Translated from *Uspekhi Khimii*, 45, 1842-1869 (1976) U.D.C. 547.911;547.921

Preparation and Properties of Oligo- and Poly-phenylenes with Functional Groups

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Methods of preparing oligo- and poly-phenylenes containing various functional groups are surveyed, together with several field of application. A list of 120 references is included.

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I. INTRODUCTION

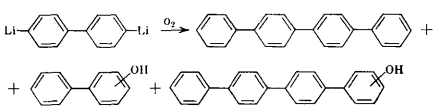
Intensive research has been undertaken during the past decade on polymers having aromatic rings in the chain and on materials based on them. Such materials are resistant not only to heat but also to various corrosive agents, including oxidants. In this respect polymers containing benzene rings in the main chain are of the greatest interest, primarily polyphenylenes, whose preparation has been reviewed several times[1-4]. However, current methods of preparation yield mainly infusible and insoluble polymers, which greatly hinders their processing and thus restricts their application.

This disadvantage might be overcome by obtaining oligophenylenes and polyphenylenes containing various functional groups. Thus polyphenylenes containing hydroxy- or carboxy-groups dissolve well in organic solvents and readily react with hydroxymethylated phenols, phenol–formaldehyde resins, oligoepoxides, metal salts, etc. to form heat-resistant, infusible cross-linked polymers[5]. The present Review surveys methods of preparation, properties, and applications of oligophenylenes and polyphenylenes containing various functional groups.

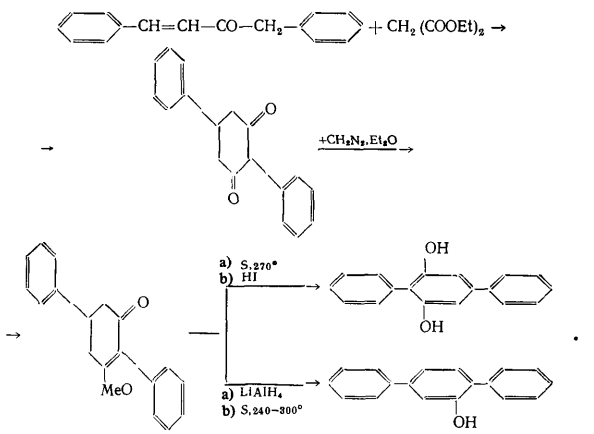
II. METHODS OF PREPARATION OF OLIGO- AND POLY-PHENYLENES WITH FUNCTIONAL GROUPS

1. Hydroxylated Oligo- and Poly-phenylenes

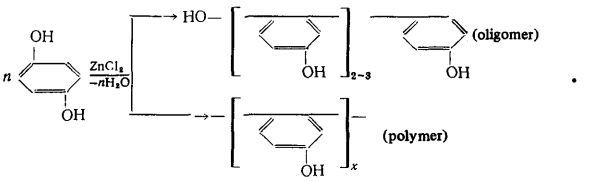
Among investigations on the preparation of hydroxylated lower oligophenylenes Pacevitz and Gilman[6] obtained *p*-phenylphenol in low yield by the oxidation with dry air of phenyl-lithium in benzene solution (at 10–15°C for 10 h). Similarly, quaterphenyl and linear oligophenylenes containing hydroxy-groups have been obtained[7] by the air oxidation of 4,4'-dilithiumbiphenyl:



The condensation of 1,4-diphenylbut-3-en-2-one with malonic ester gave[8] 2,5-diphenylcyclohexane-1,3-dione (yield ~ 80%)—the initial compound for the synthesis of *p*-terphenyl-2[5]-ol (m.p. 192–193°C, yield 45%) and *p*-terphenyl-2[2',5]-diol (m.p. 206–207°C, yield 35%):



Hydroxylated oligophenylenes and polyphenylenes were first obtained by Paushkin and his coworkers[9,10] by heating benzene-diols and -triols in the presence of zinc chloride (at 200–350°C for 6 h). On the basis of the infrared spectra these products were regarded as *o*-polyphenylenes (by analogy with Ref. 11):



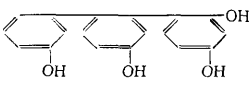
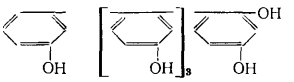
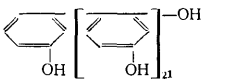
However, the suggested reaction scheme and structure of the products can only be crude approximations, since the high-temperature oxidising polycondensation of hydroxy-derivatives of benzene in the presence of a large quantity of zinc chloride may involve formation of phenyl and phenoxyl radicals, so that the structure of the products will be determined by the subsequent reactions of these radicals. Polyphenylenepolyols were obtained that were either soluble or insoluble in the usual organic solvents depending on the conditions of dehydration. Table 1 gives yields and molecular masses ($\overline{M}_n$) of soluble fractions of polyphenylenepolyols obtained from quinol, resorcinol, and pyrogallol. The yield, solubility, and molecular mass of the polymer had their maximum values in the last

case. Increase in molecular mass of fractions obtained from quinol is accompanied by a sharp rise in melting point (Table 2),[9] and the polymer having M_n = 2020 does not melt below 550°C.

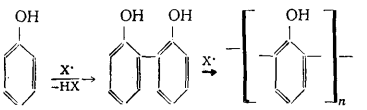
Table 1. Molecular masses and yields of hydroxylated polyphenylenes[9].

Initial diol	Yield of polymer, %		$\overline{M}_n$ of soluble fraction
	soluble fraction	insoluble fraction	
Quinol	30.6	54.4	1730
Resorcinol	67.0	9.3	1450
Pyrogallol	87.0	нет	1840

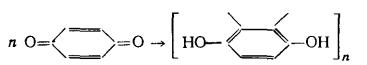
Table 2. Some characteristics of hydroxylated oligophenylene fractions from quinol[9].

Fraction	$\overline{M}_n$	Hydroxyl No., %	M.p., °C	Structure
1	330	22.8	160–180	
2	460	21.3	360–380	
3	2020	19.6	>550	

Paushkin et al. also suggested[12] polycondensation itself for the preparation of hydroxylated polyphenylenes. When phenol was heated in the presence of an equimolecular quantity of bromoform in an autoclave (at 250°C for 6 h), soluble products were obtained according to the hypothetical scheme



where n = 4–15 and X represents radicals formed by the thermal breakdown of bromoform. Fractionation of the polyhydroxyphenylene led to the isolation of oligomers having n = 4–7 (soluble in methanol) and $n \leqslant 15$ (soluble in dimethylformamide); the softening point rose from 110 to 250°C with increase in molecular mass. From the thermal stability and the composition of the hydrolysis products it was concluded[12] that the polymers had a linear structure. Polyhydroxyphenylenes soluble in alcohol, acetone, dimethylformamide, and aqueous alkalis were obtained[13] by the radical polymerisation of *p*-benzoquinone:

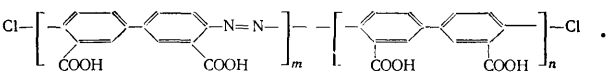


Heating phenol in the presence of iron(III) chloride at 40–90°C gave[14] poly-2-hydroxy-1,4-phenylene ("polyphenol"), an infusible dark-coloured product with $\overline{M}_n$ = 140 (determined viscometrically), soluble only in dimethylformamide. Thermogravimetric data (ΔT = 2.5 deg min^{-1}) indicate that in an atmosphere of nitrogen the polymer begins to lose weight at 350°C, and at 900°C the losses amount to 25%. It was supposed from nuclear magnetic resonance and infrared spectroscopy together with chemical investigations that the polymer contained not only hydroxyphenylene but also cyclohexadienone groups.

2. Carboxy-containing Oligophenylenes

Berlin and his coworkers[15–21] used the Sandmeyer decomposition of bisdiazo-compounds by copper(I) salts to obtain aromatic polymers. The presence of diazo-radicals $C_6H_4.N_2^{\cdot}$ accompanying the "purely" hydrocarbon radicals leads to partial incorporation of azo-groups into the polymer chain.

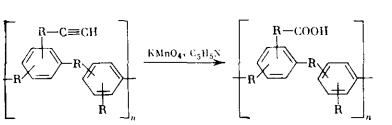
The decomposition of diazonium benzidine-3,3′-dicarboxylates[18] yielded a yellowish-brown polymer of molecular mass ~3000, which contained according to elementary analysis 1 azo-group per 6–10 benzene rings and 2 chlorine atoms per 5–16 benzene rings. Furthermore, every benzene ring contained a carboxy-group. Infrared spectroscopy suggested linear or slightly branched polymers[20], with either chlorine or peroxy as terminal groups. The structure of the products was therefore represented by the formula[18]

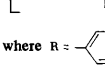


However, the general formula given is extremely arbitrary, and may not correspond to the true structure of the polymer molecule, since not only the structure of the blocks but also the alternation of azo-groups in the chain may be represented in other ways.

When heated in argon at 400°C for 1 h or at 250–400°C for 4 h, carboxylated oligophenylenes undergo complete decarboxylation without change in external appearance. Extreme losses in weight occur above 450°C. After heat-treatment at 200–400°C for 4 h the polymer was insoluble both in dimethylformamide and in aqueous alkalis[17].

Oligophenylenecarboxylic acids have been obtained[22,23] by oxidising oligophenylenes containing various carbon–carbon multiple bonds. Fractions having $\overline{M}_n$ = 1000–2200, obtained by the polycyclotrimerisation of a mixture of *p*-diethynylbenzene at phenylacetylene in the presence of various catalysts[24–26]—$TiCl_4.Al(iso\text{-}C_4H_9)_3$, $NiCl_2.2P(C_6H_5)_3 \times 2NaBH_4$, $Ni(C_5H_7O_2)_2.P(C_6H_5)_3$, and $[(C_2H_5O)_3P]_4CoBr$—and soluble in benzene and pyridine but insoluble in alcohol, were chosen for oxidation. Potassium permanganate was used[23] to oxidise the oligophenylenes (e.g. containing terminal ethynyl groups) by heating in pyridine solution:



where R = ; $n \approx 4$.

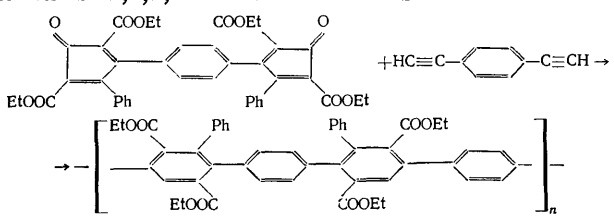
The resulting oligophenylenecarboxylic acids were light grey powders, soluble in pyridine, dioxan, oxolan, etc. Depending on the structure of the initial oligomer they had melting points of 130–280°C and acid numbers of 63–80. When the oligomeric acids were heated in argon they underwent decarboxylation, whose rate became appreciable only at 220–230°C. The resulting oligophenylenes were readily soluble in benzene, their molecular masses were closely similar to those of the original oligomers before oxidation, and they contained no carboxyls. Differential thermal analysis in helium ($\Delta T = 4.5$ deg min^{-1}) indicated that the oligomeric acids began to lose weight at ~ 230°C, vigorous decomposition occurred from 350–370 to 650°C, and the yield of the carbon residue at 900°C was 55% of the original weight of the specimen.

Oligophenylenecarboxylic acids obtained by oxidising oligophenylenes containing multiple bonds can be used as starting materials for the preparation of polyethers, polyesters, and polyamides.

3. Alkoxycarbonylated Oligo- and Poly-phenylenes

Methyl oligophenylenecarboxylates of molecular mass 1800, containing ~ 4 methoxycarbonyl groups in the oligomeric molecule, were obtained by treating the oligomeric acids with a solution of diazomethane in toluene[23]. They were grey powders, readily soluble in benzene, dioxan, chloroform, etc.

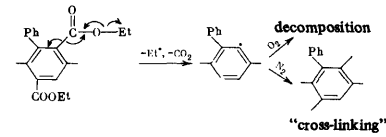
Harris and Reinhardt[27] synthesised ethoxycarbonylated oligo- and poly-phenylenes by the Diels–Alder reaction from ethoxycarbonylated biscyclopentadienones and aromatic diynes. Thus treatment of diethyl 2-oxo-4,5-diphenylcyclopentadiene-1,3-dicarboxylate with *p*-diethynylbenzene in benzene gave an approximately 97% yield of tetraethyl $1^1,1^6,3^3,3^4$-tetraphenyl-*p*-terphenyl-$1^2,1^5,3^2,3^5$-tetracarboxylate (a white powder melting at 223–224°C and readily soluble in chlorinated hydrocarbons). Similarly, ethyl carboxylates of polyphenylenes have been obtained by reaction between tetraethyl *p*-phenylenebis-4-(2-oxo-5-phenylcyclopentadiene-1,3-dicarboxylate) and *p*-diethynylbenzene in 1,1,2,2-tetrachloroethane solution:



The equation arbitrarily shows formation of a substituted poly-*p*-phenylene, although the conditions of the Diels–Alder reaction indicate the formation of both *meta*-linked and *para*-linked aromatic rings. The products had $\eta \log \simeq 3.0$ (determined at a polyphenylene concentration of 0.25 g dl^{-1} in 1,1,2,2-tetrachloroethane solution at 30°C), and formed colourless, transparent films, whose infrared spectra coincided with those of model compounds.

Differential thermal analysis showed that ethoxycarbonylated polyphenylenes begin to lose weight in the air only at 370°C, and are completely decomposed when heated to 520°C. In nitrogen intense loss of weight occurs above 370°C, and at 800°C the yield of carbon residue is 55%. Infrared spectroscopy indicated[27] that the losses in weight at 370–450°C are due to decarboxylation. Under isothermal conditions films undergo decarboxylation in nitrogen even below 300°C, with the formation of insoluble products.

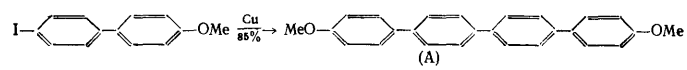
The above facts were explained[27] on the hypothesis of a free-radical mechanism for decarboxylation:



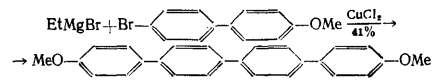
Radicals formed in the polyphenylene chain evidently undergo rapid oxidation in air. In an atmosphere of nitrogen free radicals either abstract hydrogen, giving rise to "cross-linking", or become involved in reactions leading to graphitic structures.

4. Methoxylated Oligophenylenes

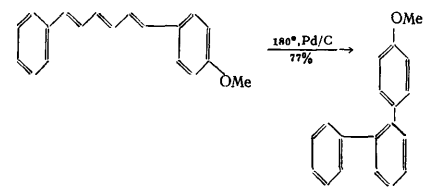
Methoxylated oligophenylenes are readily formed under the conditions of the Ullmann reaction. Thus 3,3′,5,5′-tetramethoxybiphenyl (m.p. 208°C) was obtained by heating 4-iodo-2,6-dimethoxybenzene in the presence of copper powder at 220–260°C.[28] When 4-iodo-4′-methoxybiphenyl was heated in the presence of copper bronze at 280°C for 1 h, $1^4,4^4$-dimethoxy-*p*-quaterphenyl (m.p. 338–340°C) was formed[29]:



Under conditions of oxidising dimerisation the yield of (A) is far lower[29]:



Pyrolysis of 1-*p*-methoxyphenyl-6-phenylhexa-1,3,5-triene in the presence of a palladium–carbon catalyst (10% by weight) *in vacuo* at 180°C gave *p*-methoxy-*o*-terphenyl (a colourless oil boiling at 153°C under 0.2 mmHg)[30]:



Several methoxylated *p*-oligophenylenes—from biphenyl to octophenyl—were synthesised by Kern et al.[26] from cyclic ketones and lithium aryls via intermediate hydroaromatic compounds:

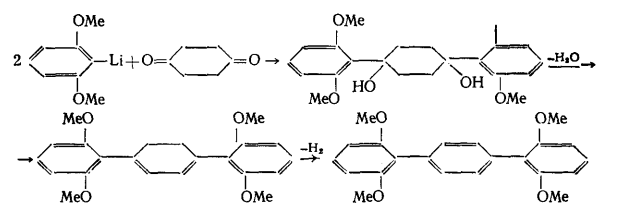
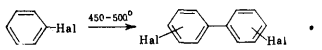


Table 3 gives the properties of the products with for comparison those of their unsubstituted analogues. It is evident that in all cases a methoxy-derivative melts at a lower temperature and dissolves better in toluene than the corresponding unsubstituted *p*-oligophenylene.

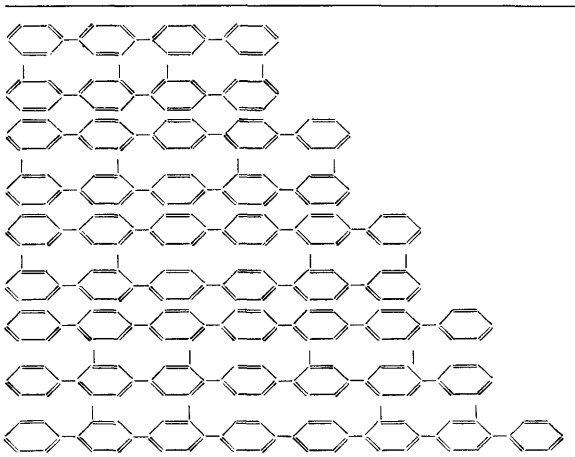
5. Halogenated Oligo- and Poly-phenylenes

Halogenated biphenyls are formed by the high-temperature treatment of halogenobenzenes: e.g. [31]

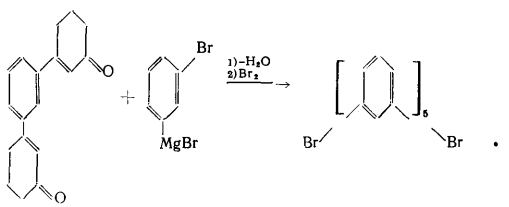


Chlorobiphenyls were found[32] among products of the pyrolysis of a mixture of *p*-nitrotoluene and chlorobenzene (at 600°C for 20 s).

Table 3. Melting points and solubilities in toluene (at 20°C) of methoxylated *p*-oligophenylenes[28].

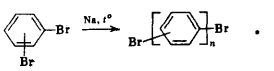
Formula	M.p., °C	Solubility, g litre^{-1}
	320	0.22
	158	22.0
	395	0.1
	165	3.5
	475	0.01
	210	2.0
	545	—
	253	0.5
	277	0.2

An interesting method[33] was used to obtain *m*-oligophenylenes containing bromine at the ends of the polymer chain:

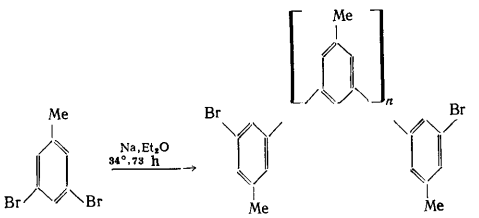


Reaction of *m*-dicyclohexenylbenzene-3′,3″-dione with *m*-bromophenylmagnesium bromide followed by dehydration and aromatisation gave a 9% yield of $1^3,5^3$-dibromo-*m*-quinquephenyl, a yellow-orange powder of m.p. 104–106°C (from alcohol). $1^3,3^3$-Dibromo-*m*-terphenyl (an uncrystallisable oil) and $1^3,6^3$-dibromo-*m*-sexiphenyl (melting at 143–145°C) were synthesised by similar methods. A multistage process is involved, and the yield of the desired product does not exceed 10%.[33]

The Wurtz–Fittig reaction has been successfully applied to the synthesis of halogenated oligophenylenes. As early as 1886 Goldschmiedt[34] obtained amorphous yellow powders, melting over the ranges 200–250 and 245–300°C, by heating *m*- and *p*-dibromobenzenes respectively with metallic sodium in ether. The reaction can be represented by the scheme (n = 8–13)



A mixture of oligomeric products having n = 2–4 and 6, containing *meta*-substituted groups, was obtained by the polycondensation of 3,5-dibromotoluene under the influence of metallic sodium[35]:



The polycondensation of *p*-dichlorobenzene in the presence of metallic sodium or a sodium–potassium alloy gives a reddish-brown powder soluble in aromatic hydrocarbons and not melting below 550°C.[36,37] Elementary analysis indicates that the polymer molecule contains ~ 5 chlorine atoms. The structure is assumed to contain not only *p*-phenylene but also *p*-quinoid groups.

A patent[38] describes the synthesis of αω-dibromo-*p*-polyphenylenes from *p*-dibromobenzene in a dioxan–xylene medium under the influence of metallic sodium.

Kovačic and his coworkers[39–42] undertook the oxidative dehydropolycondensation of benzene in various organic solvents—carbon disulphide, benzene, dichlorobenzene, etc.—in the presence of the $AlCl_3$–$CuCl_2$ catalytic system, and obtained polyphenylenes containing chlorine. When the reaction was accomplished in the presence of iron(III) chloride[43,44], small quantities of lower products, e.g. chlorobenzene, 4,4′-dichlorobiphenyl, etc., were also formed. This work showed that the thermo-oxidative stability of *p*-polyphenylenes increases with the chlorine content of the polymer (Table 4). When benzene underwent oxidative dehydropolycondensation in the presence of antimony(V) chloride, the polyphenylenes contained up to 31% of chlorine[40,45].

Table 4. Losses in weight of chlorinated poly-*p*-phenylenes in air (ΔT = 8 deg min^{-1}).[43,44]

Temp., °C	Loss (%) for Cl content		Temp., °C	Loss (%) for Cl content	
	6.0%	23.6%		6.0%	23.6%
350	0.49	0.35	500	55.50	15.55
400	0.99	0.94	550	97.00	73.0
450	16.15	2.70	600	100	99.9

Some Japanese investigators[46–48] obtained polyphenylenes by decomposing biphenyl-4,4′-bisdiazonium dichloride in aqueous solution in the presence of copper(I) and iron(II) chlorides at 50–80°C. In the polymer having $\bar{M}_n$ = 10000 one chlorine atom was present per 3–4 benzene rings. The polymer dissolved in benzene, oxolan, dioxan, and chloroform[49]. Examination of fractions of molecular

mass 3000–5000 showed the presence of 5–8 azo-groups per molecule[47]. A radical mechanism was assumed for the formation of polyphenylenes[50].

Detailed information on the preparation and properties of fluorinated oligophenylenes and polyphenylenes has recently been surveyed[51].

6. Alkylated Oligo- and Poly-phenylenes

Among the first syntheses of methylated oligophenylenes was that of $1^4,4^4$-dimethyl-*p*-quaterphenyl (m.p. 340°C) by heating 4-iodo-4′-methylbiphenyl in the presence of copper bronze[52]:

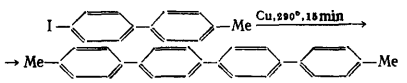
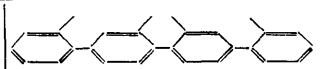
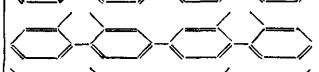
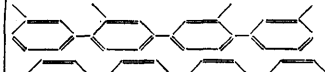
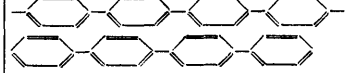
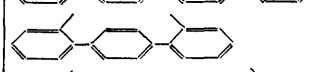
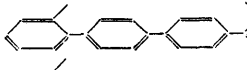
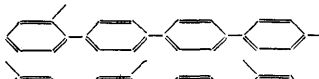
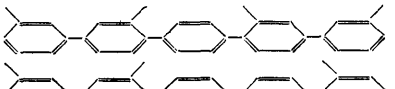
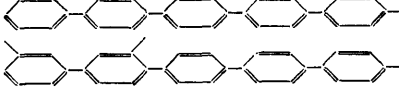
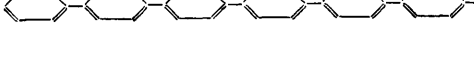
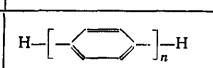
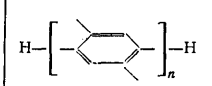
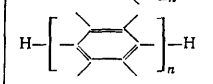


Table 5. Melting points and solubilities in toluene of methylated *p*-oligophenylenes[53–55].

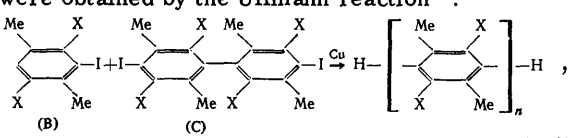
No.	Formula	M.p., °C	Solubility, g litre^{-1}
1		84	500
2		96	470
3		139	110
4		340	0.2
5		320	0.13
6		146	42
7		150	51
8		231	1.3
9		186	11
10		200	9.5
11		261	1.1

Wirth et al.[53] used the Ullmann reaction in the presence of copper powder at 230–260°C to prepare a series of methylated *p*-oligophenylenes (yield 40–50%)[53–55]. Some properties of the resulting oligomers are given in Table 5. These workers showed that the introduction of methyl groups into the $1^4,4^4$-positions of *p*-quaterphenyl (No. 5 in Table 5) has hardly any effect on the melting point or the solubility in toluene; the introduction of methyl groups into the *ortho*- and *meta*-positions lowers the melting point of the products and improves significantly their solubility in toluene. Increase in the number of methyl groups in the *p*-quinquephenyl molecule lowers the melting point and enhances the solubility in toluene (No. 8 and 9). Yet increasing the number of unsubstituted benzene rings in methylated oligophenylenes raises the melting point and lowers the solubility (No. 6–8 and 9–11). Thus methylated *p*-oligophenylenes have lower melting points and better solubility than have their unsubstituted analogues, and the solubility is better the greater the number of methylated benzene rings.

Table 6. Melting points and solubilities in toluene of *p*-oligophenylenes containing di- and tetra-methylbenzene rings[56].

No.	Formula	Degree of condensation *n*	M.p., °C	Solubility, g litre^{-1}
1		2	71	430.0
		3	215	7.4
		4	320	0.13
		5	395	0.005
2		2	54	700.0
		3	183	28.0
		4	266	1.1
		5	309	0.24
3		2	137	365.0
		3	272	24.0
		4	272	3.4

Oligophenylenes comprising *p*-xylene and *p*-durene units were obtained by the Ullmann reaction[56]:

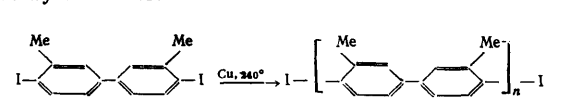


where n = 2–5 and X = H, CH_3. The highest yield (50%) of such oligophenylenes is obtained with reactants B and C in the molar proportions 10 : 1. Table 6 shows that the melting points of both unsubstituted (No. 1) and di- and tetra-methylated *p*-oligophenylenes (No. 2 and 3) rise and the solubilities in toluene diminish with increase in the degree of condensation.

Table 7. Molecular masses and melting points of fractions of methylated polyphenylene obtained by the Ullmann reaction[57].

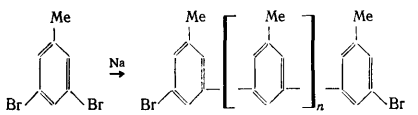
Fraction	M.p., °C	$\overline{M}_w$
1	290—310	32 000
2	225—245	3 700
3	120—140	500

The Ullmann reaction was used also for the synthesis of *p*-oligophenylenes containing a methyl group in every benzene ring[57]. The soluble methylated polyphenylenes obtained by the reaction



were fractionated by centrifugation and osmometry, when a fraction of molecular mass 300 000 was isolated. The cryoscopic method gave anomalous values of the number-average molecular mass. It was concluded[57] from viscosity, sedimentation, and diffusion results that under the given reaction conditions the polymeric molecules probably had not a linear but a branched structure, with *m*-phenylene groups in the main chain. Table 7 shows that with increase in the weight-average molecular mass of the fractions from 500 to 32 000 (determined by centrifugation) the melting point rises.

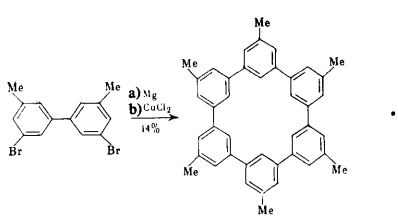
The Wurtz–Fittig reaction can also be applied to the synthesis of methylated oligophenylenes. The homocondensation of 3,5-dibromotoluene in the presence of metallic sodium in boiling ether led to the isolation[35] of oligophenylene fractions having $n = 2$ and 3 (a mixture melting below 60°C), as well as with $n = 4$ (melts above 66°C) and $n = 6$:



Each of these fractions is an amorphous yellow powder soluble in benzene and ether.

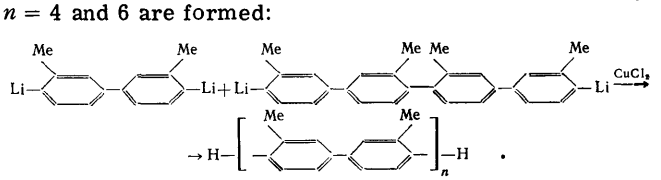
The synthesis of a methylated *p*-oligophenylene by the reaction of 4,4′-di-iodo-3,3′-dimethylbiphenyl with metallic sodium in boiling toluene was reported[58]. The resulting polymer was soluble in benzene, and melted at 150–180°C.

Organomagnesium compounds can also be used for the preparation of methylated oligophenylenes from halogenated aromatic compounds. Thus Kern et al.[59] obtained an oligophenylene by treating 4,4′-di-iodo-3,3′-dimethylbiphenyl with magnesium at 20°C. They noted that linear oligophenylenes were not formed, and concluded that the Grignard reaction, despite the milder conditions, is less suitable than the Ullmann reaction for obtaining oligophenylenes of regular structure. Bräunling et al.[60] used the Grignard reaction to synthesise methylated cyclic *m*-oligophenylenes. Thus hexamethylhexa-*m*-phenylene (m.p. 452–453°C) was obtained from 3,3′-dibromo-5,5′-dimethylbiphenyl:



3,3′-Dibromo-6,6′-dimethylbiphenyl gave a low yield of octamethylocta-*m*-phenylene (m.p. 489°C).

Furthermore, the oxidative dimerisation of dilithium derivatives of methylated aromatic compounds yields methylated oligophenylenes[61]. When a mixture of 4,4′-dilithium-3,3′-dimethylbiphenyl and $1^4,4^4$-dilithium-$1^2,2^2,3^2,4^3$-tetramethyl-*p*-quaterphenyl is treated with copper(II) chloride, methylated *p*-oligophenylenes having $n = 4$ and 6 are formed:



Similarly, $1^2,2^3,3^2,4^3,5^2,6^3,7^2,8^3$-octamethyl-*p*-octophenyl (m.p. 273°C) was obtained, together with small quantities of products having $n > 8$, from 1^4-lithium-$1^2,2^3,3^2,4^3$-tetramethyl-*p*-quaterphenyl.

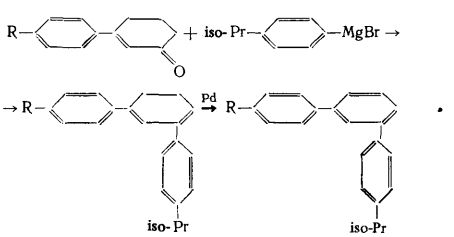
Reduction of 4-acetyl-4′-ethylbiphenyl on zinc amalgam in an acid medium gave 4,4′-diethylbiphenyl[62], which after recrystallisation from ethanol melted at 81°C.

Methylated oligophenylenes can be obtained from aromatic compounds not only by the above condensation methods but also by processes involving the formation of new benzene rings by the aromatisation of C_6 cyclic systems, as well as cycloaddition and cyclisation.

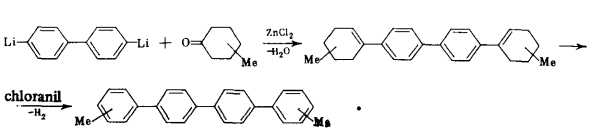
Table 8. Melting points and solubilities of methylated *p*-quaterphenyls[64].

No.	Positions of methyl	M.p., °C	Solubility, g litre^{-1}	No.	Positions of methyl	M.p., °C	Solubility, g litre^{-1}
1	1^2-	172–173	26.0	5	1^3, 4^3-	214–215	6.3
2	1^3-	244–245	3.0	6	1^4, 4^4-	338–340	0.2
3	1^4-	328–330	1.2	7	unsubst.	320	0.1
4	1^2, 4^3-	150–151	36.0				

Reaction of phenylcyclohexenone with *p*-isopropylphenylmagnesium bromide gave a diarylcyclohexadiene, whose dehydrogenation over palladium yielded an isopropyl-*m*-terphenyl[63]:



Organolithium compounds have been especially widely used in the synthesis of methylated oligophenylenes from cyclic ketones. Thus the condensation of 2-, 3-, and 4-methylcyclohexanones with 4-lithium-*p*-terphenyl or with 4,4′-dilithiumbiphenyl gave products from which the corresponding 1-methyl- and 1,4-dimethyl-*p*-quaterphenyls (Table 8) were obtained by dehydration in the presence of zinc chloride and dehydrogenation by means of chloranil in boiling xylene[64]:



Introduction of a 4-methyl group into *p*-quaterphenyl somewhat raises the melting point (cf. No. 6 and 3 with No. 7 in Table 8). Introduction of a methyl group at position 3 and especially at position 2 (cf. No. 2 and 5; 1 and 4 with No. 7) improves the solubility in toluene and lowers the melting point of the products. These effects are still more strongly developed in dimethyl-*p*-quaterphenyls substituted at the 2 or 3 positions (No. 4 and 5).

Methylated derivatives of *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl, *p*-sexiphenyl[55], and *p*-octophenyl[7] were obtained from cyclic diketones (cyclohexa-1,4-dione and bicyclohexyl-4,4′-dione) and lithium aryls via intermediate hydroaromatic compounds.

Somewhat later it was shown[53,54] that the increased solubility of methylated *p*-oligophenylenes obtained by the Ullmann reaction is explained by breakdown of symmetry of the compounds due to the combined effects of substitution and rotation, the latter associated with diminished symmetry resulting from internal molecular mobility (rotation of rings).

p-Oligophenylenes with $n \leq 14$ and containing one or two unsubstituted *m*-phenylene units in the main chain were synthesised[65]:

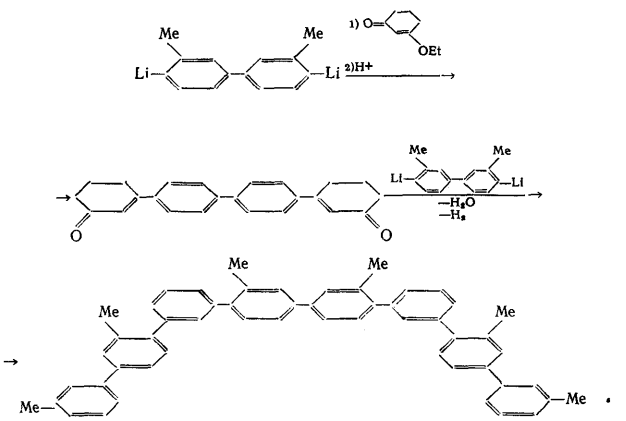


Table 9. Melting points and solubilities in toluene (at 20°C) of methylated oligophenylenes[65].

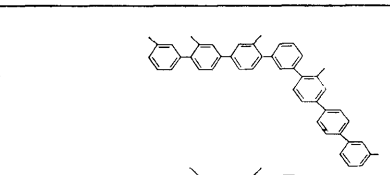
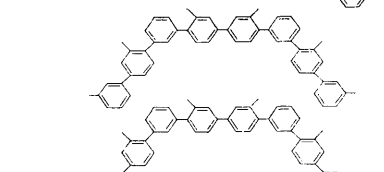
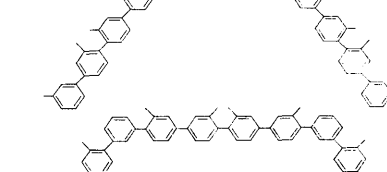
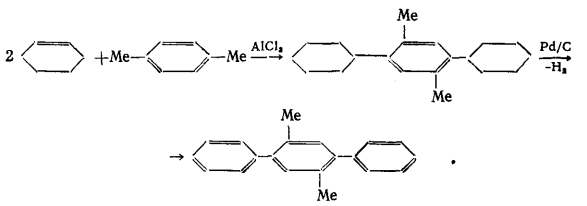
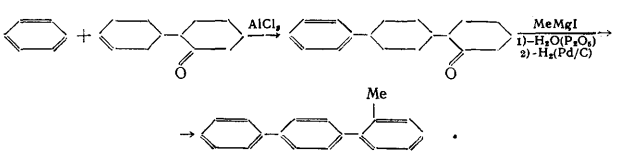
No.	Formula	M.p., °C	Solubility, g litre^{-1}
1.		202—203	12
2.		170—171	73
3.		221—222	12
4.		218—220	10

Table 9 gives the melting points and solubilities in toluene of several methylated oligomers of this type. Their infrared spectra are identical with those of *p*-oligophenylenes, whereas the ultraviolet spectra differ appreciably; the melting points are lower and the solubilities better than for the corresponding *p*-oligophenylenes.

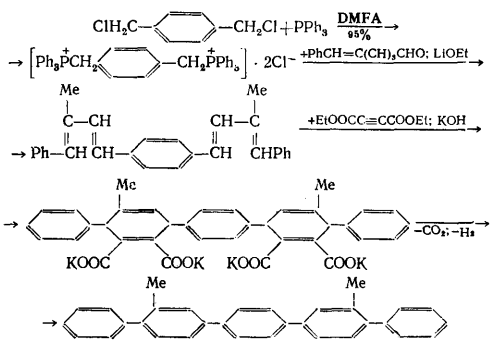
Methylated *p*-terphenyls have been obtained also by the Friedel–Crafts reaction. Deuschel[66] condensed cyclohexene with *p*-xylene in carbon disulphide in the presence of aluminium trichloride to give 2,5-dicyclohexyl-*p*-xylene, which was then dehydrogenated over a palladium–carbon catalyst to 2^2,2^5-dimethyl-*p*-terphenyl:



1^2-Methyl-*p*-terphenyl (m.p. 91–92°C) was obtained[67] from products of the condensation of 2-cyclohex-3′-enylcyclohexanone with benzene in the presence of aluminium chloride:

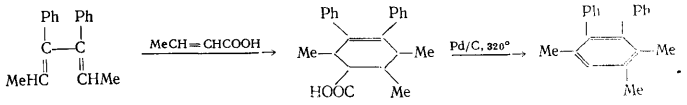


Campbell and McDonald[68] synthesised dimethyl-*p*-quinquephenyls, using cyclisation to introduce the methylated rings. Thus the reaction of *p*-xylenebistriphenylphosphonium dichloride with α-methylcinnamaldehyde gave *p*-bis-3-methyl-4-phenylbutadienylbenzene, which on the cycloaddition of diethyl acetylenedicarboxylate in the presence of potassium hydroxide formed potassium tetrahydro-2^2,4^3-dimethylquinquephenyltetracarboxylate, whose dehydrogenation and decarboxylation yielded 2^2,4^3-dimethyl-*p*-quinquephenyl (m.p. 217–218°C):

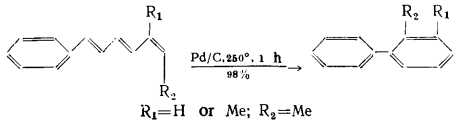


When *p*-methylcinnamaldehyde was used as initial compound, 1^4,5^4-dimethyl-*p*-quinquephenyl (m.p. 400°C) was obtained.

Langer and Wessely[69] synthesised several methylated *o*-, *m*-, and *p*-terphenyls by the dehydrogenation over a palladium–carbon catalyst of substituted cyclohexenes—products of the cycloaddition of e.g. an acrylic acid to a buta-1,3-diene:

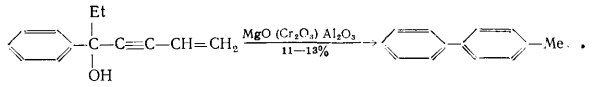


Methylated biphenyls may be formed by the high-temperature cyclisation of the side-chains of various aromatic compounds. Thus mono- and di-methylbiphenyls were obtained[30] by heating phenylalkatrienes in the presence of a palladium–carbon catalyst in a vacuum to 250°C:

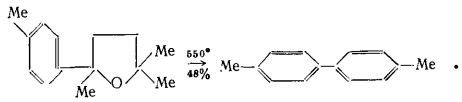


R_1=H or Me; R_2=Me

Substituted biphenyls were obtained from benzene derivatives containing at least six carbon atoms in the side-chain[70–73] (e.g. unsaturated compounds—1-ethyl-1-phenylpent-4-en-2-ynol, 1,4,4-trimethyl-1-phenylbutynediol, etc.) in the presence of a chromium–alumina catalyst:

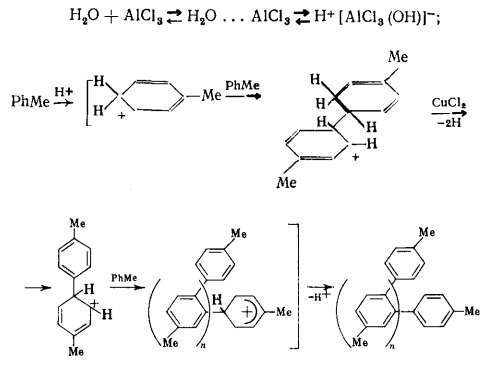


The pyrolysis of 2,2,5-trimethyl-5-*p*-tolyloxolan at 550°C yields 4,4′-dimethylbiphenyl (m.p. 121°C)[74]:

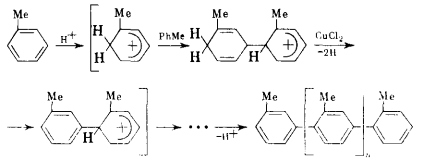


Oxidative dehydropolycondensation is currently among the best known and simplest methods for synthesising polymers having aromatic groups in the main chain. First developed by Kovačic and his coworkers in 1962,[75] it enables polyphenylenes to be obtained by the single-stage conversion of aromatic compounds in the presence of catalysts such as Lewis acids and oxidising agents at 30–37°C[39, 41, 42, 75, 76]. Several investigations have shown[43, 77, 78] that the oxidative dehydropolycondensation of benzene usually gives polymers that are infusible and insoluble in organic solvents. Mixtures of benzene with various aromatic hydrocarbons—e.g. naphthalene, biphenyl, terphenyl, toluene, xylenes, etc.—were proposed[79–87] for the production of fusible and soluble polyphenylenes. The properties of the resulting polymers were found to depend mainly on the process conditions (proportions and concentrations of initial monomers, catalyst concentrations, type of solvent, temperature, etc.).

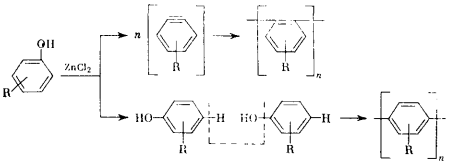
Oxidative dehydropolycondensation is catalysed most effectively[41–43, 77] by the aluminium(III)–copper(II) chloride system. In its presence toluene yielded oligophenylenes of mean degree of polymerisation n = 10–20, soluble in aromatic hydrocarbons (benzene, toluene) and having m.p. ≃ 250°C. Nuclear magnetic resonance, infrared, and ultraviolet spectroscopy together with elementary analysis of the oligophenylenes and of products formed under conditions of oxidative degradation showed that the main oligomer chain consisted of *ortho*-linked aromatic rings containing *p*-methyl groups. A certain number of *para*-linked phenylene units were also present in the chain. From this Kovačic and Ramsey[87] suggested that the mechanism of the formation of *o*-oligophenylenes from toluene (the ring bonds are delocalised) was



When a benzonium ion protonated *ortho* to the methyl group appears, growth of the oligomeric molecule leads to formation of a methylated *p*-oligophenylene:



Alkylated polyphenylenes were obtained by Paushkin et al.[9, 88] by oxidative polycondensation of the corresponding phenols. Thus phenol and its homologues (*m*-cresol, *p*-t-butylphenol, etc.) in the presence of zinc chloride (at 250–350°C for 6 h) gave polymers partly soluble in dimethylformamide, phenol, pyridine, dioxan, and concentrated sulphuric acid. The solubility of the polymers diminished with rise in temperature and increase in duration of the reaction. The mechanism was regarded as involving dehydration and polymerisation of an intermediate dehydrobenzene or as polycondensation:



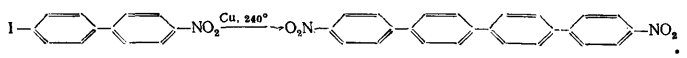
The former was regarded as the more probable, since polymers with *ortho*-linked benzene rings were mainly formed. However, the suggested mechanism can hardly be regarded as soundly based, since intermediate formation of dehydrobenzene is unlikely in the high-temperature conversion of phenols in the presence of catalysts. Processes involving phenoxy-radicals and their subsequent conversion products probably also take place under these conditions.

The unsubstituted or alkylated *o*-phenylenes (yield ≤ 32%) obtained from phenol, *m*-cresol, and *p*-t-butylphenol respectively contained 9.8–19.6% of soluble fractions having $\overline{M}_n$ = 950–1050. The presence of a small quantity of oxygen in the polymer is evidently due to terminal hydroxyls[88].

7. Nitro-substituted Oligo- and Poly-phenylenes

Several nitro-*p*-quaterphenyls were synthesised in order to ascertain the influence of nitration on the solubility of oligophenylenes. Thus 1⁴,4⁴-dinitro-*p*-quaterphenyl,

obtained from 4-iodo-4′-nitrobiphenyl by the Ullmann reaction [29]



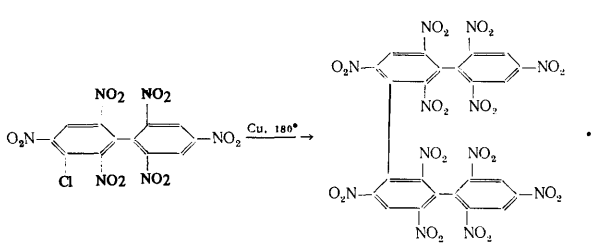
was isolated as yellow crystals of m.p. 317–320°C, insoluble in the majority of organic solvents.

Table 10. Solubilities in toluene (at 20°C) and melting points of nitrated and methylated *p*-quaterphenyls [89].

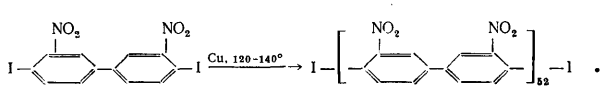
Substituted at positions	Nitro-derivative		Methyl derivative	
	solubility, g litre^{-1}	m.p., °C	solubility, g litre^{-1}	m.p., °C
2^3-	4.3	288	—	—
2^3, 3^2-	3.4	342	55	178
1^3, 4^3-	3.8	233	51	150
1^2, 2^2, 3^3, 4^2-	2.0	207	3.5	213
$1^{2,4}$, 2^3, 3^2, $4^{2,4}$-	0.85	235	470	96
	0.20	292	—	—

Comparison of the properties of methylated and nitrated *p*-quaterphenyls showed (Table 10) that the latter have rather higher melting points, but considerably lower solubilities, than their methylated analogues [89]. On the whole a nitro-group produces little enhancement of the solubility of oligophenylenes, although in polar solvents (nitrobenzene, dimethylformamide) their solubility is increased significantly.

From 3-chloro-2,2′4,4′,6,6′-hexanitrobiphenyl in dry nitrobenzene in the presence of copper bronze Dacons [90] obtained dodecanitroquaterphenyl (yield 70%), an explosive compound:

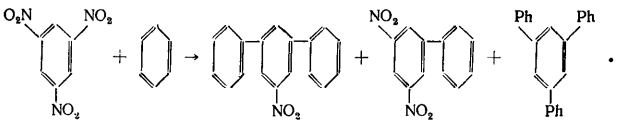


A nitro-substituted *p*-polyphenylene was obtained by the Ullmann reaction, when 4,4′-di-iodo-3,3′-dinitrobiphenyl in dimethylformamide solution in the presence of copper bronze was heated to 140°C [89]:

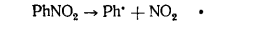


The polymer was a crystalline yellow powder, infusible and insoluble, which decomposed above 250°C.

As an alternative to the main method for obtaining nitrated oligophenylenes—the Ullmann reaction—the pyrolysis of aromatic compounds can be used for nitroterphenyls and nitrobiphenyls. Fields and Meyerson [32,91] studied the arylation of aromatic nitro-compounds at high temperatures. A 28% yield of 3-nitrobiphenyl was isolated from the pyrolysis of a mixture of *m*-dinitrobenzene and benzene (molar proportions 1 : 10) at 450°C. The reaction between 1,3,5-trinitrobenzene and benzene at 450–600°C gave a mixture of nitroterphenyl, dinitrobiphenyl, and triphenylbenzene:

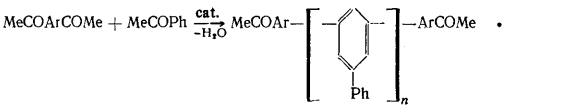


A radical mechanism is involved with intermediate formation of a phenyl radical:

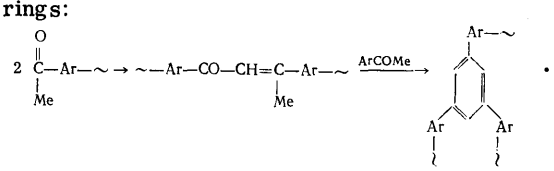


8. Oligophenylenes containing Acetyl and Acetal Groups

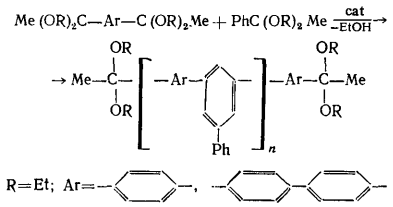
Oligophenylenes having terminal acetyl groups were first synthesised by Korshak et al. [92–94] by the polycyclocondensation of mono- and di-acetylated aromatic compounds. In the presence of an acid catalyst (hydrogen chloride, sulphuric acid, toluene-*p*-sulphonic acid) at 20°C infusible oligophenylenes, having $\overline{M}_n$ = 1500–4200, containing acetyl end-groups, and soluble in benzene, toluene, chloroform, and other organic solvents, were obtained from acetophenone with *p*-diacetylbenzene or with 4,4′-diacetylbiphenyl:



Trimerisation was shown to involve intermediate formation of a dimer containing dypnone fragments, which interacted with the acetyl group to give the 1,3,5-trisubstituted benzene rings:



The introduction of ethyl orthoformate promoted conversion of the acetyl compounds into acetals, which readily trimerised to a benzene ring. Korshak et al. [95–97] suggested that acetylated aromatic compounds should be replaced by their acetals as initial compounds, in order to diminish the significance of side-reactions in the synthesis and lower the quantity of defective structures in the polymer. The polycondensation of diacetals of diacetylarylenes with acetals of acetophenone gave oligomers ($\overline{M}_n$ = 1700–2500) having reactive terminal groups:

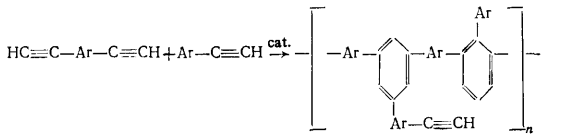


A linear structure was attributed to the resulting oligophenylenes on the basis of their elementary composition, molecular mass, and proton magnetic resonance spectra.

The oligophenylenes obtained either from acetylated aromatic compounds or from their acetals, when heated (at 400°C in the absence of a catalyst or at 300°C in the presence of toluene-*p*-sulphonic acid), set to infusible and insoluble products. Thermogravimetric results indicated that these products began to decompose at 430°C when heated in helium, and at 900°C the total losses in weight were 30%.

9. Ethynylated Oligophenylenes

The controlled synthesis of soluble aromatic polymers by the polycyclotrimerisation of a mixture of butadiyne and acetylene in an inert organic solvent, with the use of tantalum and niobium halides and oxide halides as catalysts between −30 and +200°C, was reported in the patent literature[98-100]. The chains in such polymers may terminate in ethynyl groups. Little study has been made of the properties of the products. Strongly branched oligophenylenes with terminal ethynyl groups have been obtained by the copolycyclotrimerisation of mono- and diacetylenic compounds in the presence of various catalytic systems (such as $[(AlkO)_3P]_4CoBr$,[101-103,21] $2NaBH_4.2(C_6H_5)_3P.NiCl_2$,[104] Ziegler catalysts[105], and other transition-metal complexes):



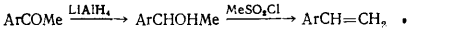
Oligophenylenes containing ethynyl groups and having molecular weights $\overline{M}_n$ = 1000–2500 (determined ebullioscopically in benzene) dissolve readily in benzene, toluene, and other organic solvents. The polymers easily set at 150–250°C to hardened products possessing high deformation heat-resistance, which increases with the number of ethynyl groups in the initial copolymer. However, the stability towards thermal oxidation of the hardened polyphenylenes diminishes with increase in the number of ethynyl groups.

Analogous soluble branched oligophenylenes having terminal ethynyl groups were obtained by Bracke[106] by the copolycyclotrimerisation of *m*-diethynylbenzene and phenylacetylene in chlorobenzene in the presence of a Fisher type of catalyst $TiCl_2.2AlCl_3$ at temperatures from −35 to +20°C. Thermogravimetry indicated that the polymer began to decompose at ~ 500°C whether in an inert gas or in air.

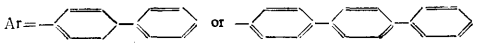
Furthermore, oligophenylenes having $\overline{M}_n$ = 10 000 (determined by gel-permeation chromatography), soluble in benzene and chlorinated hydrocarbons, were obtained by Chalk and Gilbert[107] by the copolycyclotrimerisation of phenylacetylene and *m*-ethynyltoluene with *m*-diethynylbenzene in the presence of a Ziegler catalyst (in toluene between −23 and +20°C). The products softened at 200–300°C depending on the molecular mass. The polymers were processed by extrusion.

10. Alkenylated Oligophenylenes

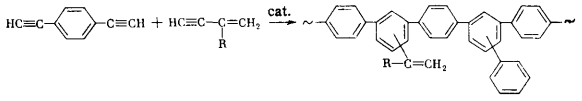
Kern et al.[108] developed a process for obtaining 4-vinylbiphenyl and 1^4-vinyl-*p*-terphenyl by reducing 4-acetylbiphenyl and 1^4-acetyl-*p*-terphenyl with lithium tetrahydroaluminate, and subjecting the resulting α-hydroxyethyl derivatives to liquid-phase dehydration in the presence of methanesulphonyl chloride in pyridine solution:



where



Branched oligophenylenes containing double bonds have been obtained[109] by the copolycyclotrimerisation of *p*-diethynylbenzene with alkenylacetylenes—butenyne or methylbutenyne—on the catalysts $[(C_2H_5O)_3P]_4CoBr$, $NiCl_2.2(C_6H_5)_3P.NaBH_4$, $(iso\text{-}C_4H_9)_3Al.TiCl_4$ (Al/Ti = 3):



The content of double bonds and the properties of the oligophenylenes depend primarily on the ratio of *p*-diethynylbenzene to alkenylacetylene in the initial mixture. Thus decrease in the ratio of the former to methylbutenyne tends to increase the solubility and the unsaturation of the oligomers and decrease their molecular mass. Completely benzene-soluble oligophenylenes were obtained at ratios of 1 : 3, when the products had $\overline{M}_n$ = 25 000 and iodine numbers of ~ 195.

Vinylated oligophenylenes obtained from *p*-diethynylbenzene and a vinylacetylene in the molar proportions 1 : 3–9 were solids only partly soluble in benzene and chloroform, probably owing to the ease of cross-linking during isolation and standing in the air. In contrast, ternary copolymers based on *p*-diethynylbenzene, butenyne, and phenylacetylene in the molar proportions 1 : 3 : 3 and 1 : 3 : 1, obtained in the presence of $(iso\text{-}C_4H_9)_3Al.TiCl_4$, dissolved completely in benzene and chloroform; their iodine numbers varied from 130 to 440.

All the alkenylated oligophenylenes were easily hardened at room temperature and on heating with the formation of infusible and insoluble products.

III. POLYMERLIKE REACTIONS OF OLIGO- AND POLYPHENYLENES

Various functional groups can be introduced into polyphenylenes by treatment with appropriate reagents, whether the polymers had been obtained by dehydrogenation of polycyclohexenes or by oxidative dehydropolycondensation of benzene. Thus Kovačic et al.[110] showed that the action of concentrated sulphuric acid on a *p*-polyphenylene yields a product in which about 60% of the aromatic rings contain sulpho-groups. Sulphonation of *p*-phenylenes with chlorosulphuric acid, oleum, or concentrated sulphuric acid gave sulphonated polymers in which the ratio of carbon to sulphur varied from 6 (one sulphur atom per aromatic ring) to 36 depending on temperature and duration of the reaction[111-113]. Specimens having ratios ≤ 9 dissolved in aqueous acetone and aqueous ethanol.

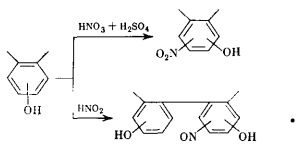
When a sulphonated polymer was fused with a mixture of sodium and potassium hydroxides 97% of the sulpho-groups were hydrolysed to hydroxy-groups[111]. The

resulting hydroxylated polyphenylenes were brittle black products, soluble only in aqueous acetone and aqueous ethanol.

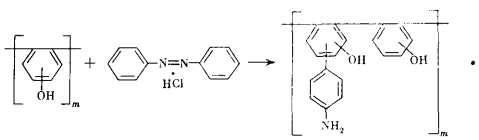
As noted earlier, the oxidative dehydropolycondensation of benzene in the presence of a Lewis acid as catalyst[39, 41-44, 77] will yield *p*-polyphenylenes having various degrees of halogenation. The hydrogen atoms of the aromatic ring are completely replaced by chlorine when the process is conducted in the presence of gaseous chlorine with $SnCl_2.AlCl_3$ or antimony(V) chloride as catalyst. In the presence of aluminium bromide brominated *p*-polyphenylenes are formed containing on the average ~ 3 bromine atoms per benzene ring[110].

One nitro-group can be introduced into every benzene ring by treating a *p*-polyphenylene with a nitrating mixture (nitric and sulphuric acids)[110]. Aminated polyphenylenes were obtained by reducing the nitro-polymers with hydrazine in the presence of Sn–HCl or $SnCl_2$–HCl in diethylene glycol solution, when conversion of nitro-groups into amino-groups reached 94–100%. The final products contained small quantities of nitro, azoxy, and other functional groups with incomplete reduction, and also because of the occurrence of side-reactions[110].

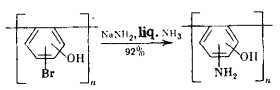
Paushkin et al.[114] used hydroxylated polyphenylenes obtained from dihydric phenols for the preparation of nitro-, nitroso-, and amino-derivatives. Thus treatment with a nitrating mixture (nitric and sulphuric acids) at temperatures not exceeding 10°C introduced a nitro-group into almost every benzene ring. Poly(hydroxynitrophenylenes) were obtained by the action of nitrous acid on a hydroxylated polyphenylene. The general trend of the nitration and nitrosation of these polymers can be represented by the scheme



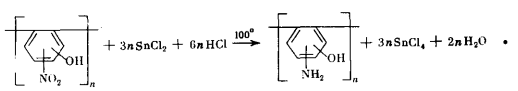
The aminophenylation of hydroxylated polyphenylenes with azobenzene hydrochloride produces polymers that are partly soluble in dimethylformamide and contain one aminophenyl group for approximately two hydroxyphenylene groups[114]:



Polymers completely soluble in dimethylformamide were obtained by the amination of poly(bromohydroxyphenylenes)[114]:



Reduction of poly(hydroxynitrophenylenes) by the action of tin(II) chloride in hydrochloric acid gave up to 70% yields of poly(aminohydroxyphenylenes):



Poly(phenylene isocycanates) were prepared by the reaction of poly(aminohydroxyphenylenes) with chloroform and alkali[114].

The above investigations have shown that the introduction of substituents into hydroxylated polyphenylenes improves their solubility but impairs their thermal stability.

IV. PRACTICAL APPLICATION OF OLIGO- AND POLYPHENYLENES CONTAINING VARIOUS FUNCTIONAL GROUPS

Much experimental information has now accumulated on the preparation and properties of oligophenylenes and polyphenylenes containing functional groups, from which conclusions can be drawn (though still preliminary) on the further development of work on these lines. Fields of practical application of the substituted oligomers and polymers, at present fairly restricted, will undoubtedly expand continuously.

When heated in a melt with alkali, polyphenylenes containing sulpho-groups form polyphenols, which are converted by treatment with formaldehyde into insoluble, infusible cross-linked products[111]. These undergo no loss in weight when heated to 400°C (in nitrogen with ΔT = 2.5 deg min^{-1}), and only at 900°C do the losses amount to 30%. The thermal stability of the products diminishes with increase in the quantity of substituents in the polymer molecule.

A heat-resistant composition was obtained also from a mixture of a chlorinated polyphenylene and a silicone grease[115].

Polyphenylenes having terminal ethynyl groups can be used as binders in polymeric antifriction materials for the production of bearings operating over the temperature range 50–320°C.[116]

Polymers obtained by treating isomeric terphenyls with benzene-*m*-disulphonyl dichloride or benzene-1,3,5-trisulphonyl trichloride at 300–350°C are used for the production of heat-resistant coatings[117]. Such coatings have been obtained also from a mixture of a soluble and a fusible polyphenylene ($\overline{M}_n$ = 500–5000), aromatic sulphonyl halides (e.g. benzene-*m*-disulphonyl dichloride), and an inorganic pigment (titanium dioxide)[118].

Thermosetting polymers of the polyphenylene type are employed as ablative coatings and for the preparation of laminates having high heat resistance[119]. Mixtures of fusible and soluble polyphenylenes were used for these purposes, with 10 wt. % of bishydroxymethylbenzenes as hardeners. $\alpha\omega$-Dibromo-*p*-polyphenylenes are used for the production of heat-resistant coatings[38].

A polymer based on *m*-dibromobenzene, containing *m*-phenylene repeating units, finds application for the manufacture of electrical insulators operating at temperatures of 23–240°C.[120] Hydroxylated *o*-polyphenylenes can be regarded as organic semiconductors[6], having conductivities of 10^{-9}–10^{-8} ohm^{-1} cm^{-1} at 50°C. Alkylated terphenyls are used as heat-transfer agents, regulators, and moderators of neutrons in atomic reactors[62]. Poly(aminohydroxy-*o*-phenylenes) have an inhibiting effect: for example, they prevent the thermal polymerisation of styrene (for up to 1.5 h at 120°C)[114].

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