CHEMISTRY OF *p*-XYLYLENE, ITS ANALOGUES, AND POLYMERS

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The development of quantum chemistry created considerable interest in hypothetical compounds, and numerous calculations were made to predict the stabilities and properties of such molecules. *p*-Xylylene (I), a hydrocarbon closely resembling the well-known *p*-benzoquinone, was one species that attracted the attention of many theoreticians. This compound was discussed as early as 1945 by Namiott, Dyatkina, and Syrkin [1] and then again by Diatkina and Syrkin [2] in 1946.

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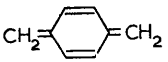
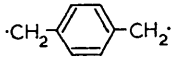
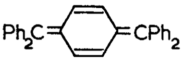




(II)

p-Xylylene is the prototype of a class of hydrocarbons known as Chichibabin hydrocarbons. These compounds can be represented either by a quinonoid structure as exemplified by (I), or by a benzenoid structure possessing two uncoupled electrons, *e.g.* as (II). Compounds corresponding to the latter should behave as diradicals and exhibit paramagnetic properties, whereas the quinonoid structure implies that the compound is diamagnetic. The magnetic properties of the known Chichibabin hydrocarbons, *e.g.*, (III) and (IV), were investigated by Müller and Müller-Rodloff [3]



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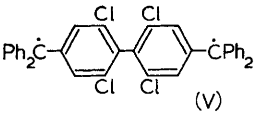

(V)

who proved that these hydrocarbons are diamagnetic, and therefore probably exist in the quinonoid form. Paramagnetic properties have been observed only in those Chichibabin compounds where the planarity of the molecule is rendered impossible by steric hindrance,[4] *e.g.*, (V), and such compounds are best described as diradicals.

The known Chichibabin hydrocarbons (III)–(V) are stabilised by the phenyl groups attached to the terminal carbon atoms. Furthermore, these phenyl groups sterically shield the reactive carbon atoms and thus prevent

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[1] A. Namiott, M. Diatkina, and J. Syrkin, *Compt. rend. Acad. Sci., U.R.S.S.*, 1945, **48**, 285.

[2] M. Diatkina and J. Syrkin, *Acta Physicochim., U.R.S.S.*, 1946, **21**, 23.

[3] Müller and Müller-Rodloff, *Annalen*, 1935, **517**, 134.

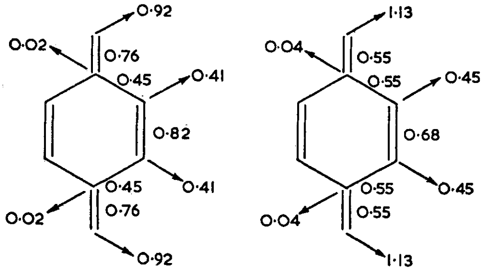
[4] Müller and Tietz, *Ber.*, 1941, **74**, 807.

dimerisation or polymerisation. On the other hand, one would expect that molecules which belong to this class of compound but possess terminal unsubstituted methylene groups would be very reactive and should be easily dimerised or polymerised.

Early theoretical consideration of the electronic structure of these compounds indicated that their triplet states are close to their singlet levels.[1, 2] Later work by Coulson *et al.*,[5] by both the valence method and the molecular-orbital method, fully confirmed the calculations of Syrkin and Diatkina. Moreover, Coulson *et al.*,[5] Daudel,[6] and Pullman *et al.*[7] calculated the bond order and free valence of *p*-xylylene both in the singlet and in the triplet state. The very high free valence computed for the terminal methylene carbons of the molecule in its ground state implies that this species should indeed be highly reactive (see Fig. 1).

FIG. 1

Molecular diagrams of p-*xylylene*



Ground state singlet *Excited state triplet*

It is understandable, therefore, that the preparation and isolation of *p*-xylylene by the classic methods of synthetic chemistry eluded the experimentalist. The first evidence for its existence was obtained in an entirely different type of experiment, namely pyrolysis of *p*-xylene,[8] and subsequent investigations of the pyrolysis of related compounds [9] proved that many analogues of *p*-xylylene can be produced by the same technique.

Formation and Reactions of *p*-Xylylene.—The pyrolysis of toluene [10] and of some related compounds [11] showed that the rupture of the $PhCH_2$–H bond is one of the primary decomposition steps. Benzyl radicals, or their derivatives, are formed by this process, and these eventually dimerise to give dibenzyl or the appropriate derivatives. The pyrolysis of *p*-xylene,[8–10] however, yields, instead of a dimer a polymer which consists, as shown later, of linearly arrayed units (VI). In view of this observation it was

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[5] Coulson, Craig, Maccoll, and Pullman, *Discuss. Faraday Soc.*, 1947, **2**, 36.

[6] Daudel, *ibid.*, p. 69.

[7] Pullman, Berthier, and Pullman, *Bull. Soc. chim. France*, 1948, **15**, 450.

[8] M. Szwarc, *Discuss. Faraday Soc.*, 1947, **2**, 46.

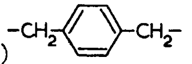
[9] *Idem*, *J. Polymer Sci.*, 1951, **6**, 319.

[10] *Idem*, *J. Chem. Phys.*, 1948, **16**, 128.

[11] M. Szwarc and J. S. Roberts, *ibid.*, p. 609.

suggested[8] that the *p*-xylyl radical (VII), initially formed in the pyrolysis, is converted into *p*-xylylene which eventually polymerises.

(VI)



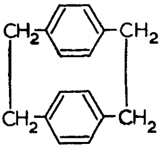
(VII)

It has been found that monomeric *p*-xylylene is remarkably inert in the gaseous phase and that polymerisation occurs only on condensation. Thus, no cloudiness or smoke .was ever perceptible in the gases flowing from the furnace, and when a 3-m. tube, heated to about 80°, separated the furnace from the cooled trap, the polymer was formed readily in the trap but not in the tube. Since the gas required about 0·5 sec. to flow through this long tube clearly no appreciable reaction of *p*-xylylene vapour takes place within this period of time. Still more convincing evidence for the inert nature of *p*-xylylene vapour was obtained in a flow system containing two traps in series, the first being cooled by ice while the second was immersed in acetone-solid carbon dioxide. Polymer was formed in both traps although the tube connecting the traps, which was maintained at room temperature, remained completely clear.[8]

To establish the identity of *p*-xylylene, iodine vapour was introduced into the ice-cooled trap in which the polymer was forming, suitable precautions being taken to prevent the iodine vapour from diffusing into the furnace. The only iodine-containing material identified at the end of the experiment was *p*-xylylene di-iodide thus confirming the existence of *p*-xylylene in the gas stream.[8, 9]

Auspos *et al.*[12] investigated the reactions between *p*-xylylene and various substrates, using the technique described above. Their observations confirmed that the addition of iodine to *p*-xylylene yields *p*-xylylene di-iodide. Furthermore, they showed that elementary chlorine and bromine react similarly, yielding the corresponding dichloride and dibromide. They also obtained products of unknown nature from the pyrolysed vapour with *NN*-diethyl-*p*-nitrosoaniline which behaves as a stable free radical. On the other hand, attempts to isolate the dinitroso- or dinitro-compounds, from *p*-xylylene and nitric oxide or nitrogen dioxide, respectively, failed to give positive results.[12, 13] However, there are indications that the respective nitrogen-containing groups are retained as the end groups of the polymers formed in those experiments.

Further evidence for the existence of *p*-xylylene was obtained from



(VIII)

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[12] Auspos, Hall, Hubbard, Kirk, Schaefgen, and Speck, *J. Polymer Sci.*, 1955, **15**, 9.
[13] Auspos, Burnum, Hall, Hubbard, Kirk, Schaefgen, and Speck, *ibid.*, p. 19.

careful studies of various by-products of the pyrolysis of *p*-xylene. Thus, Brown and Farthing [14–16] extracted from the polymer a cyclic dimer of *p*-xylylene, *i.e.* (VIII), and showed that the benzene rings in this molecule lie parallel one above the other. *p*-Xylylene is the most probable precursor of this compound which is of interest because of the highly strained structure arising from the interaction of the closely located benzene rings and to the shortness of the CH_2-CH_2 bridges [14, 16] (see Fig. 2). At the time of its isolation the compound was new; however, a few years later it was synthesised by Cram [17] who allowed a highly diluted solution of *p*-xylylene dibromide to react with sodium.

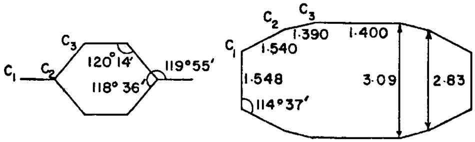


FIG. 2

*Two views of the molecule of di-*p*-xylylene at right angles, showing dimensions and distortion from planarity*

(Reproduced with permission from Brown, *J.*, 1953, 3265)

The very low yield of the cyclic dimer in the pyrolysis of *p*-xylene is attributed to steric strain. On the other hand, the strainless cyclic trimer is formed more readily in the reaction.[12, 18] This compound is identical with the trimer prepared by Baker and his colleagues [19] by means of the Wurtz reaction. Smaller quantities of a cyclic tetramer were also isolated from the products of the pyrolysis.[20] The formation of these cyclic polymers provides further proof of the existence of monomeric *p*-xylylene in the pyrolysed gases.*

The inconvenience of dealing with a short-lived labile species which was present only in the vapour introduced many limitations and difficulties in the early studies of the chemistry of *p*-xylylene. It was a great step forward, therefore, to show [21] that monomeric *p*-xylylene in admixture with *p*-xylene can be kept indefinitely in the solid state at liquid nitrogen temperature. In addition, a method has been developed [21] to produce reasonably stable solutions of *p*-xylylene in various solvents at $-80°$. This was accomplished by carrying the pyrolysed gases, containing *p*-xylylene, over a surface of a suitable and well-stirred solvent cooled to $-80°$.

[14] C. J. Brown and A. C. Farthing, *Nature*, 1949, **164**, 915.

[15] A. C. Farthing, *J.*, 1953, 3261. [16] C. J. Brown, *J.*, 1953, 3265.

[17] D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, 1951, **73**, 5691.

[18] L. Errede, unpublished results.

[19] Baker, McOmie, and Norman, *J.*, 1950, 1142.

[20] L. Errede, unpublished results.

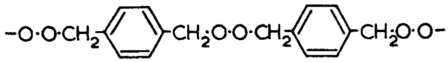
[21] L. Errede and Landrum, *J. Amer. Chem. Soc.*, 1957, **79**, 4952.

* It is not established whether these cyclic polymers are formed in the high-temperature zone or during the cooling of the exit gases. The latter is more probable.

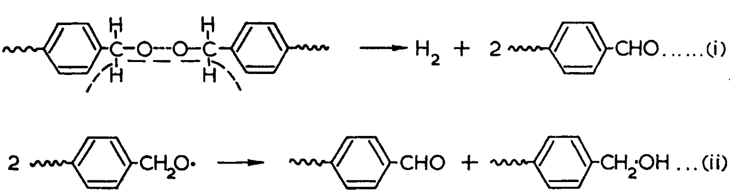
The concentration of *p*-xylylene in such solutions can be determined by withdrawing aliquot portions (using a pre-cooled pipette), mixing them rapidly with standard iodine solution, and titrating the excess of iodine. *p*-Xylylene in solution reacts readily with iodine giving *p*-xylylene di-iodide quantitatively. While both di-iodide and polymer were formed in Szwarc's original experiments where the reactants were mixed in the gaseous phase, no polymer is formed in the reaction in solution in presence of an excess of iodine.

The stability of *p*-xylylene solutions is not increased by the addition of conventional inhibitors. This is not surprising in view of its very high reactivity and of its great tendency to polymerise. Indeed, on heating these solutions polymerisation or copolymerisation takes place spontaneously, and these reactions will be discussed fully in a later section of this review.

Solutions of *p*-xylylene react also with bromine and chlorine [20, 22] giving the corresponding dihalides, and these reactions proceed more quantitatively than the corresponding reactions involving gaseous *p*-xylylene. The reactions with oxygen [23] yields a copolymer of *p*-xylylene and oxygen. If an excess of oxygen is bubbled rapidly through a solution of *p*-xylylene an alternating copolymer



results. This polymeric peroxide is precipitated as a powder, insoluble in organic solvents and in water. It is stable at room temperature but when heated carefully, *e.g.*, by suspending it in hot water, it decomposes into hydrogen, terephthalaldehyde, and to a lesser extent into the products of its disproportionation. Hydrogen evolution was used to measure the rate of the decomposition. The reaction is of first order with a first-order rate constant, $k = 4.10^{15}\exp(-34{,}000/\boldsymbol{RT})$. These observations are consistent with a mechanism involving the random rupture of the O–O bonds as the rate-determining step. This is followed either by the reaction (i) or by the



disproportionation (ii). The difference in activation energies of these two reactions was found to be approximately 13 kcal./mole. The yield of terephthalaldehyde increases at higher temperatures, approaching a maximum of 90% at about 125°. These reactions provide a basis for a novel and simple synthesis of terephthalaldehyde from *p*-xylene.

Peroxide decompositions in which hydrogen is formed have been reported

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[22] L. Errede, unpublished results.

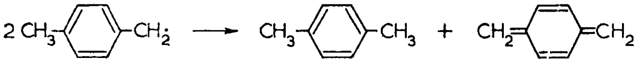
[23] L. Errede and Hopwood, *J. Amer. Chem. Soc.*, 1957, **79**, 6507.

previously. The earliest example is attributed to Blank and Finkelbeiner [24] who studied the decomposition of the peroxide ($HO{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}CH_2{\cdot}OH$) obtained from formaldehyde and hydrogen peroxide. Similar conclusions on the mechanism of this reaction have been advanced by Wieland and Wingler [25] and by Errede and Hopwood.[23] Recently, Mosher and his colleagues [26] studied the decomposition of butyl hydroperoxide which also yields hydrogen, and they proved eventually that the reaction proceeds *via* peroxide $R{\cdot}CH_2{\cdot}O{\cdot}O{\cdot}CHR{\cdot}OH$ which decomposes into hydrogen molecules without forming hydrogen atoms.[27]

Physical Properties of *p*-Xylylene.—The labile nature of *p*-xylylene adds considerable technical difficulty to the determination of its physical properties. The spectra of gaseous *p*-xylylene were studied by Tanaka [28] and by Schaefgen.[29] Absorption maxima were observed at 2520, 2560, 2680, and 2770 Å, suggesting the quinonoid (singlet) structure of the molecule.

Spectroscopic studies in solution have not been carried out, although this is now feasible. Some qualitative data are available [20] on the solubility of *p*-xylylene in solvents at −80°.

Mechanism of Formation of *p*-Xylylene.—*p*-Xylylene formed in the pyrolysis of *p*-xylene is undoubtedly produced from *p*-xylyl radicals. The presence of the latter in the reaction was proved by Farthing [15] and by Schaefgen [29] who isolated from the products of the pyrolysis the linear dimer $Me{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}Me$, the analogue of dibenzyl which is formed in the pyrolysis of toluene by the dimerisation of benzyl radicals. There are two possible reactions which might convert *p*-xylyl radicals into *p*-xylylene, namely disproportionation (iii) and decomposition (iv).



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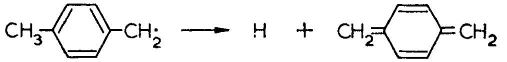

.... (iv)

When the reaction was first described, Szwarc [8] suggested disproportionation as the mode of formation of *p*-xylylene, basing his argument on kinetic observations, which in the light of more recent findings cannot be regarded as an unambiguous proof for this mechanism. The decomposition of *p*-xylyl radicals with the accompanying formation of hydrogen atoms should lead to a chain decomposition of *p*-xylene. On the other hand, no chain reaction is expected if the radicals disproportionate. The kinetics of the pyrolyses of *p*-xylene, *m*-xylene, and toluene are all alike and the last two reactions are definitely not chain decompositions. This similarity in the kinetics was advanced, therefore, as an argument in favour of disproportionation.

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[24] O. Blank and H. Finkelbeiner, *Ber.*, 1898, **31**, 2979.

[25] H. Wieland and A. Wingler, *Annalen*, 1929, **431**, 301.

[26] H. S. Mosher and C. F. Wurster, *J. Amer. Chem. Soc.*, 1955, **77**, 5451.

[27] Wurster, Durham, and Mosher, *ibid.*, 1958, **80**, 327, 332.

[28] Tanaka, *J. Chem. Soc. Japan*, 1955, **75**, 218.

[29] Schaefgen, *J. Polymer Sci.*, 1955, **15**, 230.

Since this kinetic evidence is not entirely conclusive, another approach was sought. It has been shown that the pyrolysis of benzyl bromide [30] and of its analogues [31] in a stream of toluene leads to the formation of benzyl radicals through the following sequence of reactions:

$$\mathrm{Ph{\cdot}CH_2Br \longrightarrow Ph{\cdot}CH_2{\cdot} + Br} \quad ; \quad \mathrm{Ph{\cdot}CH_3 + Br \longrightarrow Ph{\cdot}CH_2{\cdot} + HBr}$$

This pyrolysis proceeds rapidly at temperatures considerably lower than those required for the pyrolysis of *p*-xylene. It appeared, therefore, that the pyrolysis of *p*-xylyl bromide in a stream of *p*-xylene should lead to the formation of two *p*-xylyl radicals for every molecule of hydrogen bromide produced in the reaction. If the radicals disproportionate, then for every molecule of hydrogen bromide produced one *p*-xylylene unit should be formed. However, if these radicals decompose, a chain reaction should ensue and molecular hydrogen and *p*-xylylene should be formed in stoicheiometric proportions. Hence, the unequivocal discrimination between these two modes of reaction appeared to be feasible. This idea was pursued by Levy, Szwarc, and Throssell,[32] who found that at about 500° the pyrolysis of *p*-xylyl bromide proceeds rapidly; however, the products were hydrogen bromide and the linear dimer of *p*-xylyl radicals, *i.e.*, $\mathrm{Me{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}Me}$, and neither hydrogen nor polymer was formed. This means that under the conditions of their experiments *p*-xylyl radicals neither disproportionate nor decompose, but dimerise instead.

The explanation of these results was provided by Schaefgen.[29] In a system containing radicals dimerisation and disproportionation proceed simultaneously. Dimerisation requires a very low activation energy, if any. It might require, however, a third body to remove the excess of energy, particularly if the reaction proceeds at high temperature. Furthermore, at sufficiently high temperature and low pressure the reaction is reversed owing to the shift in the equilibrium position. On the other hand, disproportionation is essentially an irreversible reaction which, in this particular case, may require a not negligible activation energy. It should also be pointed out that the latter reaction does not require the presence of a third body. Hence, higher temperature, and lower partial pressure and total pressure favour disproportionation, while dimerisation should be the predominant reaction at lower temperature and higher pressure.* This was further substantiated by studying the ratio of the linear dimer to the polymer formed in the pyrolysis.

Numerous observations seem to confirm this basic picture. Various attempts were made to produce *p*-xylylene at lower temperatures under homogeneous conditions. All, however, were unsuccessful. Roper and Szwarc [33] tried to produce *p*-xylyl radicals in the low-temperature pyrolysis

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[30] Szwarc, Sehon, and Ghosh, *J. Chem. Phys.*, 1950, **18**, 1142.

[31] Leigh, Sehon, and Szwarc, *Proc. Roy. Soc.*, 1951, *A*, **209**, 97.

[32] Levy, Szwarc, and Throssell, *J. Chem. Phys.*, 1954, **22**, 1621.

[33] Roper and Szwarc, unpublished results.

* See in this connection Corley *et al.*, *J. Polymer Sci.*, 1954, **13**, 137, who showed that the conversion of *p*-xylene into the polymer is affected by the temperature of pyrolysis, pressure of the hydrocarbon and time of contact.

of *p*-xylene by introducing into the furnace small amounts of bromine or *tert.*-butyl peroxide. Although radicals are formed under these conditions, no formation of the polymer of *p*-xylylene was observed. Schaefgen [29] tried similar experiments using ethylene oxide as a source of radicals, and again the results were negative. This shows clearly that in a homogeneous gas reaction a high temperature is imperative for the conversion of *p*-xylyl radicals into *p*-xylylene.

At the same time it was found that an increase in total pressure decreases the yield of the polymer of *p*-xylylene. Szwarc [34] obtained a negligible yield of the polymer from the pyrolysis of *p*-xylene (4 mm. of mercury) in a stream of nitrogen (400 mm. of mercury). Similarly, the yield of the polymer was decreased when the pyrolysis was carried out in stream of steam at atmospheric pressure, although better results were obtained with steam at lower pressure.[33] On the other hand, the polymer yield could be improved if small amounts of chlorine or bromine were added to *p*-xylene and the pyrolysis was carried out at sufficiently high temperature and low pressure.[29]

The final proof for the disproportionation of *p*-xylyl radicals was provided by Schaefgen's studies [29] of the pyrolysis of the linear dimer $Me{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}Me$. He obtained both *p*-xylene and poly-*p*-xylylene; the formation of the former is a conclusive evidence for the disproportionation mechanism.

Although it appears to be well established that *p*-xylylene is formed through disproportionation of *p*-xylyl radicals at conventional temperatures of the pyrolysis (*i.e.*, 800—1000°), at very high temperatures and very low pressures (10^{-5} mm. or less) the decomposition of *p*-xylyl radicals into hydrogen atoms and *p*-xylylene can be observed. Such observations were reported by Lossing and his colleagues [35] who studied the pyrolysis of the xylenes at very high temperatures mass-spectrographically. While C_8H_8 was formed from *p*- or *o*-xylene, only $C_8H_9^{\cdot}$ was formed from *m*-xylene.

Many attempts have been made to find a suitable catalyst for the dehydrogenation of *p*-xylene to *p*-xylylene, but conventional dehydrogenation catalysts have proved unsuitable. The decomposition of *p*-xylene vapour on hot metal wires was also investigated and in many cases the formation of *p*-xylylene was observed. However, this method did not show any advantage over flow pyrolysis in a hot tube.[12]

p-Xylylene is probably formed as an intermediate in a few reactions other than pyrolysis, for example, the decomposition of the azide $N_3{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}N_3$ and the Hofmann degradation [36] of the base $Me{\cdot}C_6H_4{\cdot}CH_2{\cdot}NMe_3{\cdot}OH$. The latter takes place at 60—200° in a vacuum and proceeds according to the equation

$$n\{CH_3{\cdot}C_6H_4{\cdot}CH_2N(CH_3)_3^+\ OH^-\} \longrightarrow [CH_2{\cdot}C_6H_4{\cdot}CH_2]_n + nN(CH_3)_3 + nH_2O$$

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[34] Szwarc, unpublished results.

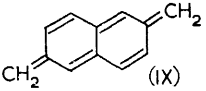
[35] Farmer, Marsden, and Lossing, *J. Chem. Phys.*, 1955, **23**, 403.

[36] Fawcett, U.S.P. 2,757,146/1956.

Formation of Analogues of *p*-Xylylene.—Pyrolysis has also proved most useful for the production of other compounds belonging to the same class as *p*-xylylene. Pyrolysis of *p*-xylene derivatives like *pseudo*cumene,* durene, *iso*durene, hexamethylbenzene, 2-phenyl-*p*-xylene, 2-chloro-*p*-xylene, 2 : 5-dichloro-*p*-xylene, 2-fluoro-*p*-xylene, and 2 : 5-difluoro-*p*-xylene leads to the formation of the corresponding substituted *p*-xylylenes, and eventually to the formation of the respective polymers.[9, 10, 37] The identity of the monomeric species was proved by analysing the structure of the polymers formed, and in a few instances by trapping the monomeric species with iodine and isolating the corresponding di-iodides.[9, 21]

It was found also that some other compounds resembling *p*-xylene yield on pyrolysis analogues of *p*-xylylene.[9] Thus, the respective polymers were formed from 1 : 4-dimethylnaphthalene, 2 : 5-dimethylpyrazine and 5 : 8-dimethylquinoline. The polymer formed from 2 : 5-dimethylpyrazine was particularly interesting, in that although it was insoluble in organic solvents at moderate temperatures, it was easily dissolved in warm dilute aqueous hydrochloric acid.

Some unsuccessful attempts were made to produce other compounds of the *p*-xylylene class. Pyrolysis of 2 : 6-dimethylnaphthalene led to the linear dimer [9] instead of the expected compound (IX). Pyrolysis of 4 : 4′-dimethyldiphenyl and 9 : 10-dimethylanthracene gave unidentified products,[9] and further study is needed in order to interpret the results so far obtained. Attempts to obtain species like (X) or (XI) from the pyrolyses of *p*-cresol and *p*-toluidine were also unsuccessful.



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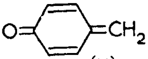

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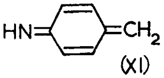
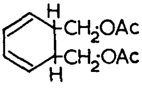


(XI)

The conventional pyrolysis of *o*-xylene, which was expected to yield *o*-xylylene, has been extensively investigated. Although none of the isolated products indicated the existence of *o*-xylylene [9] there is reason to believe that it might be formed in the reaction. Indeed, at very high temperature and at extremely low pressure the respective monomer, C_8H_8, was observed by Lossing *et al.*[35] An important side reaction in the pyrolysis of *o*-xylene involves apparently a rupture of carbon–carbon bonds since in many experiments anthracene and its methyl homologues were isolated.

Bailey [38] succeeded in producing poly-*o*-xylylene by pyrolysing the



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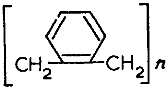

(XIII)

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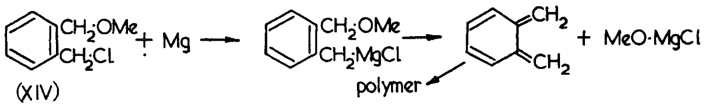
[37] Roper, U.S.P. 2,798,052/1957.

[38] See *e.g.* J. Rosenberg, Ph.D. Thesis, Wayne University, 1951.

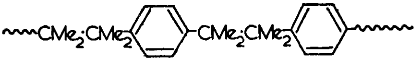
* Szwarc [6] reported that no polymer was formed from *pseudo*cumene. Later it was found that the *pseudo*cumene used was contaminated with a considerable amount of other isomers (having the same b.p.) and when experiments were repeated with the pure substance the results were positive.

diacetate (XII). The reaction probably proceeds in the usual way, yielding *o*-xylylene and acetic acid, and the former species then polymerises rapidly to (XIII). The polymer produced resembles poly-*p*-xylylene to some extent. A similar product was obtained by action of magnesium on the chloride (XIV). This reaction was investigated by Mann and Stewart [39] who suggested the following sequence of steps:



The same workers found that the *para*-isomer reacted similarly producing a *p*-xylylene polymer of low molecular weight.

Interesting work was carried out recently by Korschak ; [39a] he treated *p*-di*iso*propylbenzene with *tert.*-butyl hydroperoxide. The primary radicals abstract the tertiary hydrogen atoms of the hydrocarbon, and the recombination of the secondary radicals leads to poly-*p*-xylylene methylated in the side chain.



Because of the low temperature there are no complicating side reactions and one obtains linear, soluble, high-melting products which can be moulded, cast, or spun.*

Mechanism of Polymerisation of *p*-Xylylene.—Condensation of gaseous *p*-xylylene leads to a rapid polymerisation, and eventually a tough, coherent, and continuous film is deposited on the walls of the condenser. This film is transparent in thin but opaque or white in thick layers. Apparently, the reaction is started by the *p*-xylylene units' combining into large diradicals, *e.g.*,

$$-CH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2-$$

which continue their growth at both ends. The initiation seems to be spontaneous although it is remarkable that it does not occur in the gas but only in the condensed phase.

This lack of polymerisation in the gas merits further discussion. The first step leading to the formation of the polymer is probably the dimerisation

$$2\ CH_2{=}C_6H_4{=}CH_2 \longrightarrow -CH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2-$$

The central CH_2–CH_2 bond of such a dimer is extremely weak, since considerable binding energy is lost when two C=C double bonds are opened and form a C–C single bond leaving two electrons uncoupled. Hence, such a diradical should readily revert to the more stable xylylene units. On the

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[39] Mann and Stewart, *J.*, 1954, 2826.

[39a] Personel communication from Professor H. Mark.

* The consumption of radicals in this reaction is exceedingly high since it is not a chain process.

other hand, if four units are combined into a linear tetrameric diradical (see the formula above), then a comparatively stable species is produced and the dissociation energy of its central CH_2–CH_2 bond is probably " normal ". Rupture of this central CH_2–CH_2 bond in the tetramer produces two " true " diradicals from one diradical, and consequently no additional driving force is available to facilitate the process.* Hence, the critical stage in the polymerisation is overcome when three or four units are combined. Since a simultaneous interaction of three or four units is highly improbable in the gas but quite probable in the condensed phase, the nuclei for the polymerisation are expected to be formed readily in the condensed phase only.

There is still another factor which makes polymerisation in the condensed phase more probable than reaction in the gas. Most probably the polymerisation of *p*-xylylene involves diradicals. It was pointed out by Haward [40] and by Zimm [41] that cyclisation competes efficiently with propagation in a diradical polymerisation, particularly in the early stages of the growth when the chain is only 3 or 4 units long. In the gas, the concentration of monomer is low and therefore cyclisation is much more probable than propagation. On the other hand, the situation is probably reversed in the condensed phase, and, moreover, crystallisation of the polymer hinders the cyclisation considerably by imposing restrictions on the motion of the segments.

The creation of polymerisation nuclei is obviously a slower process than the propagation. Consequently, the polymer grows very rapidly from the initiating centres, a process favouring the formation of dendrites often observed in the reaction. However, if the nuclei are formed uniformly a homogeneous film is produced. For example, if an object to be coated with *p*-xylylene polymer is rotated in the stream of gas flowing out of the pyrolysis zone, a very uniform homogeneous film is formed.† Such films act as excellent protective materials and adhere well to the various surfaces.

Investigation conducted by the Polaroid Corporation led to the interesting observation that a laminated film is produced if the pyrolysis is interrupted and then continued again. Apparently, the growing active centres are terminated during the interruption and then on resumption of the process a new film begins to form on the surface of the old one. Most probably the termination of the growing molecules breaks the interlocking process which is responsible for the formation of a cohesive and homogeneous film.

The temperature of condensation of *p*-xylylene vapour is obviously a factor which determines the physical characteristic of the resulting polymeric film. This point was investigated by carrying out the reaction at different

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[40] Haward, *Trans. Faraday Soc.*, 1950, **46**, 204.

[41] Zimm and Bragg, *J. Polymer Sci.*, 1952, **9**, 476.

* In any *n*-meric diradical the weakest bond involves the terminal unit. In a trimeric diradical this bond would be stronger than the bond in the dimer although weaker than the central bond of tetramer.

† These experiments were performed in the M. W. Kellogg Co. laboratories.

condensation temperatures (0°, 20°, 40° and 80°). The results suggest that the molecular weight of the polymer formed, or its degree of cross-linking, increases with decreasing temperature of polymerisation.[33] On the other hand, the nature of the surface on which the condensation takes place appears not to be critical. To quote an extreme case, films of poly-*p*-xylylene were produced by carrying the vapour of the monomer over the surface of an organic liquid. The polymer formed a crust on the liquid and its properties and structure seemed to be identical with those of films formed on solid surfaces.[33]

The nature of the termination reaction in *p*-xylylene polymerisation is not known. If the growing species are diradicals, then termination cannot occur by coupling which would merely double the molecular weight of the active diradical species. Furthermore, disproportionation is impossible in polymerisation of *p*-xylylene since no terminal double bond can be formed. Hence, cyclisation seems to be the only possibility for termination involving the growing chains. Obviously this reaction is responsible for the formation of the cyclic trimers and tetramers, but it is highly improbable for production of material of high molecular weight. Nevertheless, the formation of laminated films is an obvious indication that the growing ends are somehow terminated or " buried " in the polymeric material.* The possibility of termination by impurities which act as monoradicals also should be taken into consideration, although experiments designed to check this hypothesis have not been conclusive.

Development of the technique of producing solutions of *p*-xylylene has given impetus to the study of the kinetics of *p*-xylylene polymerisation. Experiments by Errede [22] indicated that the reaction is of first order with respect to monomer and its rate is proportional to the number of existing " nuclei ". The latter are formed during the preparation of the solution and their number seems to remain constant when the solution is left undisturbed. However, if a " hot " object is immersed in the solution, *e.g.*, a pipette kept at room temperature (the polymerisation was studied at temperatures ranging from —80° to —40°), the number of nuclei apparently increases and the polymerisation is suddenly enhanced (see Fig. 3), although its new rate again obeys first-order kinetics with respect to monomer concentration. It appears, therefore, that under these conditions the polymerisation does not involve termination, each growing chain continuing its growth indefinitely.

No experimental data exist to show whether any chain-transfer process takes place in the polymerisation of *p*-xylylene. Probably the chain-transfer rate constants of poly-*p*-xylyl radicals are not significantly different from that of polystyryl radicals. However, since the propagation rate constant is obviously much greater in the *p*-xylylene system as compared with the styrene system, the corresponding chain transfer constants (k_{tr}/k_p) should be significantly smaller in *p*-xylylene polymerisation.

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* It was reported by Corley *et al.*,[44] that the concentration of free radicals, if they were indeed present in the solid polymer, is less than 10^{-10} mole/c.c., *i.e.*, less than the minimum amount detectable by electron spin resonance.

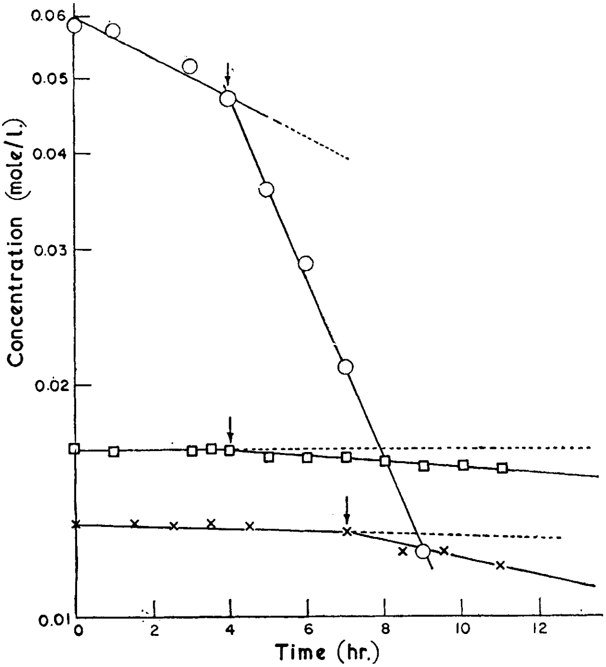
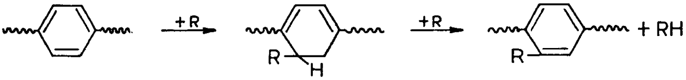


FIG. 3

Unimolecular plot representing the kinetics of polymerisation of p*-xylylene. The arrows denote the time when a warm object was introduced into solution, causing a sudden increase in the number of growing centres.*

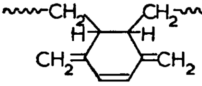
There are some indications, discussed in the last part of this review, that the *p*-xylylene polymers are crosslinked or branched. These linkages might arise from a radical-addition reaction, followed by a hydrogen abstraction:



In these equations R itself is a polymeric radical. It is to be expected that the sequence of the two reactions would be favoured by lower temperature of the polymerisation, and indeed, the decreasing solubility of the polymer formed at lower temperature of polymerisation, *i.e.*, at lower temperature of condensation, can be construed as evidence for an increasing number of crosslinks or branches.[9] Actually, a polymer isolated from traps cooled by liquid nitrogen appears to be completely insoluble,[12] and this might indicate a high proportion of crosslinks formed at this temperature.

The suggested scheme of addition of radicals to the benzene nucleus might be criticised on the ground that similar reactions can be envisaged in polymerisation of styrene although no crosslinking or branching of this nature has been discovered in polystyrene. However, the styryl radical is more shielded than the radical responsible for the polymerisation of *p*-xylylene and this may account for the difference in their behaviour.

An alternative explanation of the formation of the crosslinks or branches involves an assumption that in the propagation reaction *p*-xylylene adds in two ways: the normal addition to the methylene group, and the very infrequent addition to the benzene nucleus. The latter leads to the formation of the unit (XV) in the polymer chain, which in turn participates in the branching or crosslinking process.


(XV)

Copolymerisation.—Numerous attempts to copolymerise *p*-xylylene with various conventional monomers were mostly unsuccessful. Thus, Roper and Szwarc [33] tried to condense *p*-xylylene with styrene or butadiene, or to bubble *p*-xylylene vapour through a solution containing these monomers. In all these experiments poly-*p*-xylylene was the only polymeric material formed in the reaction. Similar techniques had been used by Kaufman *et al.*,[43] Corley *et al.*,[44] and Auspos *et al.*,[13] and only the last workers reported any success. They were able to copolymerise maleic anhydride and chloroprene with *p*-xylylene.

On the other hand, *p*-xylylene copolymerises with other monomers of the same class, *e.g.*, with monomers derived from *pseudo*cumene, chloro-*p*-xylene, and 2 : 5-dimethylpyrazine.[33] The last example is particularly interesting since the polymer of 2 : 5-dimethylpyrazine is soluble in aqueous hydrochloric acid, and thus extraction of the polymeric product with hydrochloric acid should distinguish between the true copolymer and a mixture of two homopolymers. That no polymer could be so extracted indicates that the investigated material was indeed a copolymer.* Further evidence that copolymerisation occurred is provided by studies of the *X*-ray diffraction patterns of the product.[13, 33]

Two techniques were used for the preparation of copolymers. In one a mixture of two precursors, say *p*-xylene and *pseudo*cumene, was pyrolysed, and the product condensed; in the other each precursor was pyrolysed in a different furnace and the gaseous products mixed and condensed together. The advantages of the second method are obvious, although technical difficulties encountered in this type of process are much greater. Recently, these copolymers were prepared by mixing the desired proportion of the respective monomers kept at low temperature in solution and then initiating the polymerisation by raising the temperature.[21]

Structure of Poly-*p*-xylylene Polymers.—Poly-*p*-xylylene seems to be a linear polymer of units (VI). Its oxidation by chromic acid was reported

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* One may argue, however, that the investigated material contained two homopolymers entangled to such an extent that their separation was impossible. We believe that such entanglement could slow down the extraction process, or make it less efficient, but would not prevent it entirely.

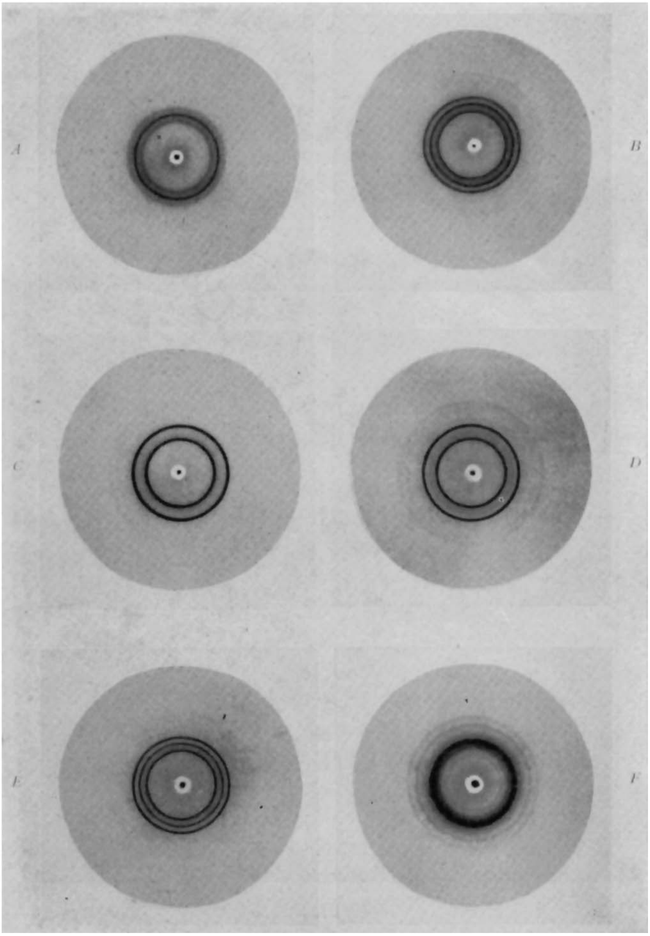

FIG. 4

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

A, Pyrolysis polymer
B, Wurtz polymer
C, α-form of polymer
D, α + small amount of β
E, α + β, approx. equal amounts
F, β-form of polymer

(Reproduced with permission from Brown and Farthing, *J.*, 1953, 3270)

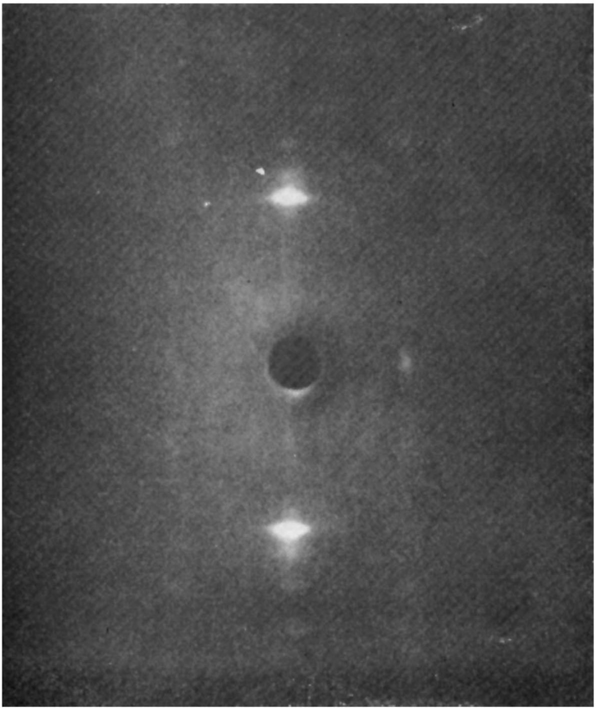

FIG. 5

X-Ray fibre diagram of poly-p-*xylylene*

(Figs. 5 and 6 are reproduced with permission from Kaufman, Mark, and Mesrobian, *J. Polymer Sci.*, 1954, **13**, 3.)

by Brown and Farthing[42] who isolated terephthalic acid as a major product, and detected only a trace (about 0·1%) of *iso*phthalic acid. The ultraviolet and the infrared spectra reveal only this grouping which is consistent with the simple linear structure. Furthermore, the *X*-ray diffraction patterns[9, 13, 42, 43] indicate a highly crystalline structure which excludes the possibility of many irregular branches or frequent cross-links in the polymeric composition.

The crystalline structure of poly-*p*-xylylene was thoroughly investigated by Brown and Farthing.[42] They were the first to point out the existence of two modifications, classified by them as the α- and the β-form. The *X*-ray pattern of the α-form shows two strong and sharp diffraction rings corresponding to the spacings of 4·0 and 5·2 Å (see Table 1), while the β-modification is characterised by a ring corresponding to the spacing of 4·4 Å. These workers suggested also that the configuration of the α-form is similar to that of the molecule of 4 : 4′-dimethyldibenzyl—the rings lie parallel to each other in the same molecule, however they are not coplanar but arranged stepwise. On the other hand, in the β-form, the benzene rings are both parallel and coplanar, as in the molecule of diphenyl.

Brown and Farthing also observed that the α-form was converted into the β-form by heat, preferentially above the melting point. This process seems to be irreversible, and it was suggested by these workers that it might involve a chemical change, namely dehydrogenation of poly-*p*-xylylene into a linear polystilbene in which each benzene ring would possess a quinonoid structure. Such structures were suggested by Goldfinger[45] for polyphenylene. In our opinion the chemical reaction suggested by Brown and Farthing does not take place under mild conditions although it might occur during pyrolysis of the polymer. Hence, we consider the β-modification to be polymorphic with the α-form.

Studies by Brown and his colleagues also showed a similarity between the crystal structures of linear poly-*p*-xylylene obtained by pyrolysis and of the polymers obtained by the Wurtz reaction from *p*-xylylene dichloride. The proportions of α- and β-modification in the polymer depend on the method of preparation and are affected by the subsequent treatment of the sample. Fig. 4, reproduced from the paper by Brown and Farthing, illustrates the observed changes in the *X*-ray diffraction patterns of polymers obtained under different conditions.

X-Ray studies of polymers obtained from other monomers of the *p*-xylylene class were reported by Szwarc[9] and by Kaufman, Mark, and Mesrobian.[43] Their results are also included in Table 1. Moreover, Kaufman, Mark, and Mesrobian studied the structure of fibres obtained by stretching samples of poly-*p*-xylylene, poly*pseudo*cumene and polydurene. The high melting points of these polymers made it necessary to stretch the fibres at temperatures above 150°. The phenomenon of "necking down",

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[42] Brown and Farthing, *J.*, 1953, 3270.

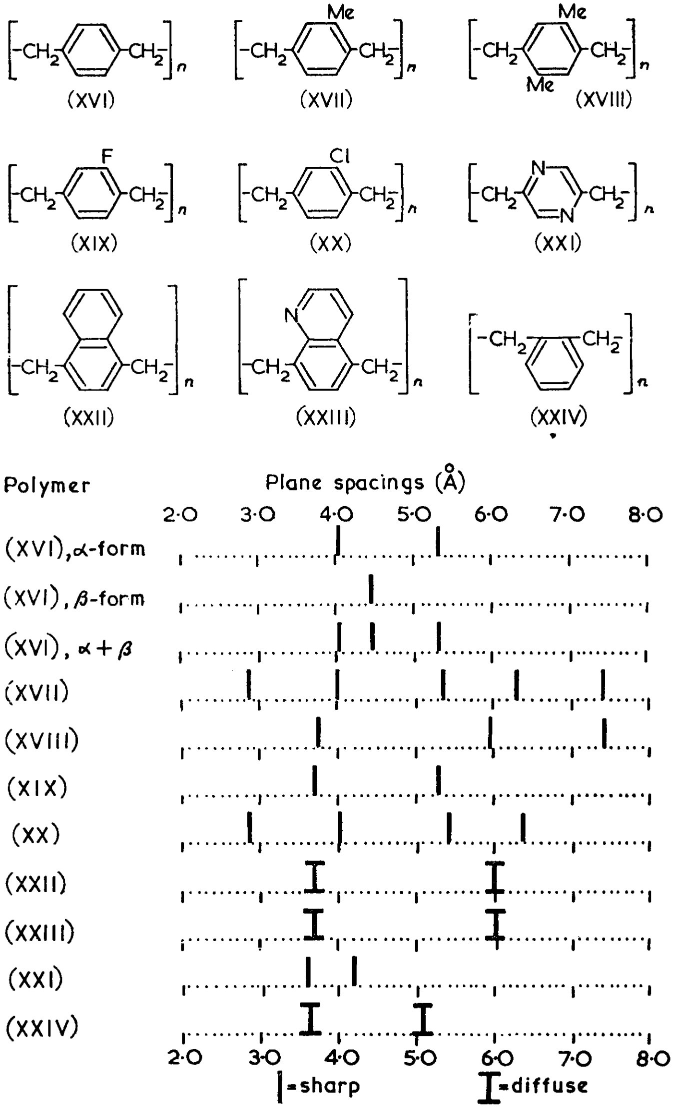
[43] Kaufman, Mark, and Mesrobian, *J. Polymer Sci.*, 1954, **13**, 3.

[44] Corley, Haas, Kane, and Livingstone, *ibid.*, p. 137.

[45] Goldfinger, *ibid.*, 1949, **4**, 93.

frequently associated with the cold drawing of crystalline polymers, was noted during the elongation of poly-*p*-xylylene films. This phenomenon is typical of polymers of high molecular weight and is therefore further evidence that poly-*p*-xylylene obtained by pyrolysis has a high molecular weight.

TABLE 1. X-*Ray diffraction patterns of various polyxylylenes*



Evidence for the formation of a well-oriented fibre is apparent from the *X*-ray fibre diagrams shown in Fig. 5. The repeat distance calculated from the diagram is 6·55 Å, corresponding to an ordered sequence of *p*-xylylene units (see Fig. 6). The calculated value for such a configuration is 6·52 Å, while a repeat distance of 6·37 Å was calculated for the disordered configuration shown also in Fig. 6. The former repeat distance was found also for the oriented poly*pseudo*cumene and polydurene.[43]

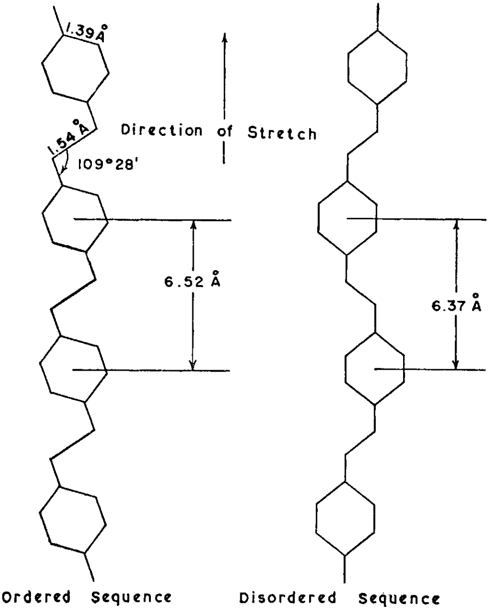


FIG. 6

Schematic representation of the arrangement of p*-xylylene chains under stretch.*

Determination of the molecular weight of poly-*p*-xylylene presents technical difficulties because of its insolubility and high melting point. In work carried out at the Du Pont laboratories over 250 chemicals were tried as solvents for these polymers;[13] the best were the chlorinated diphenyls, benzyl benzoate, α-methylbenzylphenols, and the terphenyls. The polymer does not dissolve, however, below 250°, and precipitates again if the temperature of the solution falls below 200°.[9, 13, 43] Some degradation probably takes place during dissolution, this degradation apparently continuing if the solution is kept at these high temperatures.[13]

Some observations by Kaufman, Mark, and Mesrobian[43] should now be mentioned. These workers claim that poly-*p*-xylylene dissolves only if oxygen is present during the heating, and when this was rigorously excluded a sample of the polymer did not dissolve when heated for two days with a suitable solvent at 250°. They concluded, therefore, that some cross-links exist in the polymer and that oxygen accelerates their rupture.

The viscosity of diluted solutions of poly-*p*-xylylene was measured by Auspos *et al.*[13] who developed a viscosometer suitable for work at high temperatures (around 300°). They found that all "soluble" polymers, *i.e.*, materials which could be dissolved at 302° in less than 5 minutes, had low inherent viscosity. The viscosity increased, however, as the rate of solution of the polymers decreased. The relevant results are collected in Table 2 and indicate that the molecular weight of some samples is at least 20,000. Similar results were obtained by Kaufman *et al.*[43] who determined the molecular weight of a soluble fraction of poly*pseudo*cumene by measuring the osmotic pressure of its solution in chloroform ($\bar{M}_n \sim 24{,}000$).

Further evidence for the high molecular weight of poly-*p*-xylylene is provided by Kaufman, Mark, and Mesrobian,[43] namely its ability to be stretched to give highly oriented fibres, the swelling in water of sulphonated poly-*p*-xylylene, and the nondiffusibility of the polymer solution through a sintered-glass membrane, which allegedly prevents diffusion of polymers of molecular weight above 20,000. In connection with the ability of poly-*p*-xylylene to yield fibres, it is generally recognised among fibre chemists that crystalline polymers must have a minimum molecular weight in order to exhibit spinnability and drawing capacity; for polyesters this is above 8000.

TABLE 2. *Viscosities of poly-*p*-xylylene*

Preparation	Time to soln., min.	Concn., g./100 c.c.	ln η_r/c
Pyrolysis	40	0·768	0·27
Pyrolysis	25	0·673	0·325
Pyrolysis [a]	6	0·504	0·153
Wurtz reaction [b]	10 [e]	0·838	0·095
Wurtz reaction [c]	11 [e]	0·865	0·15
Pyrolysis	5	0·261	0·35
Pyrolysis [d]	30	0·618	0·73

[a] Polymer is drawable at 150° before dissolving.

[b] Reaction at −30°. Polymer melts at 390–400° when heated rapidly; degradation quite slow at 259°.

[c] Reaction at −60°. Viscosity at 259° (more soluble polymer).

[d] Swollen gel present after 5 min. Dissolution after 30 min., the solution becoming amber.

[e] At 259°.

There are several indications that the network chains in (unstretched) poly-*p*-xylylene are deposited on the walls of the condenser in some unique manner. First, the transparent polymer film exhibits negative birefringence when viewed edge-on,[43, 44] and, secondly, the sulphonated polymers swell anisotropically.[43] Since the sulphonated polymer exhibits pronounced swelling in length and width but not in thickness, it might be assumed that the network chains are lying approximately parallel to the flat face of the polymer film. Attempts to define this arrangement more exactly by *X*-ray diffraction were unsuccessful; however, it has been reported that in the detection of chain orientation *X*-ray measurements are less sensitive than optical birefringence measurements or anisotropic swelling behaviour.[46]

A very pronounced birefringence develops in films of poly-*p*-xylylene during stretching. The stretching birefringence constant is positive and very high,[44] namely + 0·2, while considerably lower values characterise other polymeric films [*e.g.*, poly (vinylacetate) + 0·035, "Ethocel" + 0·016, cellulose acetate + 0·005, poly(methyl methacrylate) − 0·001 and polystyrene − 0·024 to − 0·031]. At the same time, films of poly-*p*-xylylene exhibit a positive and very high Brewster constant[44] of $+ 75.10^{-13}$ cm.^{2}/dyne (the corresponding value for polystyrene is + 10 in the same units). The high and positive birefringence stretching constant and Brewster constant make poly-*p*-xylylene a very good photoelastic material.

Intractability of poly-*p*-xylylene polymers is frequently attributed to the combination of crystallinity and cross-linking. It is difficult to separate the two effects for no amorphous polymer has ever been obtained—even the polymer produced at − 190° shows crystallinity.[13] Presence of *ortho*-substituents in the repeating units only slightly lessens the crystallinity.

The polymer does not dissolve until the temperature of the solution approaches that of the crystalline melting point.[13] This observation led many to believe that the intractable nature of the polymer is due solely to its extreme crystallinity. However, this property alone cannot explain the following observations: (1) Although *ortho*-substituents somewhat lower the crystallinity of the polymer they do not lower the flow point; for example, the melting point of crystallites of poly-*p*-xylylene and poly*pseudo*-cumene are 400° and 250°, respectively, while their flow points are at about 400°.[13] (2) Although the swellability is increased by this structural modification, the solubility is hardly affected.[13] In fact, the poly-(2-phenyl-*p*-xylylene), the least crystalline of this class of polymer, is even less soluble than poly-*p*-xylylene.[13] One is forced, therefore, to assume that the polymer is cross-linked in addition to being crystalline, although neither infrared spectra nor *X*-ray examination indicates the presence of cross-links. However, it was pointed out by Powers and Austin[47] that these analytical devices are not sensitive enough to detect the presence of cross-links in amounts that still could impart marked effects on the physical properties.

Poly-*p*-xylylene undergoes many of the reactions typical of *p*-xylene itself, although the rate is markedly retarded because of the polymer's insolubility. The polymer is not attacked appreciably[9] by concentrated sulphuric acid at 150°. Sulphonation occurs readily however in the presence of traces of silver ion,[13, 43, 44] and the product contains one sulphonic acid group per benzene ring.[43] The sulphonated product swells about 100-fold in water and about 400-fold in dilute aqueous base without dissolving.[43] The swelling is anisotropic, that is the sulphonated film expends in length and width but not in thickness.

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[46] K. H. Meyer, " Natural and Synthetic High Polymers ", 2nd edn., Interscience Publ., New York, 1950, p. 89.

[47] Powers and Austin, *J. Polymer Sci.*, 1951, **6**, 775.

The polymer can be chlorinated by treatment with sulphuryl chloride in pyridine in the presence of ultraviolet light.[44] Chlorination occurs predominantly at the ethylene groups although some aromatic substitution and chlorinolysis also take place. The final product again displays anisotropic swelling and it contains 2—4 chlorine atoms per *p*-xylylene unit. The chlorinated product is fairly soluble in low-boiling solvents, such as toluene and xylene, because of chain scission. Clear pale yellow polymeric films are deposited when the solutions are evaporated to dryness. These films are reported [44] to be tough and flexible and can be cold-drawn. The product melts with darkening at about 200° The once-solubilised chlorinated polymer is amorphous and is readily soluble in low-boiling solvent such as dioxan or benzene.

Nitration occurs [13] when the polymer is immersed in concentrated nitric acid at 50° for a prolonged period giving poly(dinitro-*p*-xylylene). This material is a high explosive with the sensitivity of pentaerythritol tetranitrate and with the power of trinitrotoluene. The nitrated product is soluble in nitrobenzene and in *cyclo*hexanone but films cast from these solutions are of very poor quality.[13]

Poly-*p*-xylylene is unaffected by prolonged treatment with boiling 5N-nitric acid.[42] About one half of the available polymer is oxidised, however, by 24 hours' treatment with excess of chromic oxide in boiling acetic acid,[42] yielding terephthalic acid as the main product. The polymer is slowly oxidised at high temperature by atmospheric oxygen and the material burns fiercely when ignited.[13]

Degradation of the polymer takes place on melting at about 400°. It was expected that the polymer would decompose into monomeric units, *i.e.*, *p*-xylylene molecules, which would re-polymerise on condensation. Hence, a pseudosublimation of the polymer was attempted by heating it in one end of an evacuated tube cooled at the other end by solid carbon dioxide. The experiment failed, however, and closer examination of the results showed that dehydrogenation occurred readily.[34] Madorsky and Strauss [48] have studied the decomposition of poly-*p*-xylylene in a vacuum and observed random chain scission at 415°. Benzene, toluene, xylene, *p*-methylstyrene, and *p*-ethyltoluene were identified as volatile products of the decomposition. The activation energy was reported to be 76 kcal./mole. These workers compared the thermal stability of numerous polymers and found poly-*p*-xylylene to be second to " Teflon " in this respect.

We thank the National Science Foundation for their support. We also express our appreciation to the late Dr. F. Kind, Dr. H. Steiner, Dr. W. E. Hanford, and Dr. J. W. Copenhaver for encouragement and interest.

[48] Madorsky and Strauss, *J. Res. Nat. Bur. Stand.*, 1955, **55**, 223.