649. lin-*Poly*-p-*xylylene. Part III.* Preparation by the Wurtz Reaction, and Investigation of Structure.*

By C. J. Brown and A. C. Farthing.

lin-Poly-*p*-xylylene is prepared from *p*-xylylene dichloride by the Wurtz reaction and is shown by *X*-ray methods to be identical with the polymer prepared by pyrolysis of *p*-xylene. Oxidative degradation shows the polymer to be linear; it is dimorphic, both forms, α and β, being characterised by *X*-ray powder patterns, and they can be separated by fractionation methods. The α- is converted into the β-form by heat, but the transformation could not be reversed. *X*-Ray evidence indicates that the α-form has a stepped structure whilst the β-form is planar.

The production of a polymeric substance during the pyrolysis of *p*-xylene at low pressures by Szwarc (*J. Chem. Phys.*, 1948, **16**, 128) gave rise to the question of its structure. It was decided to examine the preparation of similar material by a classical organic synthetic method which might be expected to afford greater control, and then to compare the product, by *X*-ray diffraction, with polymer formed by pyrolysis. Wurtz condensation of *p*-xylylene dichloride did not occur at all in benzene, and only very slowly in toluene to give an amorphous polymer. *p*-Xylene was thought to be a suitable medium because if it took part in the Wurtz reaction by trans-metallation or radical interchange then the product would be of unchanged structure. The Wurtz reaction took place rapidly in *p*-xylene, yielding a solid product which on purification generally had a diffraction pattern identical with that of polymer prepared by the pyrolysis method. When dioxan was used as solvent reaction was extremely rapid and violent.

Friedel–Crafts condensation of phenethyl chloride gave an amorphous polymer, no doubt owing to reaction at both *o*- and *p*-positions on the ring, whereas formation of *lin*-poly-*p*-xylylene requires reaction exclusively at the *p*-position.

Oxidation of the pyrolysis polymer yielded terephthalic acid along with only 0·1% of *iso*phthalic acid. This indicated primarily a structure (I), the traces of *iso*phthalic acid arising from *m*-xylylene units in the chain, which were probably formed by isomerisation of the *p*-xylene in the pyrolysis apparatus. An alternative structure (II), based on the known pyrolysis of *p*-xylene to dimethylanthracenes (Part I), is ruled out.

Wurtz condensation of 4-methylbenzyl chloride yielded only 4 : 4′-dimethyldibenzyl,

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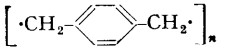
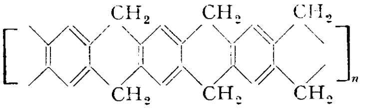
* Part II, preceding paper.

and by analogy it is likely that *p*-xylylene dichloride would react similarly to give poly-*p*-xylylene. It has been shown (Szwarc, *Discuss. Faraday Soc.*, 1947, **2**, 39) that the bond between the aliphatic carbon atoms in dibenzyl is stabilised by resonance and this stabilisation may occur in the polymer.

(I)





(II)

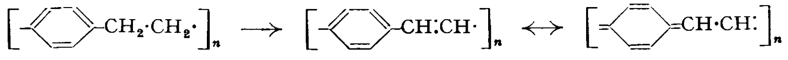
The polymerisation in the pyrolysis apparatus is a combination of free radicals, and the literature shows three cases of dimerisation of *p*-xylene, probably by a homolytic mechanism. Aqueous potassium persulphate oxidises *p*-xylene to 4 : 4′-dimethyldibenzyl, (Part I); the decomposition of phenyl azide in *p*-xylene gives the same compound (Bertho, *Ber.*, 1924, **57**, 1138); and when a solution of benzophenone in *p*-xylene is exposed to sunlight (Paterns and Chieffi, *Gazzetta*, 1909, **39**, II, 428) 4 : 4′-dimethyldibenzyl is among the products. By analogy, the higher polymer formed from the free radicals would be expected to have the same structure as the dimer formed from the same radicals. This argument is supported by the occurrence of both the linear dimer (4 : 4′-dimethyldibenzyl) and the cyclic dimer (di-*p*-xylylene) in the pyrolysis polymer.

Although polymer prepared by both the Wurtz and the pyrolysis method gave similar *X*-ray diffraction patterns, it was observed that the relative intensities of certain rings on the powder photographs were different. By adjusting the conditions of preparation of the polymer the ratio of these intensities could be varied. The evidence pointed to the presence of two components, and these were separated by making use of their differential solubilities. For example, extraction of the Wurtz polymer with chloroform (Soxhlet) removed only the α-modification; and when the pyrolysis polymer was dissolved in boiling benzyl benzoate, and cooled, the portion separating first was the β-modification.

The α- was transformed into the β-form by heating above the melting point, but numerous attempts to carry out the reverse process were unsuccessful.

Probable structures of the two modifications of the polymer were suggested by comparing their *X*-ray powder photographs with the powder photographs and known structures of corresponding monomeric substances. It is not generally possible to derive an unambiguous crystal structure from a powder photograph of a substance of low symmetry, but in the case of the two forms of *lin*-poly-*p*-xylylene there are two series of closely related substances whose structures are already known, and these were of great assistance in deducing the probable structures of the polymers.

The unit-cell dimensions suggested for the α- and the β-form of the polymer account for all the reflexions observed in their powder photographs as shown in Tables 2 and 4. The configuration of the α-form of the polymer was taken to be similar to that of the molecule of 4 : 4′-dimethyldibenzyl; the benzene rings lie parallel to each other in the same molecule but are not co-planar; they are arranged stepwise. In the β-form of the polymer, the benzene rings are both parallel and co-planar as in the molecule of diphenyl; it follows that the $\cdot CH_2\cdot CH_2\cdot$ grouping also lies in the plane of the rings whereas in the α-modification it forms the step. It is not impossible that the β-form may be quinonoid as has been suggested by Goldfinger (*J. Polymer Sci.*, 1949, **4**, 93) for polyphenylene, but if this is so, two hydrogen atoms would be lost from each $\cdot CH_2\cdot CH_2\cdot$ grouping, and this might account for the irreversibility of the transition from α to β :



This difference, especially in a polymer of very low solubility, would be extremely difficult to detect.

EXPERIMENTAL

Preparation of Polymer by the Action of Sodium on p-*Xylylene Dichloride.*—Apparatus for Wurtz reactions and for immediate manipulation of reagents was dried by baking at 100° for several hours. *p*-Xylylene dichloride was dried (over $CaCl_2$) for several days. Solvents were dried over sodium and distilled directly into the apparatus. Exits from the apparatus were protected by tubes containing " Drierite " ($CaSO_4$).

(a) *Preparation in* p-*xylene.* In a 1-l. flask fitted with a rapid stirrer and reflux condenser *p*-xylylene dichloride (30 g.), *p*-xylene (100 c.c.), and sodium (10 g., an excess of 2·1 g.) were heated carefully. When the b. p. was reached a spontaneous reaction occurred and subsided in 1 min. The precipitate formed was deep purple. The mixture was then heated under reflux for a further 1·5 hr. The solid was filtered off, washed with ethanol, and stirred for 2 hr. with water, during which the blue mixture became pale cream in colour. It was then stirred with water for a week (the water being changed daily), filtered, washed with ethanol, and dried *in vacuo* ($CaCl_2$). The product (sample 5, 16·45 g.; 93·5%) was more soluble than sample 4 (prepared in toluene); it swelled and partly dissolved in hot naphthalene, ditolylmethane, and *m*-cresol. The solutions were not viscous. It was almost completely soluble in boiling benzyl benzoate and dibenzyl terephthalate, but " ghosts " of swollen particles were just visible (Found: C, 88·8; H, 7·45; Cl, 1·0; residue, 1·9%; C : H = 1). The *X*-ray photograph showed three rings of spacing 3·9, 4·4, and 5·3 Å, showing a moderate degree of crystallinity. The intensities of the 3·9 and 5·3 Å rings were greater than that of the 4·4 Å ring, and the photograph bore a marked resemblance to those of polymer obtained by pyrolysis of *p*-xylene. Reproductions of typical diffraction patterns are shown in the Plate.

(b) *Preparation in absence of solvent.* When sodium and excess of *p*-xylylene dichloride were warmed together in a test-tube, with suitable protection, a spontaneous reaction occurred after the dichloride had melted. A spongy solid formed round the sodium and swelled up the tube. When cold, the polymer was washed and dried as before. It was similar in appearance to the polymer sample 5, but not quite as soluble.

(c) *Further preparations of polymer.* The experimental procedure was similar to that adopted above. Some of the results are summarised in the Table.

Polymer sample no.	*p*-Xylylene dichloride: charged (g.)	unreacted (g.)	Yield of polymer: (g.)	(%)	Na (g.)	Solvent (c.c.)	
6	30	18	6·5	95	10	*p*-Xylene	250
10	30	—	2	—	10	Ditolylmethane	250
7	30	5	13	90	10	*p*-Xylene	164
8	30	—	8	—	10	Dioxan	250
9	10	—	2	—	4	Dioxan	250

Sample 6. The polymer had similar properties to sample 5. The *X*-ray photograph showed that the degree of crystallinity, judged by visual comparison, was slightly higher, and the three principal diffraction rings were roughly of equal intensity.

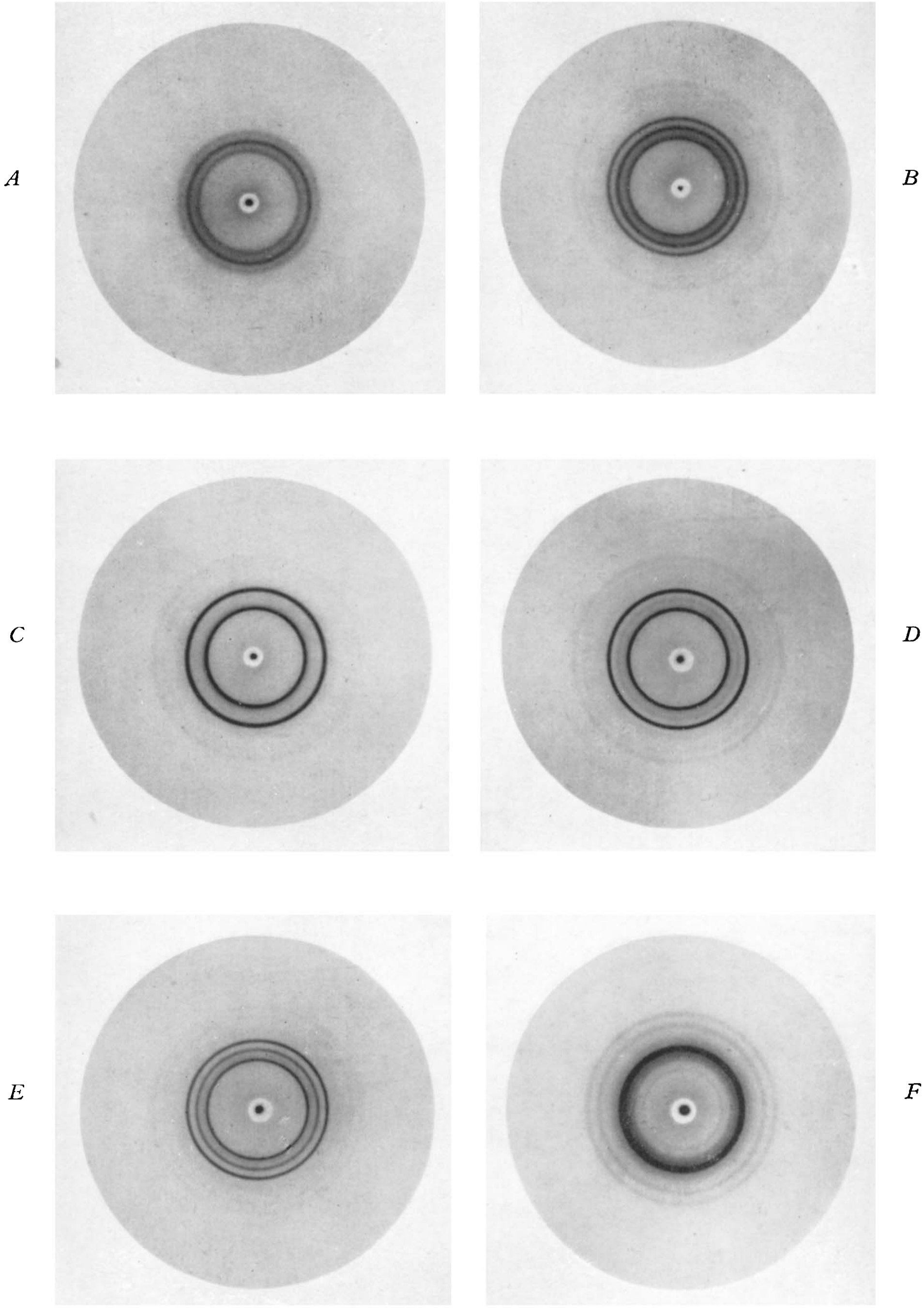
Sample 10. The solvent (mixed isomers from methylene dichloride and toluene) was not distilled directly in the reactor. Reaction was slow at 200°. After 10 min. at 220° the solution was black. The polymer was filtered off, and washed thoroughly with ethanol and benzene. It was swollen by hot naphthalene and acenaphthene, but remained generally insoluble. The *X*-ray photograph showed the sample to be mainly amorphous, but there was indication of three crystalline rings due to spacings of 3·9, 4·4, and 5·3 Å.

Sample 7. This was apparently identical with sample 6.

Sample 8. The Wurtz reaction in this case was very violent and material was ejected from the reactor. However, the residue in the flask was worked up in the usual manner. The polymer was almost pure white and was more powdery than the other preparations. It was the most soluble of the polymers prepared by the Wurtz reaction, but did not completely dissolve in hot naphthalene, acenaphthene, benzyl benzoate, or dibenzyl terephthalate; faint " ghosts " of swollen particles were just visible in the solution. The *X*-ray photograph showed the same three principal diffraction rings as the previous samples 4—7, but the relative intensities were markedly different. The middle of the three rings was considerably more intense than the other two. This gave the first hint about the composition of the polymer.

Sample 9. The sodium was added in 0·5-g. portions. In solubility it resembled sample 8, but the *X*-ray diffraction pattern was identical with that of samples 6 and 7.

Polymer samples 30 and 31. In a 3-l. flask were placed *p*-xylene (1475 c.c.) and sodium (10 g.). The *p*-xylene was gently boiled over an oil-bath. *p*-Xylylene dichloride (30 g.) was added in small portions during 4½ hr., and the mixture boiled for a further 4½ hr. The mixture was concentrated to *ca.* 200 c.c. and filtered hot. The residue was worked up in the usual way, to yield polymer sample 31, which resembled samples 5, 6, and 7 except that it was paler in colour. The *X*-ray photograph showed rings due to the usual spacings of 3·9, 4·4, and 5·3 Å,



X-*Ray diffraction patterns of* lin-*poly*-p-*xylylene*.

A, Pyrolysis polymer (sample 22).
B, Wurtz polymer (sample 12).
C, α-Form of polymer (sample 13).
D, α + small amount of β (sample 14).
E, α + β, approx. equal amounts (sample 15).
F, β-Form of polymer (sample 29).

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but the middle ring was very weak. There was also a background of scattering due to amorphous material. The filtrate from the hot reaction mixture was concentrated on the steam-bath at the water-pump, to about 20 c.c. On cooling, a gummy precipitate appeared. This was washed with acetone and dried to give sample 30. It melted at 120—150° to yield a viscous liquid. It was soluble in hot pyridine and was precipitated as a sludge on cooling. No di-*p*-xylylene could be detected. The *X*-ray photograph was well defined, showing the material to be of high crystallinity. It had rings corresponding to the three common spacings but there were also additional rings resembling those of 4 : 4′-dimethyldibenzyl.

Self-condensation of Phenethyl Chloride.—Phenethyl chloride, freshly distilled, was polymerised by anhydrous aluminium chloride after Sizido and Kato (*Chem. Abs.*, 1941, **35**, 3246). The product was washed free from aluminium chloride and phenethyl chloride. On drying in air a hard brittle solid (sample 32) remained. The *X*-ray photograph of sample 32 was that of amorphous material. Freshly distilled phenethyl bromide gave a similar product.

Wurtz Condensation of p-*Di-2-chloroethylbenzene.*—*p*-Di-2-chloroethylbenzene (4·85 g., Part I) and sodium (2 g., an excess) in *p*-xylene (47 c.c.) in a 250-c.c. 3-necked flask were used, the technique described above being followed. The reaction proceeded exactly as with *p*-xylylene dichloride. The blue-brown precipitate of polymer was similarly treated to produce 1·6 g. (50%) of pale yellow polymer (sample 33). It was insoluble in all common organic solvents, but it was swollen readily by the solvents which swelled the *lin*-poly-*p*-xylylene prepared by the Wurtz reaction. It had a slightly lower m. p. than Wurtz *lin*-poly-*p*-xylylene. A comparison was made with sample 16 in an electrically heated capillary m. p. apparatus by use of a 550° mercury-in-glass thermometer which took two tubes and enabled comparison to be made. Results were not exactly reproducible, but poly-*p*-xylylene had the higher m. p., 420—430°, as against 395—415° for sample 33. Sample 33 gave an *X*-ray diffraction pattern characteristic of amorphous material. The mother-liquors from the Wurtz reaction on evaporation to dryness in air and finally *in vacuo* gave a viscous orange-coloured resin (1·3 g., 40%) free from the odour of *p*-di-2-chloroethylbenzene.

Wurtz Condensation of p-*Dichlorobenzene.*—*p*-Dichlorobenzene (redistilled, 30 g.) and sodium (11 g., an excess) in *p*-xylene (350 c.c.) failed to react after prolonged boiling. In dioxan (100 c.c.) a smooth reaction occurred on boiling. As the reaction started, a cold-water bath was applied for a moment. The liquors became brown and a deep blue solid was precipitated. The mixture was left to cool, and methanol (800 c.c.) slowly added, causing a sludge to be formed. The mixture was stirred overnight, and the residue was collected and washed as usual, to yield a brown powder (sample 36), m. p. 220° (cf. Goldfinger, *loc. cit.*, m. p. >300°), soluble in benzyl benzoate (Found: C, 82·55; H, 4·6; Cl, 10·65. Calc. for $[C_6H_4]_8Cl_2$: C, 84·8; H, 4·7; Cl, 10·5%). *X*-Ray examination showed sample 36 to be amorphous even after melting (sample 37). The filtrate from the isolation of sample 36 from the reaction mixture was concentrated and yielded a series of fractions of varying solubility. The more soluble ones smelt of diphenyl. The least soluble fraction (sample 38) was submitted to *X*-ray analysis and shown to be crystalline, but there was some amorphous background. The general appearance of the rings on the photograph was closely similar to that of the rings of β-*lin*-poly-*p*-xylylene, sample 21.

Investigation of the Structure of lin-*Poly*-p-*xylylene.*—Polymer obtained by pyrolysis of *p*-xylene ("pyrolysis polymer") was completely soluble in boiling benzyl benzoate and acenaphthene (F. D. Hartley and F. Lord, of these Laboratories, personal communication). Polymer from *p*-xylylene dichloride ("Wurtz polymer") was not completely soluble, as described above. Both Wurtz and pyrolysis polymer were insoluble in common organic solvents.

Degradative oxidation of pyrolysis polymer. Polymer (samples 1—3) freed from substances of low molecular weight by chloroform extraction (Part I) was unchanged by boiling 5N-nitric acid for 24 hr. The polymer (2·25 g.) was heated in boiling glacial acetic acid under a reflux condenser, and *ca.* 0·3-g. portions of chromium(VI) oxide added until spontaneous oxidation ceased. A further portion of oxidant was added, and the mixture boiled for 15 min., but chromate was still present. The mixture was poured into water (250 c.c.) and filtered. The residue was washed free from chromium with water, stirred with excess of dilute aqueous ammonia, and filtered. The residue was unchanged polymer (1·15 g.). The filtrate was acidified, and the precipitate collected (1·1 g.) and converted into methyl ester by methanol–sulphuric acid. The esters were largely dimethyl terephthalate, m. p. and mixed m. p. 140°, which contained 0·1% of dimethyl *iso*phthalate. The latter was estimated by infra-red spectrometry after separation of the terephthalate by *cyclo*hexane.

Separation of the Polymorphic Forms of the Polymer

(*a*) A sample of pyrolysis polymer was examined and a single piece of film selected. This was cut in two pieces and one piece reserved as a control (sample 20). The other piece was dissolved in hot benzyl benzoate, and the solution cooled. A sludge separated and was filtered off, washed with benzene, ethanol, and then dry ether, and dried on the filter to give sample 21. The X-ray photograph of polymer sample 20 showed the usual outer and inner rings of spacing 3·9 and 5·3 Å with a weak middle ring of spacing 4·4 Å. That of sample 21 showed a predominantly strong ring at 4·4 Å with a number of weaker ones. This form, characterised by the strong ring due to a 4·4 Å spacing, is designated β-*lin*-poly-*p*-xylylene.

(*b*) Polymer sample 7 was finely ground in a mortar and put in two test-tubes in an oil-bath at 200°. After 1 hr. one tube was withdrawn and plunged into an oil-bath at room temperature to give sample 11. The other tube was annealed by allowing the oil-bath to cool to room temperature during 1 hr., giving sample 12. The X-ray photographs of samples 11 and 12 were identical and resembled that of sample 7.

(*c*) Polymer sample 7 (6·6 g.) was ground in a mortar and extracted with chloroform (Soxhlet) for 5½ hr. The extract was yellow. On removal of the chloroform there remained a yellow solid (0·2 g.; sample 13), m. p. 184—220°, melting to a viscous liquid. The polymer remaining after extraction (sample 16) appeared unchanged and this was confirmed by its X-ray diffraction pattern. However, sample 13, the extract, showed only the outer and the inner diffraction ring, corresponding to spacings of 3·9 and 5·3 Å. This form, characterised by these two rings, is designated α-*lin*-poly-*p*-xylylene. A portion of sample 13 was melted in an air-bath at 240° and left to cool to give sample 14. Sample 14 showed a change in internal structure, as in its diffraction pattern the middle ring, corresponding to 4·4 Å, had appeared and was faintly visible. Accordingly, a further portion of sample 13 was melted, held at 300° for 2 min., and allowed to solidify during 5 min., giving sample 15. In this case the amount of change was greater, the middle ring on the diffraction pattern having become almost as intense as the other two rings. The diffraction patterns of samples 13, 14, and 15 are reproduced in the Plate. A further portion of sample 13 was dissolved in boiling benzyl benzoate and precipitated on cooling. The sludge was filtered off, washed with benzene, ethanol, and ether, and spread on a microscope slide to dry. After 4 weeks at room temperature it was still wet with benzyl benzoate and so it was finally dried at 84° in an oven (sample 17). Its diffraction pattern was similar to that of sample 13. Sample 17, m. p. 217°, was melted in a flame and immediately cooled by spraying the tube with ethanol to give sample 18. The X-ray photograph of sample 18 showed that the middle ring had appeared in considerable strength.

(*d*) Wurtz polymer, sample 5 (10·4 g.), was extracted for 24 hr. with chloroform (Soxhlet). There was obtained a yellow solid extract (0·07 g.; sample 19). The X-ray photograph of this product resembled that of sample 30 and also bore certain similarities to the powder photograph of 4 : 4′-dimethyldibenzyl.

(*e*) Pyrolysis polymer was extracted with chloroform as in Part I. The extracted polymer (sample 22, 4·85 g.) was dissolved in boiling benzyl benzoate (85 c.c.). A few lumps of swollen gel which were difficult to dissolve were removed with forceps. The solution was left to cool, and then filtered, and the residue washed with cold benzene, ethanol, and ether to yield 4·1 g. of a brown powder (sample 23). This was extracted with chloroform for several hours (Soxhlet). The extract, sample 24 (0·1 g.), was a brown solid. Three portions of the extracted matter (sample 26) were melted in test-tubes with a free flame; one was left to cool in air (sample 27), one was left to cool wrapped in cotton-wool (sample 28), and the last quenched by plunging into cold water (sample 29). X-Ray examination of each of these samples showed the following sequence of changes. Sample 22, the parent sample, showed a preponderance of β-structure, *i.e.*, the middle ring of the diffraction pattern was several times more intense than either of the other two. Sample 23 was almost completely the β-structure, as the rings due to the α-structure had largely disappeared. Sample 24 was completely α-, with a little amorphous matter, but sample 25 was largely β-, with a trace of α-structure. Sample 26 was largely β-, as also were samples 27, 28, and 29, but these three samples had a greater degree of crystallinity than 26, as shown by an increase in the sharpness of the rings.

(*f*) Wurtz polymer, sample 16, was placed in a Carius tube which was then flushed three times with nitrogen, evacuated, and sealed. On being heated in an air-bath at 430° the solid shrank from the walls of the tube and did not melt. The air-bath was removed, and the polymer partially melted with a free flame. The polymer was removed and showed a skin of melted and resolidified polymer (sample 34), then a circular zone of sintered material (sample 35), and finally a core of loose powder. Both samples 34 and 35 were swollen by boiling benzyl benzoate, as was sample 16. This melting treatment was shown by the diffraction patterns to result in the complete conversion of a mixture of the α- and β-structures into the β-structure.

X-*Ray Experimental Procedure*.—Each sample was photographed in an *X*-ray diffraction camera on a flat film placed at 2·90 cm. from the specimen, which was powdered and pressed by hand into a $\frac{1}{16}''$ hole in a piece of 0·03″ celluloid, and mounted on the end of a 0·05 × 5 cm. lead-glass collimator. Exposure times were generally 2 hr. with a tube current of 20 mA at 50 kv. Although the majority of the photographs were taken for qualitative comparison purposes only (see Table 5), those of samples 17, 27, and 38 were calibrated and measured accurately in order to obtain the unit cell dimensions of polyphenylene and of the α- and the β-form of *lin*-poly-*p*-xylylene.

Structures of the Polymers.—In general it is not feasible to determine the crystalline structure of a complex compound from its *X*-ray powder photograph. The problem is especially difficult in the case of polymers on account of the relatively small number of reflexions. In cases where well-oriented specimens are obtainable, *e.g.*, nylon, *X*-ray photographs comparable with those from single crystals can be taken, and the interpretation of these is straightforward (Bunn and Garner, *Proc. Roy. Soc.*, 1947, *A*, **189**, 39). The *lin*-poly-*p*-xylylene polymers, however, are of low molecular weight and show no tendency to form films or fibres; neither have sufficiently large crystals for single-crystal photographs been grown, and so only *X*-ray powder photographs were obtainable. The interpretation of these was simplified by the existence of a series of compounds which are closely related to the polymers and which gave somewhat similar powder photographs; in this way unit cell dimensions for the polymers were found which were related to those of the monomeric compounds. By analogy, structures were then postulated for the polymers.

α-lin-*Poly*-p-*xylylene*. The powder photograph of sample 17 bore certain resemblances to that of 4 : 4′-dimethyldibenzyl; the two strong rings (Photograph *C*, on Plate) were similar, both in position and intensity, to two rings on the powder photograph of 4 : 4′-dimethyldibenzyl. As there was a correspondence of the same kind between the photographs of the β-polymer and diphenyl, it was thought reasonable to investigate the relation between the structures of the α-polymer and 4 : 4′-dimethyldibenzyl. The structure of 4 : 4′-dimethyldibenzyl was not known, and it was necessary to work it out. This was done on the basis of structural similarity between it and the closely related iso-structural series comprising dibenzyl, stilbene, tolane, and *trans*-azobenzene (Robertson, Prasad, and Woodward, *Proc. Roy. Soc.*, 1936, *A*, **154**, 187). The unit-cell dimensions of these compounds, together with those of the α-polymer and 4 : 4′-dimethyldibenzyl, are shown in Table 1.

TABLE 1. *Crystal structures related to* α-lin-*poly*-p-*xylylene*.

Unit-cell dimensions	*a*, Å	*b*, Å	*c*, Å	*β*
α-*lin*-Poly-*p*-xylylene	11·68	6·10	9·16	102½°
4 : 4′-Dimethyldibenzyl	2 × 11·68	6·10	9·16	100½
Dibenzyl	12·77	6·12	7·70	116
Stilbene	12·35	5·70	2 × 7·96	114
Tolane	12·75	5·73	2 × 7·83	115
trans-Azobenzene	12·20	5·77	2 × 7·70	114

The relationship of the last four compounds with 4 : 4′-dimethyldibenzyl is dealt with fully in the paper describing its structure (Brown, *Acta Cryst.*, 1953, in the press); the comparison between the α-form of the polymer and 4 : 4′-dimethyldibenzyl is made here. The powder photograph was indexed by Ito's method ("*X*-Ray Studies on Polymorphism," Maruzen Co. Ltd., Tokyo, 1950), and the unit cell reduced by Delaunay's method (*Z. Krist.*, 1933, **84**, 132). Before the limit of reduction was reached, it was found that one representation of the lattice corresponded very closely with that of 4 : 4′-dimethyldibenzyl. This is the monoclinic cell shown in Table 1, approximately half the size of the body-centred 4 : 4′-dimethyldibenzyl cell. The indexing of the reflexions of the powder photographs of the two compounds is shown in Table 2.

Allowance being made for the doubling of *a*, and consequently *h*, owing to the body-centring of the dimethyldibenzyl lattice, the strong reflexions on each are seen to correspond. Plane (110) which is strong in the α-polymer is absent from the dimethyldibenzyl because the corresponding plane (210) is a forbidden reflexion owing to body-centring. The two strong planes in the α-polymer (110) and $(20\bar{2})$ give a rough indication of the orientation of the molecular chains, and on this basis an approximate structure can be postulated, as shown in Fig. 1. This is, of course, in no sense an accurate structure determination as would be evident from atomic co-ordinates and lists of structure amplitudes; such would indeed be pressing the

TABLE 2. *Comparison of powder photographs of* 4 : 4′-*dimethyldibenzyl and* α-lin-*poly*-p-*xylylene.*

4 : 4′-Dimethyldibenzyl						α-*lin*-Poly-*p*-xylylene					
hkl	*d* (Å)	*I*	*hkl*	*d* (Å)	*I*	*hkl*	*d* (Å)	*I*	*hkl*	*d* (Å)	*I*
(200)	11·50	m	$(31\bar{2})$	3·48	m	(110)	5·38	s	$(11\bar{2})$	3·64	m
(400)	5·75	m	(312)	3·10	m.s.	(011)	5·06	m	(020)	3·06	w
(011)	5·05	v.s.	$(51\bar{2})$	3·07		(111)	4·42	w	$(12\bar{1})$	2·84	m
(002)	4·51	m	(020)	3·05		$(21\bar{1})$	3·98	s	$(22\bar{1})$	2·64	v.w.
$(20\bar{2})$	4·49		(710)	2·89	m	$(20\bar{2})$	3·95		$(21\bar{2})$	2·41	v.w.
$(41\bar{1})$	4·00	s	$(41\bar{3})$	2·61	m						
$(40\bar{2})$	3·91	s	(613)	2·05	w						
$(11\bar{2})$	3·66	m									

analogy further than the *X*-ray diffraction photographs from this class of substance justify, but it is a reasonable interpretation of the data available, and one which appears to fit all the facts at present known. There is no evidence of monoclinic symmetry; the simplest unit cell is triclinic, but the monoclinic representation is retained in order to show the relation to 4 : 4′-dimethyldibenzyl. It is concluded that the α-form of the polymer crystallises in a very similar manner to 4 : 4′-dimethyldibenzyl and has the same characteristic "stepped" structure.

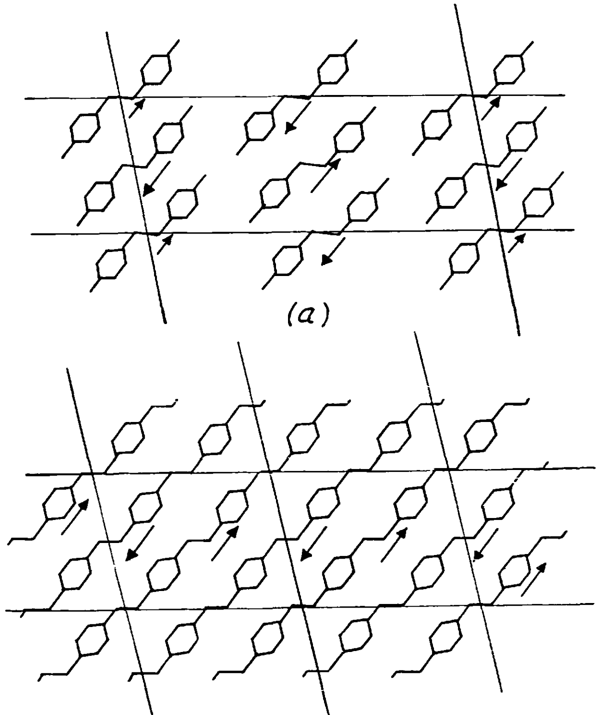


FIG. 1. *Diagrammatic projection of crystal structures of* (*a*) 4 : 4′-*dimethyldibenzyl and* (*b*) α-lin-*poly*-p-*xylylene.*

The arrows indicate the direction of inclination with respect to the plane of the paper.

β lin-*Poly*-p-*xylylene and polyphenylene.* The *X*-ray powder photograph of the β-form of the polymer (sample No. 27) showed, as its outstanding characteristic feature, one strong ring at a spacing of 4·4 Å, together with a number of less intense ones. A powder photograph of diphenyl taken under similar conditions also exhibited a very strong ring at a similar, although not identical, spacing, and it was suggested that the similarity of the two diffraction patterns might be due to a resemblance of molecular packing in the two substances. If this were so, the β-form of the polymer would fall into a crystallographic series of a number of hydrocarbons whose structures are well known (Table 3).

The molecular packing of the first three members of this series is identical with respect to the *a* and *b* axes, *c* being sufficient to accommodate the length of the molecule. The hypothesis for the polymers is that the cross-sectional packing shall again be the same, but that [*c*] should be the length of one repeat unit in the molecular chain. With unit cells derived in this way, the indexing of the photographs is as shown in Table 4.

TABLE 3. *Crystal structures related to* β-lin-*poly*-p-*xylylene.*

Unit-cell dimensions	*a*, Å	*b*, Å	*c*, Å	*β*
Diphenyl	8·11	5·67	9·57	94½°
Terphenyl	8·08	5·60	13·59	92
Quaterphenyl	8·14	5·64	18·4	97
β-*lin*-Poly-*p*-xylylene	8·10	5·25	6·53	95
Polyphenylene	8·10	5·35	4·22	95

TABLE 4. *Comparison of powder photographs of diphenyl, polyphenylene, and* β-lin-*poly*-p-*xylylene.*

Diphenyl			Polyphenylene			*β*-*lin*-Poly-*p*-xylylene		
hkl	*d*, Å	*I*	*hkl*	*d*, Å	*I*	*hkl*	*d*, Å	*I*
(001)	9·53	w	(110)	4·47	s	(001)	6·53	w
(110)	4·64	s	(201)	4·22	w	(10$\bar{1}$)	5·32	w
(11$\bar{1}$)	4·25	m	(10$\bar{1}$)	3·84	w	(101)	4·88	w
(111)	4·10	w	(11$\bar{1}$)	3·12	w	(110)	4·40	s
(20$\bar{1}$)	3·83	m	(020)	2·68	w	(200)	4·05	w
(201)	3·62	w				(111)	3·58	w
(20$\bar{2}$)	3·15	m				(201)	3·32	m
						(102)	2·95	m
						(120)	2·51	w
						(121)	2·32	w
						(22$\bar{1}$)	2·12	w
						(400)	2·02	w
						(22$\bar{2}$)	1·87	w

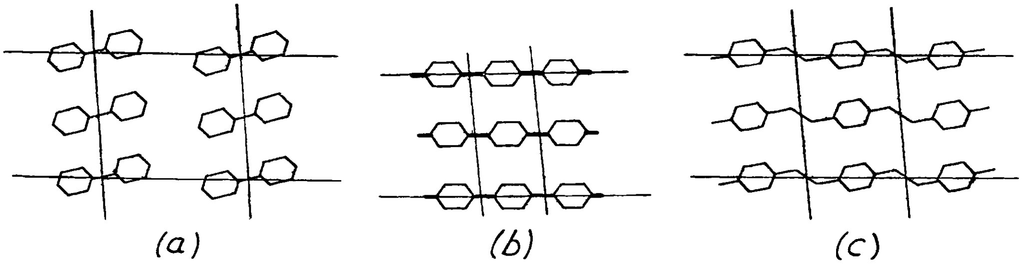
TABLE 5. *Summary of samples and* X-*ray photographs.*

		Intensity of rings :		
Sample No.	Description	inner, 5·3 Å	middle, 4·4 Å	outer, 3·9 Å
1	Pyrolysis	m	m	m
2	Pyrolysis	s	w	s
3	Pyrolysis	m	s	m
4	Wurtz reaction in toluene		*	
5	Wurtz reaction in *p*-xylene	s	w	s
6	Wurtz reaction in *p*-xylene	m	m	m
7	Wurtz reaction in *p*-xylene	m	m	m
8	Wurtz reaction in dioxan	w	s	w
9	Wurtz reaction in dioxan	s	m	s
10	Wurtz reaction in ditolylmethane		*	
11	Sample 7 heated to 200°, quenched	m	m	m
12	Sample 7 heated to 200°, annealed	m	m	m
13	Chloroform extract of Sample 7	s	—	s
14	Sample 13 melted at 240°	s	w	s
15	Sample 13 heated to 300° for 2 min.	s	m	s
16	Sample 7 after extraction by chloroform	m	m	m
17	Sample 13 recryst. from benzyl benzoate	s	—	s
18	Sample 17 melted	m	s	m
19	Chloroform extract of Sample 5	s	w	s
20	Pyrolysis	s	w	s
21	Sample 20 recryst. from benzyl benzoate	—	s	—
22	Pyrolysis	m	s	m
23	Sample 22 recryst. from benzyl benzoate	w	s	w
24	Chloroform extract of Sample 23	s	—	s
25	Sample 24 melted	w	s	w
26	Sample 23 after extraction by chloroform	w	s	w
27	Sample 26 melted	w	s	w
28	Sample 26 melted	w	s	w
29	Sample 26 melted	w	s	w
30	Wurtz in *p*-xylene at low concentration	s	w	s
31	As Sample 30, but higher mol. wt.	s	w	s
32	Phenethylchloride : Friedel–Crafts		*	
33	Polyphenylene butylene		*	
34	Sample 16 heat-treated	—	s	—
35	Sample 16 sintered	—	s	—
36	Polyphenylene		*	
37	Sample 36 melted		*	
38	Polyphenylene	—	s	—

* Amorphous.

On the basis of this indexing, the (110) plane gives the outstandingly strong reflexion in all three cases. This plane depends on the lengths of (*a*) and (*b*), and since these are very similar in all these compounds (Table 3), it would seem that they are determined by the dimensions of the benzene rings and how closely they can pack together. The molecules of diphenyl are known to be planar, and as the lateral dimensions are so similar it is most likely that the molecular chains of the polymers polyphenylene and β-*lin*-poly-*p*-xylylene will be planar also. The molecular arrangements of these three related substances are shown in Fig. 2.

FIG. 2. *Digrammatic projection of crystal structures of* (*a*) *diphenyl,* (*b*) *polyphenylene, and* (*c*) β-lin-*poly*-p-*xylylene.*


(a) (b) (c)

The configuration around the aliphatic carbon atoms in the β-form of the polymer is uncertain. The whole molecular chain is, in all probability, planar, but if the central C–C bond is single, the usual tetrahedral angle may be expected. If there is a loss of hydrogen, as Goldfinger suggests, the angle will be greater than this. Such small differences can scarcely be detected on the basis of unit-cell measurements. It is, however, plain that this type of molecular packing must be correct as it is the only one which accounts for the diffraction pattern.

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