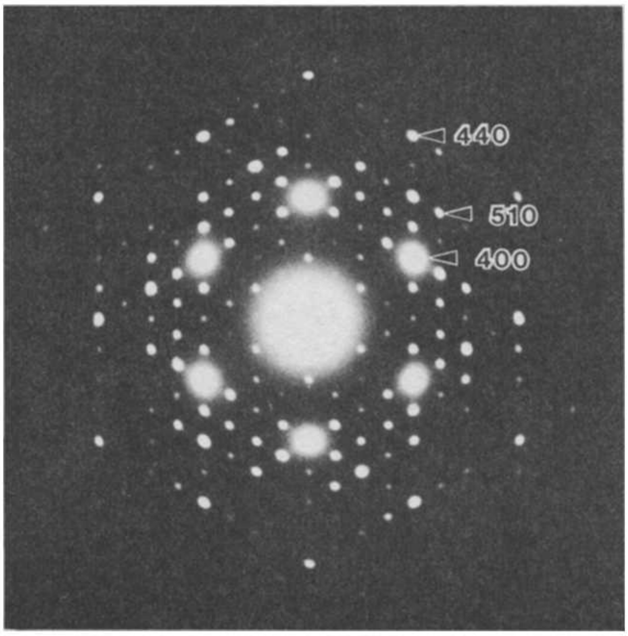


Figure 2 Electron diffraction pattern of β-form PPX single crystal. The incident electron beam direction is parallel to the *c*-axis, that is perpendicular to the basal plane of the crystal. A large unit cell dimension with a=2.052 nm is observed. The pattern shows no systematic absence of reflections. The asymmetric features denote only the 6-fold symmetry on the electron diffraction pattern, for example strong 510 but weak 150. All six sectors yield identical diffraction patterns

tensity with a reference optical density grade. The intensities of electron diffraction are not so accurate because of the incorrect orientation of a crystal relative to the electron beam. The intensities of many diffraction patterns were averaged and eventually a set of intensity data was obtained. The correction of $1/d_{hk0}$ was applied as the Lorentz factor correction[6]. Even in the case where many overlappings of diffraction spots occur in the X-ray measurement, electron diffraction displays all *hk*0 reflections separately and then it is indispensable for determining the symmetry of PPX. In the electron *hk*0 reflections of *Figure 2*, a large unit cell with $a = 2.052$ nm is shown. Only the 6-fold symmetry is observed and the two-dimensional symmetry group is considered to be p6 or p3. The figure shows no systematic absence of reflections. The total number of independent electron reflections used to refine the projected structure by the least-squares method is 25.

X-ray measurement

X-ray diffraction patterns were taken to prepare more accurate three-dimensional data of structure amplitude. Fibre photographs from a drawn β-form PPX sample, which is made by stretching an as-polymerized film six times at 285°C in an oil bath, were taken with a cylindrical camera. *Figure 3* shows the diffraction pattern of β-form PPX. The Cu K_α radiation monochromatized with a graphite crystal was used. The diffraction intensities of the film were measured using the same procedures as in the case of electron diffraction and corrected for the Lorentz and polarization factors and multiplicity. No absorption correction was carried out. Overlapped diffraction peaks were separated with a curve matching program using the least-squares method[7]. The peaks that were inseparable by this method were treated in a lump for the structural analysis. The total number of independent reflections used for the refinement of the crystal structure is 57.

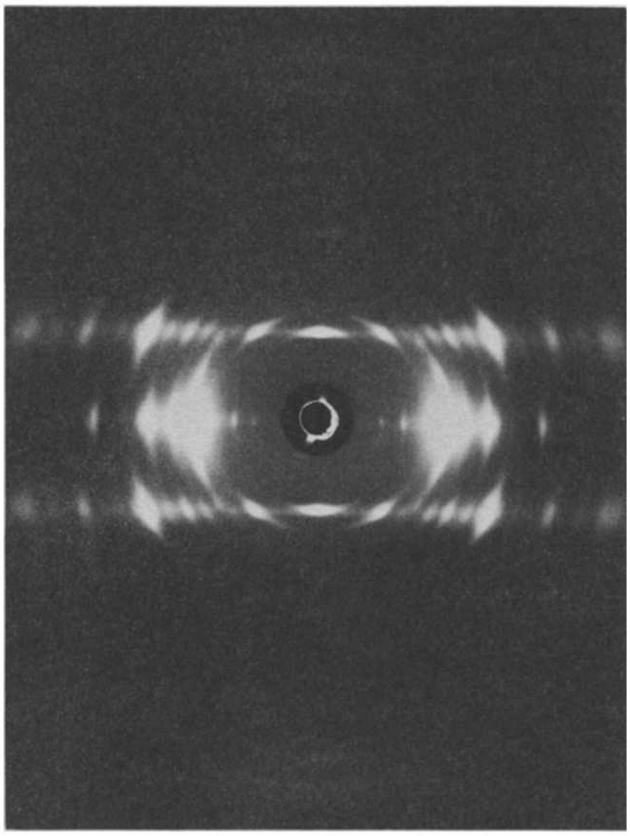
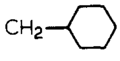


Figure 3 X-ray diffraction pattern from drawn PPX of the β-form taken by the rotating crystal method. The direction of the *c*-axis coincides with the axis of the cylindrical camera and is vertical in this figure

Least-squares method

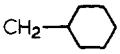
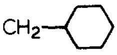
A full matrix method was adopted. The weight factors of all reflections are assumed to be 1.0 and the damping factor is 0.33. Parameters used are scale factor, isotropic temperature factor common for all atoms, the fractional coordinates of the centre of the molecule (the centre of the benzene ring) and the orientations of molecules in the *ab*-plane. Sixteen molecules should be contained in the unit cell and they are considered to take the same chain conformation. With regard to the chain conformation, only the internal rotation about the



bond is taken into account. This is the simplest case of the constrained least-squares method[8,9].

STRUCTURAL ANALYSIS

Structure model

The hexagonal or trigonal unit cell has been proposed for β-form PPX[4,5], but the molecular packing of this form was not presented. In our case, X-ray and electron reflections are indexed by the unit cell parameters of $a = b = 2.052$ nm, $c = 0.655$ nm and $\gamma = 120°$. The *c*-axis dimension is the same in the α-form and corresponds to the *trans* zigzag conformation shown in *Figure 4*. One chemical repeating unit makes up the fibre period. This *c* dimension is deduced from the assumption that $d(CH_2–CH_2) = 0.154$ nm, *d*() = 0.153 nm, *d*(CH–CH in benzene ring) = 0.1395 nm, *d*(C–H) = 0.107 nm, angle CCC = 109.5° and all angles in a benzene ring are 120°. The internal rotation angle ϕ of the ring about the  bond has no effect on the fibre period, and then ϕ is a parameter for the refinement.

First of all, we have to construct a two-dimensional model of the *ab*-plane projection which follows from the high-resolution image and the requirements of packing and density. From the density measurement by the floating method, the highest density of PPX bulk material which was annealed in oil bath at 270°C is 1.15 g cm^{-3}. This requires that 16 molecular chains should be contained in the unit cell. The calculated density of β-form PPX crystal is 1.158 g cm^{-3} (the density of the α-form was calculated at 1.18 g cm^{-3}). The fact that 16 molecular chains are included in the unit cell was also ascertained from the high-resolution image.

The high-resolution electron microscopic image is shown in *Figure 5*. In this figure, each dark portion corresponds to a projected molecule along the polymer chain axis. It is clear that 16 chains pass through the unit cell and that this two-dimensional unit cell has roughly p6 symmetry as regards the positions of molecules. This image gives a very important starting point for the analysis of the unknown structure of β-form PPX. In the present case, the resolution of about 0.25 nm is preserved, since 440-spots ($d_{440} = 0.257$ nm) were observed on the optical diffractogram of the original micrograph[2]. The detailed orientations of the projected molecules on the *ab*-plane are scarcely resolved, but approximate positions of molecules in the unit cell can be determined. Molecules do not align straight, but in a wavy fashion, for example along ⟨100⟩ direction. The feature of the wavy arrangement of molecular centres in the high-resolution image is exaggerated in *Figure 6*.

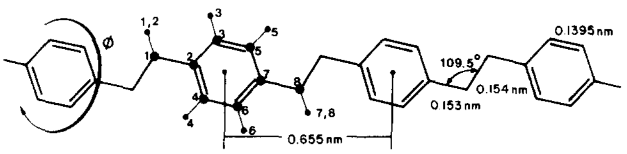


Figure 4 Molecular conformation in PPX crystals. This *trans* zigzag conformation has the fibre period of 0.655 nm. A benzene ring can rotate without a change of fibre period. In the refined β-form structure, the plane containing the benzene ring makes an angle of ϕ=90° with that of a CH_2–CH_2 zigzag unit, just as in the α-form. Eight carbon (larger circles) and eight hydrogen (smaller circles) atoms are numbered as in the figure

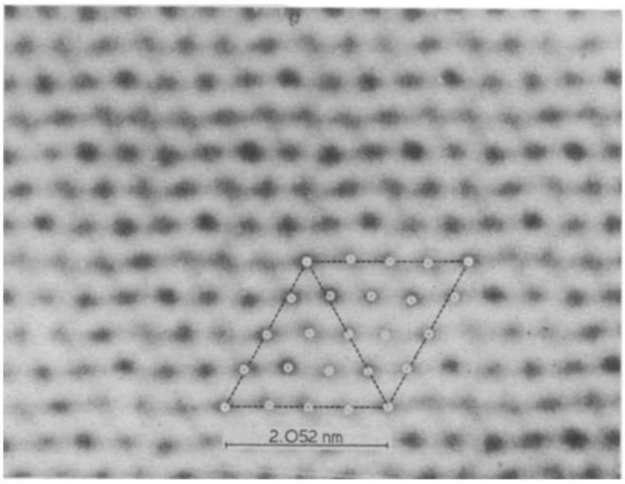


Figure 5 High-resolution image of a PPX β-form single crystal taken with JEM-500. Each dark portion corresponds to one molecule projected onto the basal plane along the polymer chain axis. The rhombus shows the large unit cell of β-form PPX. One unit cell contains 16 molecules. White circles show the centres of molecules in the unit cell. Molecules are not aligned straight, but in a characteristic wavy fashion along the ⟨100⟩ direction

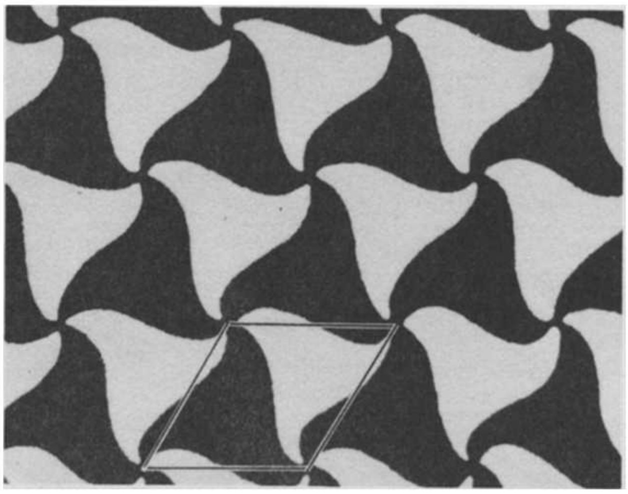


Figure 6 A two-dimensional pattern called 'Chidori' is a nice representation of wavy alignment of molecules in β-form PPX. The rhombus shows the unit cell corresponding to that of PPX

Before the molecular packing is determined, an important point must be scrutinized; how can 16 molecules be packed in the unit cell, preserving the p3 or p6 symmetry? The hexagonal and trigonal structures of polymers already reported are summarized in *Table 1*. They are classifed into three groups. Group 1: each chain itself has the 3- or 6-fold axis or screw axis. The number of molecules in a unit cell (N) is 1 or an integral multiple of 3. Group 2: each chain has cylindrical or nearly cylindrical symmetry. In this case, a unit cell must be made up of only 1 molecule and the symmetry is restricted to be hexagonal or pseudo-hexagonal. Group 3: a set of identical molecules produces the 3- or 6-fold symmetry, though one molecular chain itself has no symmetry features of group 1 or 2. A unit cell is formed with such sets and N is an integral multiple of 3.

A PPX molecule itself does not have symmetry such as group 1 or 2 and the number of molecules ($N = 16$) is not an integral multiple of 3 such as in group 3. The PPX β-form crystal does not suit any of the above mentioned prerequisites and the 3- or 6-fold rotational symmetry could not be realized in the present lattice. Consequently to preserve the present symmetry of crystal lattice, one molecule at the special position in the unit cell must be assigned to occupy statistically one of three equivalent orientations with equal probability and the residual 15 molecules are settled in orientation and position so as to satisfy approximately the symmetry of P6 in the *ab*-plane by taking the van der Waals' radii into account. Other packing models could be possible to satisfy the present symmetry, for example four or all molecules statistically distributed, and the refinements were also carried out for these models.

Projected two-dimensional structure (*the* ab-*plane*)

The two-dimensional symmetry is found to be roughly p6 from the high-resolution image and the electron diffraction pattern. The p6 symmetry is assumed in the *ab*-plane and independent molecules in structural analysis are as follows: $i = 1, 2, 3$ and 7 in *Figure 7*. The molecule of $i = 1$ is assigned to be the special one as described before. The molecule with one of three equivalent orientations is shown with the nearest-neighbour molecules in *Figure 7a*. *Figure 7b* shows the two-dimensional structure refined from electron diffraction intensity. For this model, the number of parameters for the least-squares method is 12; scale factor, temperature factor, four θ_i, three u_i and three

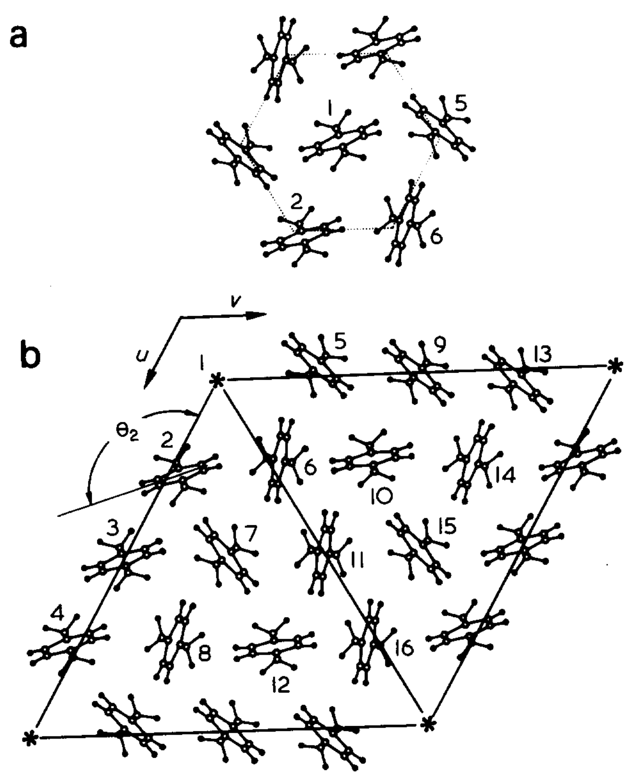


Figure 7 Two-dimensional structure (the *ab*-plane projection) refined by electron diffraction intensity (*b*). Open circles denote carbon atoms and filled circles hydrogen atoms. Molecules in the unit cell are numbered as $i = 1$ to 16. The orientation of each molecule is defined by θ_i, as shown in the figure. The three 6-fold symmetry axes are on the $i = 1$ molecule and on the centres of two triangles formed by $i = 7$, 8 and 12 and by $i = 10$, 14 and 15. From the requirement of p6 symmetry, the molecule of $i = 1$ may occupy one of three equivalent orientations with equal probability (*a*)

Table 2 Crystal parameters obtained by electron diffraction analysis. u_i and v_i are fractional coordinates of molecular centres (the centres of benzene rings in the main chain). θ_i denotes the orientation of a molecule defined in *Figure 7* and the results of θ_i and $\theta_i + 180°$ are equivalent. The temperature factor B is about 0.075 nm^2 and ϕ is 90°

i	u_i	v_i	θ_i (deg)
1	0.00	0.00	−33, 87, 207
2	0.25	0.03	−42
3	0.50	0.00	139
7	0.51	0.27	−110

Table 1 Grouping of polymer crystal structures belonging to hexagonal or trigonal systems[10]. N is the number of molecules per unit cell; H, hexagonal; T, trigonal; PH, pseudo-hexagonal

Group	Polymer	Crystal system	Molecular conformation	N
1	it-Polypropylene (β-form)	H	helix (3/1)	9
	Polyoxymethylene	T	helix (9/5)	1
	it-Polystyrene	T	helix (3/1)	6
	it-Poly-1-butene (form I)	T	helix (3/1)	6
	Poly-1,3-dioxolane (form III)	H	helix (6/1)	3
	it-Poly(vinyl methyl ether)	T	helix (3/1)	6
	Polytetrafluoroethylene (above 19°C)	T	helix (15/7)	1
2	Polytetrafluoroethylene (below 19°C)	PH	helix (13/6)	1
	Polychlorotrifluoroethylene	PH	helix (16.8/1) on average	1
	Nylon-7,7 (γ-form)	PH	(1/0)	1
3	Polyoxacyclobutane (form II)	T	glide-type (2/0)	9

v_i. Parameters u_1, v_1 and ϕ are fixed during the calculation. On termination the reliability factor:

$$R=\sum||F(\text{obs})|-|F(\text{calc})||/\sum|F(\text{obs})|$$

is 0.31. The parameters that result are listed in *Table 2*. The overall temperature factor is about 0.075 nm^2. The meaning of the parameter θ_i is read from *Figure 7* and u_i and v_i are the fractional coordinates of the centres of benzene rings. The plane containing the benzene ring is perpendicular to that of a $-CH_2-CH_2-$ plane and this chain conformation ($\phi=90°$) is the same as in the case of the α-form. In the model that four ($i=1,3,9,11$) or all molecules are statistically distributed, factor R is about 0.35 and higher than in the case where one molecule is statistically distributed.

Three-dimensional structure

Three-dimensional structural analysis was carried out using X-ray diffraction intensity. The p6 symmetry is considered in the two-dimensional case, but p6 is not possible in the three-dimensional case. Since the plane of the benzene ring is not parallel to the c-axis, the two orientations of a molecule, that is θ_i and $\theta_i+180°$, must be distinguished in the three-dimensional case. Retaining this three-dimensional characteristic of chain conformation, the molecular packing shown in *Figure 7* cannot satisfy both 6-fold and translational symmetries simultaneously; an equivalent molecule of $i=11$ produced by the $60°\times 3$ rotation around the origin cannot coincide with one produced by translation along $\langle\bar{1}\bar{1}0\rangle$. Thus the space group is P3 and the independent molecules are $i=1$, 2, 3, 6, 7 and 10. Two-dimensional parameters (u_i, v_i and θ_i) are roughly determined in the last section, but the positions along the c-axis (w_i) are not known. Four values of w_i along the c-axis, i.e. 0, $\pm c/4$ and $c/2$ displacements relative to the molecule of $i=1$, are initially examined for each molecule of $i=2, 3, 6, 7$ and 10. The refinements were started from these models and the structure with the lowest R value was chosen. The number of parameters used for the least-squares calculation is 24, i.e. temperature factor, scale factor, five sets of (u_i, v_i, w_i), six θ_i, ϕ, and u_1, v_1 and w_1 are fixed during the calculation.

The structure that results is shown in *Figure 8* and their parameters are listed in *Table 3*. The overall temperature factor is about 0.09 nm^2. In this structure, chain conformation is also the same as the α-form, that is $\phi=90°$. The molecule of $i=1$ is presented as a superposed molecule with three equivalent orientations at the origin of the unit cell. As for the atomic coordinates of each atom, the fractional coordinates of $i=1$ molecule with the special orientation, $\theta_1=206°$, are listed in *Table 4*. The molecule of $i=3$ and equivalent molecules ($i=9$ and 11) are displaced by $c/2$ along the c-axis in comparison with other molecules. The ab-plane arrangement of this structure is nearly the same as in *Figure 7*. The two-dimensional symmetry of the ab-plane projection in *Figure 8* is approximately p6, but actually p3. The resulting R factor is 0.21. Observed and calculated structure factors are tabulated in *Table 5*. For comparison between calculated and observed structure factors, the calculated ones are tabulated also in a lump, that is

$$\left(\sum_m |F_m(\text{calc})|^2\right)^{1/2}$$

The summation over m means the summation over all overlapped peaks. The value of

$$\left(\sum_m |F_m(\text{calc})|^2\right)^{1/2}$$

is shown as F(calc) in *Table 5*.

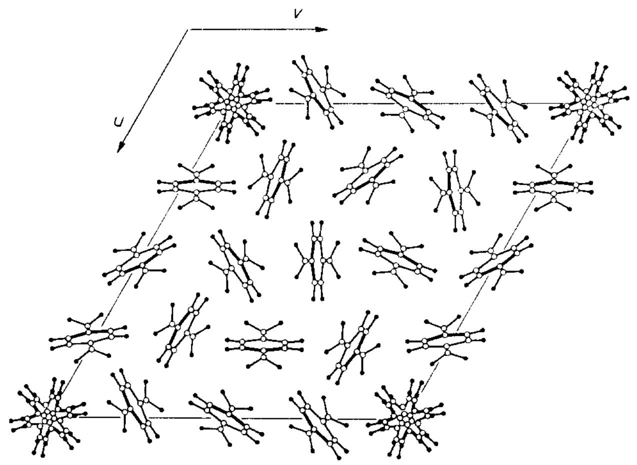


Figure 8 Three-dimensional structure of the β-form is shown as the *ab*-plane projection. Open and filled circles represent carbon and hydrogen atoms, respectively. Bold lines in a molecule represent the upper part of a benzene ring. The molecule of $i=3$ and its equivalents are displaced by $c/2$ along the c-axis and the others align on the same level. The molecule of $i=1$ is presented as a superposed molecule with the three equivalent orientations, one of which is actually occupied in a real crystal

Table 3 Three-dimensional parameters refined by X-ray diffraction. u_i, v_i and w_i are the fractional coordinates of the molecular centres. The temperature factor is about 0.09 nm^2. ϕ is also 90°

i	u_i	v_i	w_i	θ_i (deg)
1	0.00	0.00	0.00	−34, 86, 206
2	0.26	0.04	0.00	−59
3	0.50	0.00	0.50	151
6	0.23	0.25	0.00	170
7	0.51	0.28	0.00	−82
10	0.22	0.50	0.00	122

Table 4 Atomic coordinates of the molecule of $i=1$ ($\theta_1=206°$). The atom number corresponds to that of *Figure 4*

Atom number		u	v	w
Carbon	1	0.002	0.033	−0.435
	2	0.001	0.015	−0.208
	3	0.068	0.036	−0.104
	4	−0.066	−0.021	−0.104
	5	0.066	0.021	0.104
	6	−0.068	−0.036	0.104
	7	−0.001	−0.015	0.208
	8	−0.002	−0.033	0.435
Hydrogen	1	−0.046	0.036	−0.468
	2	0.056	0.081	−0.468
	3	0.120	0.064	−0.184
	4	−0.118	−0.038	−0.184
	5	0.118	0.038	0.184
	6	−0.120	−0.064	0.184
	7	−0.056	−0.081	0.468
	8	0.046	−0.036	0.468

Table 5 Absolute values of calculated and observed structure factors. *d* is the calculated lattice spacing

h k l				*d* (nm)	*F*(calc)	*F*(obs)
1 0 0				1.777	11.7	2.6
1 1 0				1.026	13.2	7.7
2 0 0				0.889	23.9	20.4
2 1 0,	1 2 0			0.672	54.2	47.6
3 0 0				0.592	14.5	2.8
2 2 0				0.513	18.1	8.8
3 1 0,	1 3 0			0.493	105.9	120.3
4 0 0				0.444	362.4	369.2
3 2 0,	2 3 0			0.408	81.9	95.8
4 1 0,	1 4 0			0.388	101.2	113.7
5 0 0				0.355	24.8	45.2
3 3 0				0.342		
4 2 0,	2 4 0			0.336	110.9	121.0
5 1 0,	1 5 0			0.319	57.1	52.6
6 0 0				0.296	32.6	39.9
4 3 0,	3 4 0			0.292		
5 2 0,	2 5 0			0.285	32.7	32.6
6 1 0,	1 6 0			0.271	31.9	27.5
4 4 0				0.257	88.1	114.3
5 3 0,	3 5 0,	7 0 0		0.254		
6 2 0,	2 6 0			0.246	42.6	39.1
7 1 0,	1 7 0			0.235	26.0	20.1
5 4 0,	4 5 0			0.228	35.7	40.3
6 3 0,	3 6 0			0.224		
1 0 1,	0 1 1			0.617	29.8	5.8
1 1 1,	$\bar{1}$ 2 1,	0 2 1		0.554	21.6	9.6
2 0 1				0.529	50.2	62.7
2 1 1,	1 2 1,	$\bar{2}$ 3 1,	$\bar{1}$ 3 1	0.470	48.7	41.1
3 0 1,	0 3 1			0.440	40.0	15.4
2 2 1,	$\bar{2}$ 4 1			0.405	16.0	17.0
3 1 1,	1 3 1,	$\bar{3}$ 4 1,	$\bar{1}$ 4 1	0.395	98.7	89.6
4 0 1,	0 4 1			0.368	20.2	49.3
3 2 1,	2 3 1,	$\bar{3}$ 5 1,	$\bar{2}$ 5 1	0.347	49.3	24.3
4 1 1,	1 4 1,	$\bar{4}$ 5 1,	$\bar{1}$ 5 1	0.334	96.9	91.5
5 0 1,	0 5 1			0.313	78.2	22.8
3 3 1,	$\bar{3}$ 6 1			0.303	170.3	163.6
4 2 1,	2 4 1,	$\bar{4}$ 6 1,	$\bar{2}$ 6 1	0.299		
5 1 1,	1 5 1,	$\bar{5}$ 6 1,	$\bar{1}$ 6 1	0.287	91.3	70.2
6 0 1,	0 6 1			0.270	90.4	92.5
4 3 1,	3 4 1,	$\bar{4}$ 7 1,	$\bar{3}$ 7 1	0.267		
5 2 1,	2 5 1,	$\bar{5}$ 7 1,	$\bar{2}$ 7 1	0.261	109.3	98.4
6 1 1,	1 6 1,	$\bar{6}$ 7 1,	$\bar{1}$ 7 1	0.251		
4 4 1,	$\bar{4}$ 8 1			0.239	26.1	23.0
5 3 1,	3 5 1,	$\bar{5}$ 8 1,	$\bar{3}$ 8 1,	0.237	118.9	122.9
0 7 1,	7 0 1					
5 4 1,	4 5 1,	$\bar{5}$ 9 1,	$\bar{4}$ 9 1	0.215	121.9	134.8
1 1 2,	$\bar{1}$ 2 2			0.313	5.7	6.6
2 0 2,	0 2 2			0.309		
2 1 2,	1 2 2,	$\bar{1}$ 3 2,	$\bar{2}$ 3 2	0.295	10.6	8.4
3 0 2,	0 3 2			0.288		
2 2 2,	$\bar{2}$ 4 2			0.277	15.7	9.6
3 1 2,	1 3 2,	$\bar{1}$ 4 2,	$\bar{3}$ 4 2	0.274		
4 0 2,	0 4 2			0.264	5.9	10.4
3 2 2,	2 3 2,	$\bar{2}$ 5 2,	$\bar{3}$ 5 2	0.256	19.4	11.6
4 1 2,	1 4 2,	$\bar{1}$ 5 2,	$\bar{4}$ 5 2	0.251		
5 0 2,	0 5 2			0.241	17.5	12.5
3 3 2,	$\bar{3}$ 6 2			0.237		
4 2 2,	2 4 2,	$\bar{4}$ 6 2,	$\bar{2}$ 6 2	0.235	22.4	38.0
5 1 2,	1 5 2,	$\bar{5}$ 6 2,	$\bar{1}$ 6 2	0.229		
6 0 2,	0 6 2			0.220	24.4	37.6
4 3 2,	3 4 2,	$\bar{4}$ 7 2,	$\bar{3}$ 7 2	0.218		
5 2 2,	2 5 2,	$\bar{5}$ 7 2,	$\bar{2}$ 7 2	0.215	32.7	15.7
6 1 2,	1 6 2,	$\bar{6}$ 7 2,	$\bar{1}$ 7 2	0.209	29.7	16.6
5 3 2,	3 5 2,	$\bar{5}$ 8 2,	$\bar{3}$ 8 2	0.201	77.6	86.3
7 0 2,	0 7 2,	4 4 2,	$\bar{4}$ 8 2			
6 2 2,	2 6 2,	$\bar{6}$ 8 2,	$\bar{2}$ 8 2	0.197	63.8	61.5
7 1 2,	1 7 2,	$\bar{7}$ 8 2,	$\bar{1}$ 8 2	0.191		
5 4 2,	4 5 2,	$\bar{5}$ 9 2,	$\bar{4}$ 9 2	0.187	71.7	87.0
6 3 2,	3 6 2,	$\bar{6}$ 9 2,	$\bar{3}$ 9 2	0.185		
8 0 2,	0 8 2			0.184		
4 0 3,	0 4 3			0.197	96.0	117.1
3 2 3,	2 3 3,	$\bar{3}$ 5 2,	$\bar{2}$ 5 3	0.193		
4 1 3,	1 4 3,	$\bar{1}$ 5 3,	$\bar{4}$ 5 3	0.191	48.0	21.1
5 0 3,	0 5 3			0.187	46.2	22.8
3 3 3,	$\bar{3}$ 6 3			0.185		
4 2 3,	2 4 3,	$\bar{4}$ 6 3,	$\bar{2}$ 6 3	0.184	67.2	86.7
5 1 3,	1 5 3,	$\bar{5}$ 6 3,	$\bar{1}$ 6 3	0.181		
6 0 3,	0 6 3			0.176	72.5	33.5
4 3 3,	3 4 3,	$\bar{3}$ 7 3,	$\bar{4}$ 7 3	0.175		
5 2 3,	2 5 3,	$\bar{2}$ 7 3,	$\bar{5}$ 7 3	0.174		
6 1 3,	1 6 3,	$\bar{1}$ 7 3,	$\bar{6}$ 7 3	0.171		
4 4 3,	$\bar{4}$ 8 3			0.167	42.8	58.3
5 3 3,	3 5 3,	$\bar{5}$ 8 3,	$\bar{3}$ 8 3,	0.166		
7 0 3,	0 7 3					

DISCUSSION

The crystal structure of β-form PPX has been obtained, starting from the high-resolution image of this crystal. Now, one should examine whether the structure obtained above can reproduce the actual image. The high-resolution image is greatly affected by the defocus and the spherical aberration through the contrast transfer function in phase-contrast electron microscopy. Therefore it is necessary to compare the image actually obtained with a simulated image to confirm authenticity of the high-resolution image as well as the result of structural analysis.

On the basis of the refined structure of the β-form, an electron microscopic image projected onto the *ab*-plane is simulated using the kinematical imaging theory. The extinction distance of 400 reflection ξ_{400} is about 160 nm, calculated from the refined β-form structure. ξ_{400} is much larger than the thickness of the β-form single crystal and so the kinematical imaging theory is applicable. The resolution limit is assumed to be 0.25 nm, the defocus value 45 nm (the optimum focus in the present case), the wavelength 0.00142 nm and the spherical aberration coefficient 1.06 nm. The simulated image shown in *Figure 9* closely resembles the image actually obtained. Thus a high-resolution image is found to give good guidance in structural analysis, especially in a very complicated structure. The structural analysis, however, cannot be performed only with the high-resolution images. X-ray and/or electron diffraction data are inevitable for quantitative analysis. To obtain a high-resolution image, it is necessary that the polymer must be strong against electron radiation and easily crystallized as a single

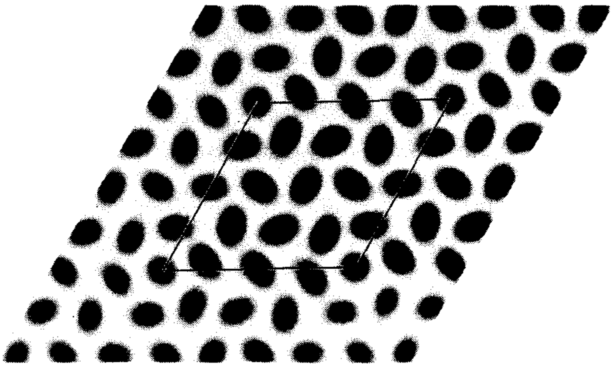


Figure 9 An image simulated on the basis of the refined β-form structure as the *ab*-plane projection. The rhombus corresponds to the unit cell

crystal. Because of these conditions, structural analysis using a high-resolution image is restricted to special polymers at the present time, though a high-resolution method is going to be a very important method for studying crystal structure.

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REFERENCES

1. For example, Nobel Symposium 47, *Chemica Scripta* 1978/1979, **14**
2. Tsuji, M., Isoda, S., Ohara, M., Kawaguchi, A. and Katayama, K. *Polymer* 1982, **23**, 1568
3. Iwamoto, R. and Wunderlich, B. *J. Polym. Sci.* 1973, **11**, 2403
4. Niegisch, W. D. *J. Appl. Phys.* 1966, **37**, 4041
5. Kubo, S. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1972, **10**, 1949
6. Vainshtein, B. K. 'Structure Analysis by Electron Diffraction', Pergamon Press, New York, 1964, Ch. 3
7. Kawaguchi, A., Matsui, R. and Katayama, K. *Bull. Inst. Chem. Res., Kyoto Univ.* 1980, **58**, 470
8. Arnott, S. and Wonacott, A. J. *Polymer* 1966, **7**, 157
9. Takahashi, Y., Sato, T. and Tadokoro, H. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 233
10. Wunderlich, B. 'Macromolecular Physics', vol. 1, Academic Press, New York, 1973; Takokoro, H. 'Structure of Crystalline Polymers', John Wiley and Sons, New York, 1979