

Electron Microscopical Studies on *p*-Polyphenyls

Akiyoshi KAWAGUCHI*, Masaki TSUJI*, Sakumi MORIGUCHI*, Akio UEMURA*,
Seiji ISODA*, Masayoshi OHARA*, Jürgen PETERMANN**
and Ken-ichi KATAYAMA*

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The unit cell of *p*-hexaphenyl was determined to be an orthorhombic form with cell dimensions; $a=0.7758$, $b=0.5530$ and $c=5.46$ nm. In the electron diffraction pattern of *p*-hexaphenyl which was grown on the (100) surface of KCl, the diffuse streaks were observed. From this observation, it was concluded that the shift disorder along the molecular axis was marked. High resolution electron microscopic images of *p*-hexaphenyl having a resolution up to 0.32 nm were obtained. The images supported the crystal structure derived from the analysis of electron diffraction pattern. High resolution electron micrographs of poly(1,4-phenylene) in which lattice fringes run in the direction parallel to the molecular axis were also obtained. It was found from the length of fringes that the length of the polymer ranges from several to ten nm.

KEY WORDS: *p*-Hexaphenyl/ Poly(1,4-phenylene)/ Crystal structure/
Electron diffraction/ High resolution electron microscopy/

INTRODUCTION

Development of highly conducting polymers is a exciting topic in the field of polymer research at the present time. Poly(1,4-phenylene) (PPP), $(-C_6H_4-)_n$, is one of such polymers with the electrical conductivity. The polymer itself is not so conductive, but its conductivity is enhanced by improving the physical state by doping with Lewis acids such as AsF_5 , SbF_5 and so on^{1,2)}. Usually, the polymer is synthesized by the Friedel-Craft reaction from benzene³⁾ or with the transition metal catalyst from *p*-dihalobenzene.⁴⁾ The polymer has also been prepared by the solid-state synthesis from the PPP oligomers ($2 \leq n \leq 6$) by doping with AsF_5 .⁵⁾ The crystal structure of PPP is not fully understood yet, as some points still remain controvertible.⁶⁾ To make clear the problems, the oligomers have been studied as model substances of PPP. Since the crystalline structure of higher members ($n \geq 5$) of homologues is not well-defined yet, it is very interesting for us to analyse their crystal structure itself. Focusing on *p*-hexaphenyl, we examined the crystal structure of these oligomers using an electron microscope mainly and compared their structure with that of PPP.

EXPERIMENTAL

p-Hexaphenyl produced by ICN Pharmaceutical, Inc., USA was used. Crystals

* 河口昭義, 辻 正樹, 森口作美, 植村明夫, 磯田正二, 小原正義, Jürgen Petermann, 片山健一:
Laboratory of Polymer Crystals, Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu,
611.

** Present Address; Technische Universität Hamburg-Harburg, Hamburger Schloßstraße 20, 2100
Hamburg 90, WEST GERMANY.

which are small and thin enough for electron microscopical observation were prepared by the following two methods.

1) *p*-Hexaphenyl was dissolved in the dilute solution (<0.05 wt%) in α -chloronaphthalene at its boiling temperature and was crystallized by slow cooling. A sedimented mat of crystals was prepared from the suspension of crystals by filtration and examined by X-ray diffraction.

2) The material was evaporated in vacuum and deposited on some substrates. The cleavage surface of alkali halides (NaCl, KCl, KBr and KI) was selected as substrates. The following evaporation condition was suitable for the present purpose; the evaporation temperature was 430–450°C and the temperature of substrate 200°C.

A thin film of PPP for electron microscopy was prepared from benzene.^{3,6)}

An electron microscope used here was JEM 200 CS of JEOL and it was operated at 200 kV.

RESULTS

Figure 1 shows the morphology of *p*-hexaphenyl crystallized from the dilute solution in α -chloronaphthalene and the corresponding electron diffraction pattern. The diffraction pattern is indexed well on the basis of the unit cell with $a=0.7758$ and $b=0.5530$ nm. The b -axis is in the direction of long axis of leaf-shaped crystals. The $h00$ and $0k0$ diffractions with h and k odd are clearly observed in the electron diffraction pattern. In the X-ray diffraction pattern of the sedimented mat, these reflections are not seen (see Fig. 2). This shows these reflections are intrinsically extinct. These reflections in the electron diffraction pattern are caused by the secondary effect, probably by the double diffraction. It is found from this extinction that the

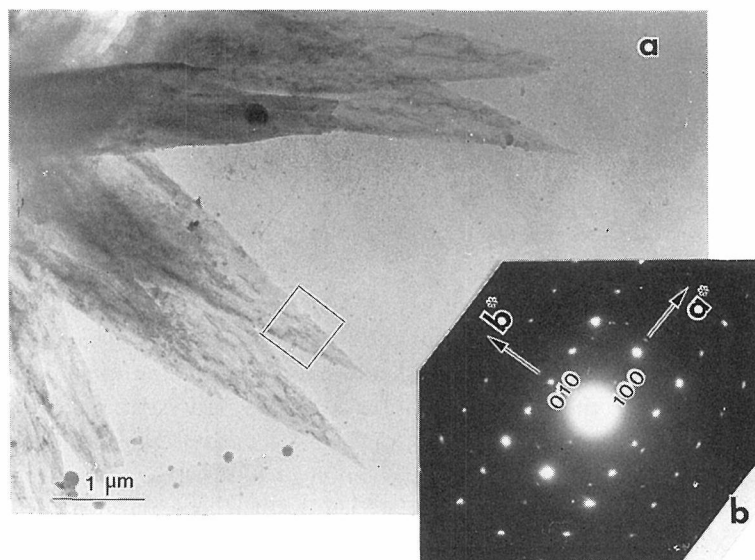


Fig. 1. (a) Crystals grown from the dilute solution in α -chloronaphthalene and (b) the electron diffraction pattern corresponding to the part enclosed by a rectangle.

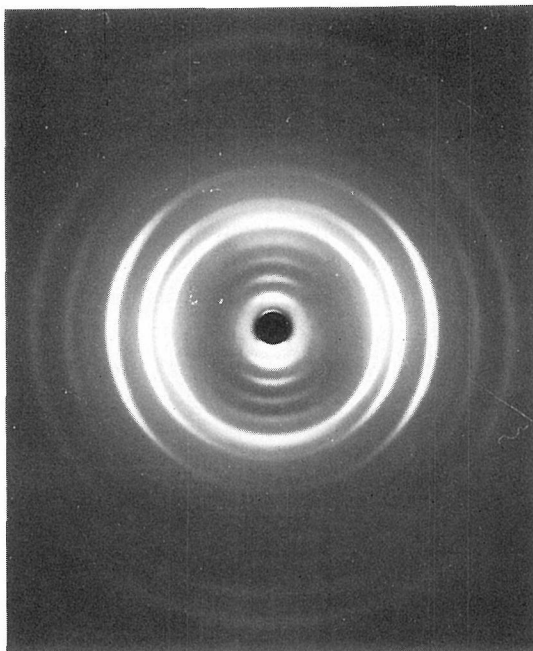


Fig. 2. X-ray diffraction pattern taken from the sedimented mat of *p*-hexaphenyl. The surface of the mat is horizontal and the incident X-ray is parallel to it.

projection of this crystal structure on the **a**-**b** plane has the 2_1 screw axis in the direction parallel to **a**- and **b**-axes: the two-dimensional space group is $p2gg$.

Figure 3(a) shows the high resolution electron micrograph taken from the solution-grown crystal. The photographing condition is as follows; the direct magnification is $\times 10^5$, exposure time 3 secs. and the image-recording film used is FG, the product for electron microscopy by Fuji Photo Film Co., Ltd. The computer-simulated image (b) is inset. The optical diffraction pattern obtained from the original negative of Fig. 3(a) is shown in Fig. 3(c). It is quite similar to the electron diffraction pattern in Fig. 1(b). The similarity of both diffraction patterns indicates that the high resolution image reproduces well the molecular arrangement within the crystal in the **a**-**b** projection. It will be discussed below in detail in the relation with the computer simulated image.

Figure 4 shows the electron micrograph of *p*-hexaphenyl deposited on the {100} surface of KCl. Its electron diffraction pattern is compared with that of PPP in Fig. 5. Many diffraction spots can be distinguished along the meridian in Fig. 5(a). From these meridional spots, the **c**-axis dimension is "apparently" estimated at 2.730 nm. The value 2.730 nm is comparable to the molecular length of *p*-hexaphenyl calculated on the basis of crystal data of its lower homologues.^{7,8)} It is sure from this that molecules are deposited on the KCl surface with chain axes parallel to the surface. Though the X-ray diffraction pattern of the mat arcs, it shows that the $00l$ reflections are on the meridian. This means that molecular chains are normal to the lamellar surface in the case of solution-grown lamellae. Figure 6 shows the enlarged electron

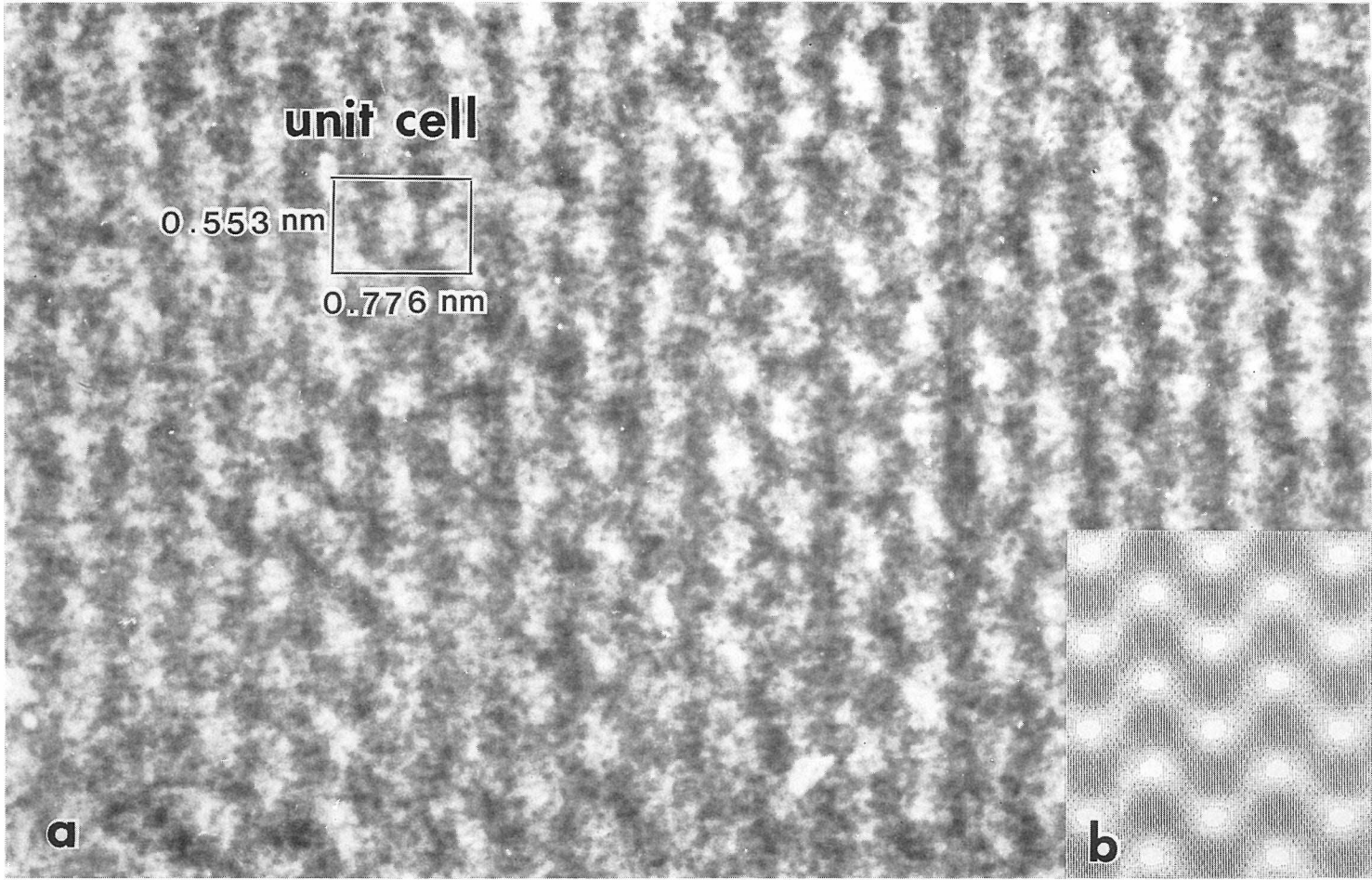


Fig. 3.

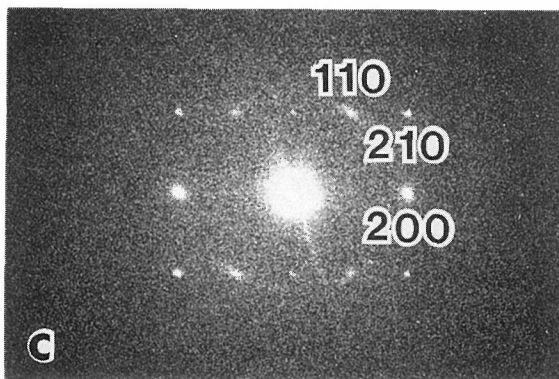


Fig. 3. (a) High resolution electron micrograph of *p*-hexaphenyl crystal grown from the solution, (b) the computer-simulated image and (c) the optical diffraction pattern. Computer-simulation was carried out on the condition; the amount of defocus Δf is -90 nm and the spherical aberration coefficient $C_s=2.8$ mm.

diffraction pattern to pay attention to the diffraction on the 6th, 13th and 19th layer lines, which are indexed in terms of the above “apparent” *c*-axis. The diffraction spots on the respective layer lines are not on the same straight line, as shown in the figure. Only when the *c*-axis dimension is doubled, i.e. 5.46 nm, all these diffractions can be indexed consistently as in Fig. 6. Thus, the unit cell should be orthorhombic and its cell dimensions are $a=0.7758$, $b=0.5530$ and $c=5.46$ nm.

It is seen from Fig. 4 that many long, thin crystals are arranged putting together perpendicularly with one another. Their long axes are aligned parallelly to the $[100]$ direction on $\{100\}$ surface of KCl. The electron diffraction pattern shows that molecular chains are perpendicular to the long axis of the crystal. In the electron diffraction pattern of Fig. 5(a), only $0k0$ diffraction spots are seen along the equator. This means that the (010) plane is normal to the substrate. On the surface of other alkali halides, NaCl, KBr and KI, molecules were also grown epitaxially in the same

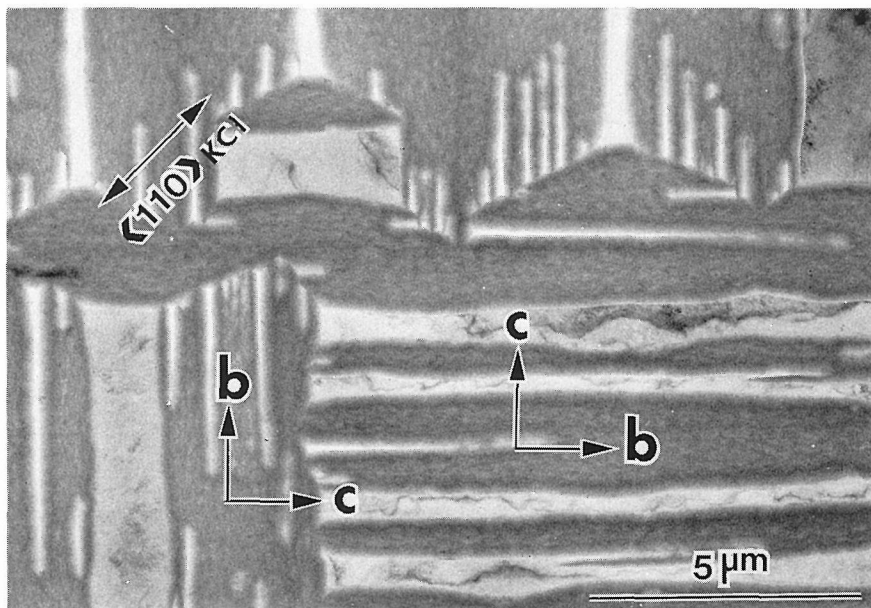


Fig. 4. Electron micrograph of *p*-hexaphenyl deposited on the KCl surface.

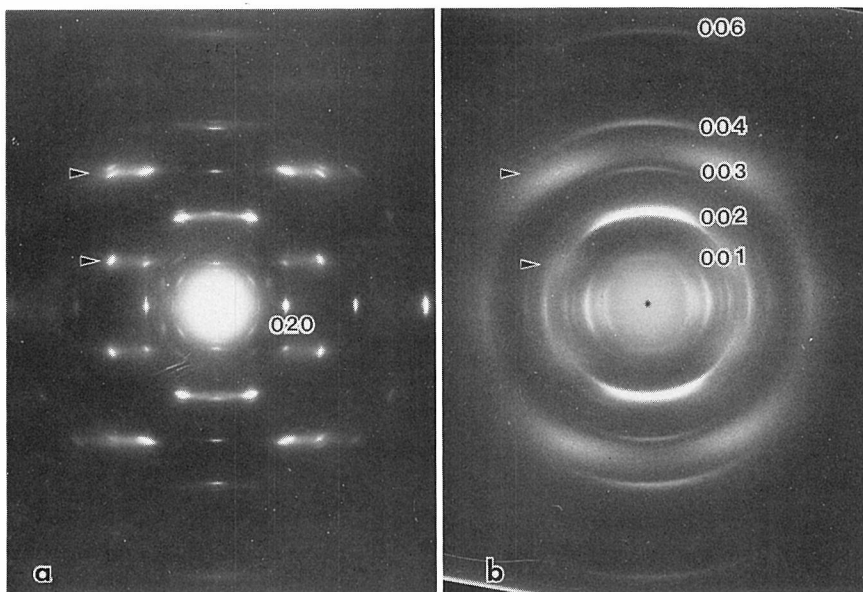


Fig. 5. (a) Electron diffraction pattern of a *p*-hexaphenyl crystal of Fig. 4. The long axis of the crystal is horizontal. (b) The electron diffraction pattern of PPP thin film.

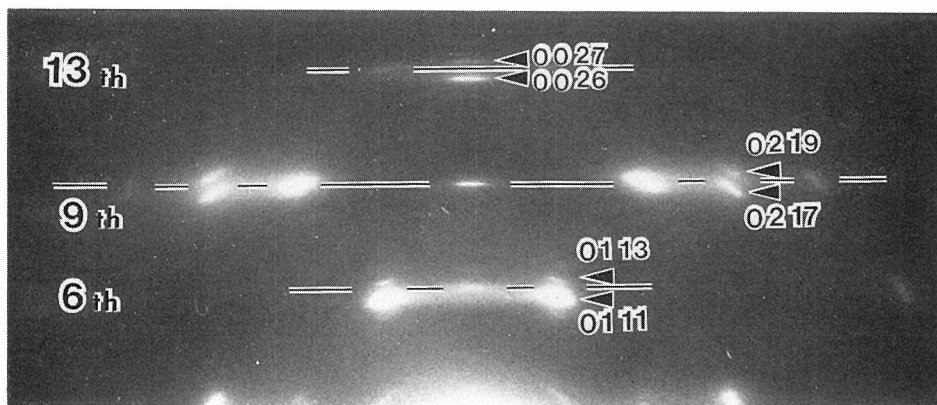


Fig. 6. Enlarged electron diffraction pattern of Fig. 5(a). Numbers in the left side denote the layer lines which are indexed in terms of the "apparent" *c*-cell dimension. Arrows denote the diffractions off from the layer lines.

way as in the case of KCl. In most cases, however, crystal growth with molecules being normal to the substrates is predominant.

Figure 7 shows the high resolution electron micrograph of *p*-hexaphenyl grown on the KCl surface. It was also taken at a direct magnification of $\times 10^5$. The optical diffraction pattern inset in Fig. 7 shows clearly diffraction spots corresponding to the lattice spacings of 2.73 nm and its half. The lattice images are composite of two kinds of lattice fringes running parallelly to the crystal edge. The lattice fringes are not continuous but staggered at some parts (shown by arrows) by the shift of the half of 2.73 nm lattice spacing.

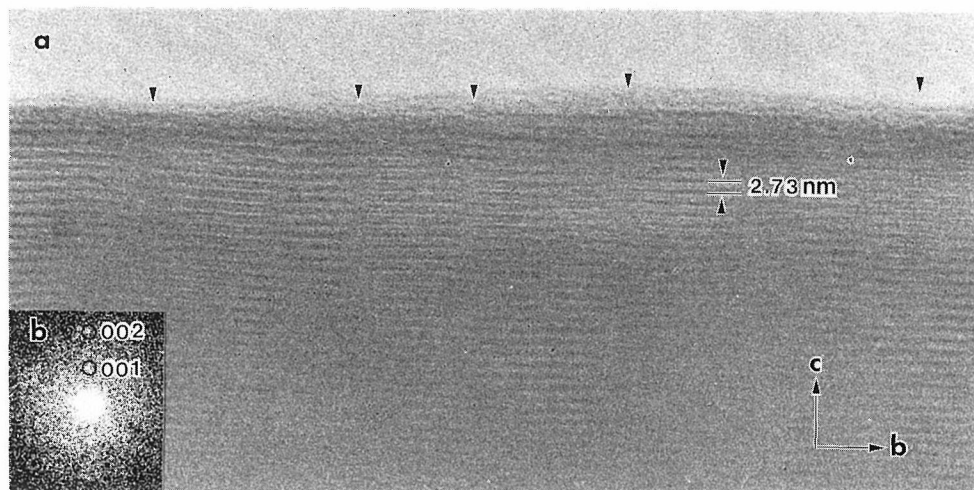


Fig. 7. (a) High resolution electron micrograph of *p*-hexaphenyl grown on the KCl surface and (b) the optical diffraction pattern taken from the negative of (a).

DISCUSSION

Crystallographic data of *p*-polyphenyls and PPP which were reported so far are listed in Table 1. Only the present unit cell of *p*-hexaphenyl is orthorhombic and has a large **c**-cell dimension corresponding to the length of two molecules. The cell size on **a**-**b** plane of PPP is comparable to that of *p*-hexaphenyl. This shows that both crystal structures have the analogous molecular packing on the **a**-**b** projection.

Though diffraction patterns of Figs. 1 and 5(a) taken in the two different directions are available for structure analysis, the information is too restricted to set up

Table 1. Lattice parameters of *p*-polyphenyls and poly(1,4-phenylene)

	a(nm)	b(nm)	c(nm)	$\beta(^{\circ})$	space groupe	Ref.
Biphenyl	0.812	0.563	0.951	95.1	P2 ₁ /a	[9]
<i>p</i> -Terphenyl						
(high temp. form)	0.8106	0.5613	1.3613	92.1	P2 ₁ /a	[10]
(low temp. form)	1.601	1.109	1.353	92.0	P2 ₁ /a	[7]
<i>p</i> -Quaterphenyl	0.811	0.561	1.791	95.8	P2 ₁ /a	[8]
<i>p</i> -Quinquephenyl	0.804	0.5485	2.199	92.0	P2 ₁ /a	[11]
<i>p</i> -Hexaphenyl	0.809	0.560	2.623	91.8		[11]
	0.7758	0.553	5.46			
poly (1,4-phenylene)	0.781	0.5553	0.420			[3]
	0.793	0.553	0.426	100	P2 ₁ /a	[3]
	0.778	0.562	0.426	79	P2 ₁ /a	[12]
	0.781	0.553	0.426	100	P2 ₁ /a	[13]
	0.798	0.555	0.424			[14]
	0.780	0.556	0.420			[15]
	0.778	0.552	0.430			[6]

the three dimensional structure of *p*-hexaphenyl. In consideration of their diffraction features, however, the molecular packing in the unit cell may be as follows. According to the data of molecular structure of *p*-terphenyl⁷⁾ and *p*-quaterphenyl,⁸⁾ the length of structural unit $\text{—}\text{C}_6\text{H}_4\text{—}$ is 0.436 nm and the C-H bond length of end group $\text{H—C}_6\text{H}_4\text{—}$ 0.112 nm. Using these values, the molecular length of *p*-hexaphenyl is estimated at 2.69 nm. The sum of the length of two molecules is comparable to the *c*-cell dimension. From the size of *a*-*b* plane, it is found that two molecular chains should be contained in it. Resultingly, four molecules must be involved in the unit cell. From the extinction of *h*00, 0*k*0 and 00*l* diffractions with *h*, *k* and *l* odd respectively, it is expected that four molecules must be arranged in the unit cell to have 2_1 screw axis in the direction of *a*-, *b*- and *c*-axes. By taking account of these packing requirement together, it is presumed that molecules should be packed as depicted in Fig. 8. This packing manner is just the same as that of normal long chain paraffins with the orthorhombic form.^{6,17)} The structure factors of *hk*0 reflections were calculated on the basis of this model, as the angle (θ in Fig. 8) between the *a*-axis and the plane in which the "averaged" planar molecules are contained is changed. When the calculated intensities are compared with the intensity data obtained by visual evaluation, the setting angle θ for the best fitting of both data is determined to be about 60° . The structural model of *p*-quaterphenyl of Fig. 9 is quoted from Delugeard et al.⁸⁾ In this crystal structure, molecules are shifted progressively along their axes in the same direction. If the molecule C is shifted by 0.082 nm ($a \cdot \cos \beta$) along the molecular axis as shown in Fig. 9, the orthorhombic structural model proposed here could be reproduced. Molecules are alternatively shifted up and down in this form. The intermolecular relation in packing between A and B is equivalent to that between B and C'. Consequently, there is no problem about the molecular packing in this

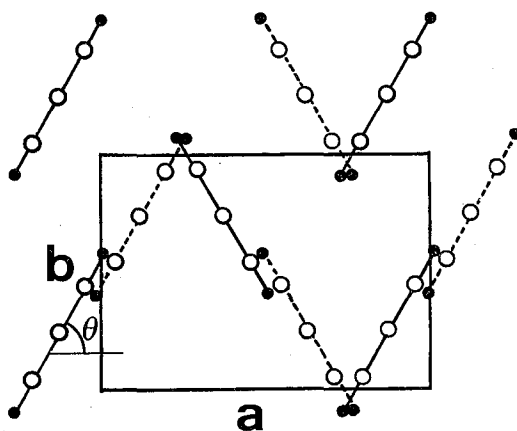


Fig. 8. Projection of the expected structural model on the *a*-*b* plane. Molecules projected in the direction of *c*-axis (molecular axis)—the plane containing the benzene rings—are depicted. Open and solid circles denote the positions of carbon and hydrogen atoms, respectively. The molecular planes indicated by dotted lines denote that molecules are at the level shifted upward in the direction of *c*-axis by $1/2 c$.

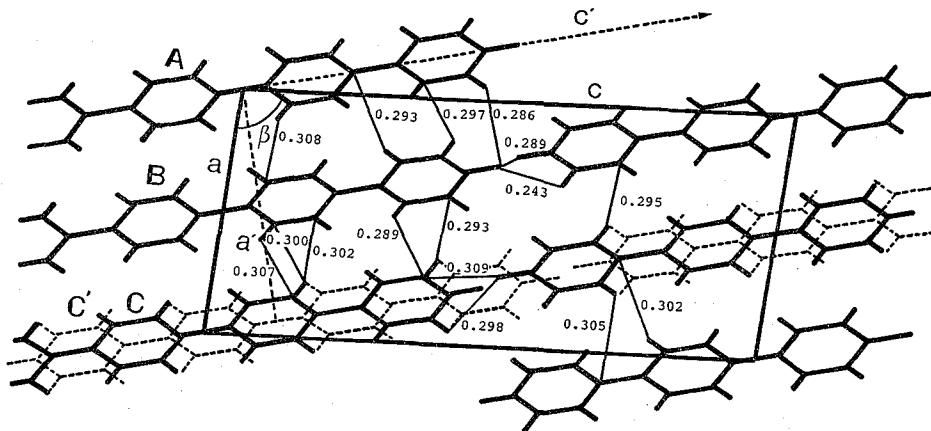


Fig. 9. Structural model of *p*-quaterphenyl in the *a*-*c* projection (after Delugeard et al.). The molecule indicated by dotted lines, *C'*, is displaced from the molecule *C* in the direction of molecular axis by $a \sin \beta$. In combination of *A* and *C'* molecules, the orthorhombic structural model is formed. Figures denote the interatomic distances.

form in terms of interatomic distances. The former type of molecular packing (the result by Delugeard et al.) is very similar to that of the monoclinic modification of *n*-hexatriacontane¹⁸⁾ and the latter (the present form of *p*-hexaphenyl) to that of its orthorhombic form.¹⁷⁾ The structural model analogous to the present form has been proposed for the PPP by Kawaguchi and Petermann.⁶⁾ Detailed examination is in progress.

The high resolution electron micrograph of Fig. 3 corresponds to the crystal image of *p*-hexaphenyl projected on the (001) plane. Accordingly, dark parts in the figure represent probably the images of molecules projected on the (001) plane in the direction of molecular axes. (Since there is no accurate information of the amount of defocus of this image, we can not uniquely allocate molecules to these dark parts.) The unit cell is shown by a rectangle in Fig. 3, and the molecular arrangement quite similar to that of Fig. 8.—zig-zag patterns which we feel tempted to identify as the projected arrangement of molecules—is seen from place to place. The simulated image in Fig. 3(b) was computed on the basis of the structural model in Fig. 8 by Cowley's method on the assumption of kinematical diffraction.¹⁹⁾ In the simulation, the zig-zag molecular arrangement is reproduced on the under-focus condition of $\Delta f = -90$ nm. Appearances of both the observed and computed images are quite similar. This similarity proves that the structural model of Fig. 8 is reliable.

In the electron diffraction pattern of Fig. 5(a), the diffraction peaks on the equator are sharp, but those on the layer lines tail off along the layer line and moreover diffuse streaks overlap on it. The sharp equatorial reflections prove that the lateral packing of molecules is rather regular. It is shown theoretically that the diffraction peaks on the layer line become broadened along the layer line, when the shift disorder of molecules along their axes is marked.^{20,21)} The diffraction pattern of PPP in which equatorial reflections are sharp and other sharp reflections are only on the meridian is

the extreme case (see Fig. 5(b)). It is thus concluded that PPP has the paracrystalline nature with a large shift disorder along the chain axes as in the nematic state of liquid crystals.⁶⁾ The diffraction features of diffuse streaks in Fig. 5(a) (shown by arrows) are also caused by the same disorder as in PPP, though the degree of disorder is less.

In the *p*-terphenyl and *p*-quaterphenyl crystals, molecules can not take the planar conformation that the planes containing benzene rings are in the same plane.^{7,8)} Since the hydrogen atoms protruding from the neighboring benzenes are too near, repulsion between them is serious. To reduce the repulsion, molecules must twist about the C-C bond connecting benzene rings. Thus, twisting of benzene rings around the molecular axis occurs clockwise and anticlockwise with equal probability statistically so that they could settled down in an energetically favorite position deviated from the planar structure. Though the orientation of the benzene rings changes thus randomly, a chain has a planar conformation as an average, because the center of gravity of benzenes is not displaced. If the distance between neighboring chains is sufficiently large, such "averaged" planar chains could be packed side-by-side keeping the distance between them fixed. As their conformation is irregular, however, the chains may not be settled in a regular positions in the direction of their axes and then the shift disorder along the molecular direction increases. This is the cause of large shift disorder along the molecular axis. The existence of high and low temperature phases in *p*-terphenyl and *p*-quaterphenyl evidences this disorder. As regards the energetical stability of these molecules, a benzene ring holded between two adjacent benzene rings— for example the central benzene ring of *p*-terphenyl— has two potential minimums which are located on either side of planar conformation. At high temperatures, the rings could move around back and forth between two potential wells. The thermal motions result in the "averaged" planar conformation. Since thermal motions are restricted at low temperatures, the benzene rings fall into either of the potential minimums. The conformation that a benzene ring is settled down in one of potential minimums is to be distinguished from that for the other. A large unit cell incorporating these two types of molecules is formed at low temperatures.^{7,8)} At present time, however, it is not found that *p*-hexaphenyl has this type of crystal form at low temperatures such as liquid nitrogen temperature.

The high resolution electron micrograph of Fig. 7 shows the projection of *p*-hexaphenyl crystals on the (100) plane in the direction of $\langle 100 \rangle$. The lattice fringes of 2.73 nm run parallelly to the edge of crystal. This proves that molecular chains are normal to the edge. The characteristic staggering of fringes is seen in Fig. 7. Staggering is probably produced by such lattice defects as stacking faults, dislocations and so on. When the thickness variation exists in the crystals, however, the lattice fringes meander due to gradual change of thickness and shift due to step in thickness.²²⁾ Since no other lattice image except 00 ℓ ones are observed, the cause of staggering can not be sought further.

The electron diffraction pattern of PPP is the fiber pattern and shows that the molecular axis is preferentially aligned parallelly to the film surface. Figure 10 shows the high resolution image of PPP thin film. The 110 lattice fringes of 0.45 nm are seen in the image. The 200 lattice fringes of 0.38 nm are also observed in another part.

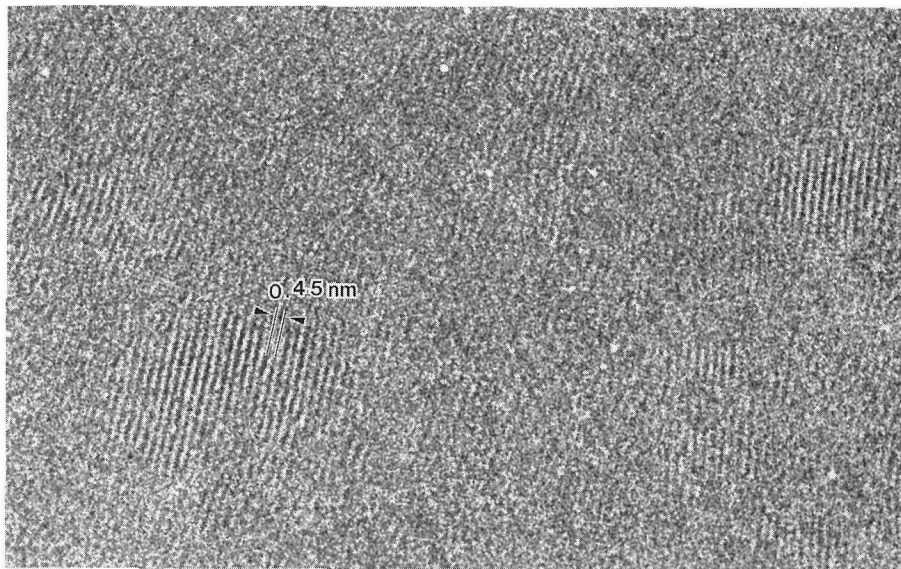


Fig. 10. High resolution electron micrograph of PPP. The 110 lattice fringes of 0.45 nm are seen. The fiber axis is vertical.

Judging from the molecular orientation, it is reasonable to consider that these fringes should be the projection of PPP crystallites in the direction normal to the molecular axis on some planes: the 110 fringe is the projection on the plane normal to the (110) plane and the 200 fringe on the (010) plane in the $\langle 010 \rangle$ direction. There are no images of long spacing observed, conveying information of molecular length and direction as in Fig. 7. This implies that PPP molecules are "long" and uneven in length in contrast with *p*-hexaphenyl. The same kind of lattice images from fiber specimens have been obtained in other polymers; poly(*p*-phenylene terephthalamide),²³⁾ poly(*p*-phenylene benzobisthiazole),²⁴⁾ (SN)_x²⁵⁾ and isotactic-polystyrene.²⁶⁾ What happens at the boundary where the lattice images disappear in Fig. 10? When the diffraction condition is not fulfilled by the change in the orientation of crystallites, the lattice images could not be formed. Intuitively, PPP molecular chains are considered to be rigid from their chemical structure. Detailed examination of the diffraction pattern of PPP shows surely that the PPP chains are rigid and rectilinear enough to be regarded as a linear grating.⁶⁾ It is thus unlikely that the orientation of a crystallite might change at the boundary where fringes terminate. Assumedly, the length of each fringe could be compared to that of a single molecule.²⁷⁾ In this consideration, molecular length was estimated at several to ten nm. According to the chemical analysis, the degree of polymerization is about 16 as an average.¹⁾ A comparable value is obtained from the analysis of X-ray diffraction profile.²⁸⁾ The length of lattice fringes observed here is in good agreement with those obtained by the above degree of polymerization.

p-Polyphenyls are so tough for electron irradiation that high resolution electron micrographs can be taken. Structural studies on these materials with the use of

a high resolution electron microscope was partly successful. Further study on these materials by this methods is expected to be fruitful.

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