U.D.C. 541.64:678.674

Aromatic Polyethers

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Aromatic polyethers which have found industrial application are surveyed. The formation, structure, and properties of poly(phenylene oxides) are described. A list of 361 references is included.

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I. INTRODUCTION AND CLASSIFICATION

Aromatic rings and ether bonds are among the chemical groupings which possess great resistance to heat and to thermal oxidation. It is not surprising, therefore, that aromatic polyethers—poly(arylene oxides)—have found wide application as high-temperature materials. Furthermore, the benzene rings in phenyl ethers are not coplanar, but are inclined at an angle to one another[1]. Such arrangement results in absence of resonance conjugation between these rings, so that they can easily rotate relative to one another through a solid angle of 120°.[2] Because of this combination of stability and mobility the arylene oxide unit is very frequently used to confer flexibility on the macromolecules of thermostable polymers. The introduction of such units into macromolecules usually results in an improvement in the solubility and the elasticity of the polymer, while its mechanical and thermal stability are maintained, as has been confirmed experimentally on series of such polymers as the polybenzimidazoles, polybenzothiazoles, polybenzoxazoles[3], polypyromellitimides[4-7], polythiazoles[8], polycarbonates[9-12], polyamides[13], poly-1,3,5-triazines[14], polyesteramides[15], polyquinoxalines[16], polysulphones[17-20], polysulphonamides[21], polybenzylenes[22,23], polyperfluorobenzylenes[24], polyphenylenes[25,26], poly(phenylene borates)[27], etc.

The Dowtherm high-temperature heat-transfer agents—eutectic mixtures of diphenyl ether with biphenyl and naphthalene—which have been known since the 1930s, may be regarded as the first industrial materials of this type[28,29]. The principal subsequent developments on these lines have been due mainly to chemists working for the Dow and Monsanto firms, and in recent years the General Electric Company.

Poly(arylene oxides) are met in Nature only in the form of poly(phenylene oxide) resins having molecular weights up to 5000, in which the ether bonds are oriented in the *meta*-position relative to one another. These resins can be isolated from certain petroleums by repeated reprecipitation with petroleum ether from oxolan solution[30]. No such results are yet available for the *para*-isomers. The possibility of the existence of poly-(*o*-phenylene oxides) is doubtful because of steric hindrance, although they are mentioned in some patents.

With few exceptions the aromatic polyethers which have hitherto been synthesised and investigated have been benzene derivatives. In the literature they are denoted by several different terms. In the present Review we shall use the name *phenylene oxides*. The reason for this choice is that, although all the terms equally reflect the chemical structure of the compounds, only the above name corresponds to those adopted in the chemistry of macromolecular compounds, such as poly(phenylene sulphides), poly(phenylene sulphoxides), polyphenyleneimines, etc.

Phenylene oxides of low and of high molecular weight differ substantially in methods of preparation, properties, and fields of application, and merit separate consideration. In the present Review, therefore, all phenylene oxides are divided into three classes—(*a*) oligomeric phenylene oxides, containing up to 10 benzene rings in the molecule, (*b*) meso(phenylene oxides), containing 10—100 benzene rings, and (*c*) poly(phenylene oxides), containing more than 100 benzene rings, and exhibiting all the properties of high polymers.

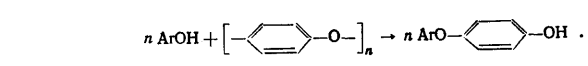
II. OLIGO(PHENYLENE OXIDES)

Oligo(phenylene oxides) can in turn be provisionally divided into two groups—neutral, consisting only of ether bridges and benzene rings having alkyl or halogen substituents; and functional derivatives, containing such groups as hydroxyl, carboxyl, amino, sulpho, etc. in the framework.

1. Synthesis of Neutral Oligo(phenylene Oxides)

The chief method of synthesis consists in building up the chain step by step by the Ullmann condensation of alkali-metal phenoxides or phenoxyphenoxides with aryl halides in the presence of catalytic quantities of copper powder[31-33]. A mechanism of heterolytic substitution had been suggested earlier for this process, but evidence has recently been obtained that the reaction involves the formation of free radicals of phenoxyl type[34,35]. A search for optimum conditions for the synthesis of oligo(phenylene oxides) has shown that, in order to increase the purity and the yield of the required product, the process must be conducted in solution or in suspension in a highly polar organic solvent having a high boiling point, especially in one which is a single-electron carrier, whether in the form of a solvated electron (ether)[36,37] or in the form of a radical-anion (ketone)[38,39]. In several cases copper salts and their complexes are used instead of metallic copper as catalyst. It is sometimes useful to activate the reaction with ultraviolet radiation, iodine, or a free-radical catalyst[40].

The structure of the oligomers is determined by that of the initial compounds: isomerisation has not been observed during synthesis. The initial phenoxyphenols are usually obtained also by Ullmann condensation. A promising method of preparing phenoxyphenols is the "radical acidolysis" of poly(phenylene oxides)[41,42]:



The aryl halides are prepared by the usual methods, and if necessary are isomerised by means of aluminium chloride[43]. The greatest influence on the reactivity of phenoxyphenols in the Ullmann condensation is exerted by substituents located *ortho* and *para* to the hydroxy-group, the reactivity being diminished by electron-acceptor substituents, and increased by electron-donor substituents. The halogen in the aryl halide and the process conditions have a considerably greater effect. It has been found that the activity sequence of the halogens is $I \simeq Br > Cl \gg F$ [44]; in the synthesis of the polyethers $I > Br > Cl$ and *para* > *ortho* ≫ *meta*.

It has been noted several times that the synthesis of oligo(phenylene oxides) is accompanied by several side-reactions. The effect of oxygen is especially injurious, quinones and biphenylquinones being formed in its presence. Since these impurities catalyse decomposition of the oligomers, purification of the final product becomes particularly important. Ordinary fractional distillation and recrystallisation are usually ineffective. The best results are obtained by treatment with silica and alumina in a flow system (chromatography) or in solution with subsequent filtration and fractional distillation, by zone melting, or by treatment with ion-exchange resins or alkali metals[45-50].

2. Synthesis of Oligo(phenylene Oxides) containing Functional Groups

Functional groups are introduced into oligo(phenylene oxides) either by the choice of appropriate initial compounds containing protected functional groups, e.g. alkoxylated aromatic compounds, the protection being removed after condensation, or by appropriate chemical treatment of the neutral oligomers. Since an aromatic ether bond possesses great chemical stability, both methods are quite effective. Thus dihydroxylated oligo(phenylene oxides) have been obtained[10,51] by hydrolysing the dimethoxy-compounds, diepoxy-derivatives[52], and sulpho-derivatives, by treating neutral oligomers with oleum[53], etc. A mixture of mono- and di-hydroxylated oligomers is formed by the action of aqueous alkali on a monochlorodiphenoxide in the presence of copper at 250–350°C.[54] An interesting and evidently promising method for the synthesis of the monohydroxylated oligomers is the oxidative polycoupling of phenols terminated in its early stages. It has been shown experimentally[55-57] that oligomers containing 2–7 benzene rings and one terminal hydroxyl can be obtained in this way. The decomposition of poly(phenylene oxides) of high molecular weight may also yield oligomers containing one or two terminal hydroxy-groups[58,59].

3. Physical Properties of Oligo(phenylene Oxides)

Almost all known oligo(phenylene oxides) are clearly identified chemical compounds. The series of *para*-isomers are crystalline solids, and the *meta*-isomers are viscous liquids at room temperature. The characteristics of some of these compounds are listed in Table 1.

X-Ray examination of a series of oligo-(*p*-phenylene oxides) has shown that the parameters of the unit cell are independent of the length of the molecular chain. All these compounds give the same indices of type *h*, *k*, 0, corresponding to interplanar spacings of 6.79, 5.05, 4.58, 4.22, 3.94, 3.42, 3.67, 2.88, 2.71, 2.56, 2.32, 2.12, 1.89, 1.82, 1.66, 1.60, and 1.50 Å, which represent a crystal lattice having the parameters $a = 9.6$ Å, $b = 6.45$ Å, and $\gamma = 90°$.[60]

Table 1. Characteristics of oligo(phenylene oxides) of general formula $C_6H_5.[OC_6H_4]_n.H$.

n	M.p., °C	B.p., °C	Ref.
	para-Isomers		
2	77	—	2
3	111.0–1.5	—	60
4	153.0–3.5	-	60
5	180.0–1.0	-	60
6	211	—	60
7	222	—	61
	meta-Isomers		
2	61.5	220/0.18	33,62
3	—	214–7/0.7	63
4	—	292–4/2.8	63
5	—	280–3/0.15	63
6	—	318–24/0.15	63
p-$(C_6H_5OC_6H_4)_2$	53.5–4.5	245–811.5	64–66

All neutral oligo(phenylene oxides) are excellent dielectrics, having volume resistivities of the order of $10^{11}-10^{12}$ ohm cm. The electrical conductivity of the series of *meta*-oligomers over this range can be explained by convection currents[67]. A more interesting rule has been observed in the series of *para*-oligomers, whose conductivity at room temperature diminished with increase in the length of the molecular chain; it varied exponentially with rise in temperature, the activation energy being 5.2–7.2 eV, and near the melting points reached a value of the order of 10^{-9} ohm^{-1} cm^{-1}, which was approximately the same for all the compounds investigated[60].

The viscosity of the oligomers diminishes with rise in temperature, but nevertheless remains sufficiently high for them to be used as high-temperature lubricants. In order to obtain oligo(phenylene oxide) lubricants which do not thicken at low temperatures, halogen atoms[68,69] or alkyl groups[70,71] are introduced around the phenylene oxide chain, or else ester or carbonyl groups are included in the chain itself[72-74].

The dielectric properties of the oligomers are preserved over wide ranges of frequency and temperature. Thus *p*-*p'*-chlorophenoxyphenyl phenyl ether has a dielectric constant of 4.57–5.98, a dielectric loss angle of tan^{-1} 0.001–0.0071, and a volume resistivity of 3.1×10^{10} to 3×10^{12} ohm cm.[75]

The infrared spectra of oligo(phenylene oxides) contain all the typical absorption bands of aromatic compounds having the given type of substitution. The characteristic bands due to an aromatic ether bond lie in the range 1210–1230 cm^{-1} and in the region of 1270 cm^{-1} in the cases of the *para*- and *meta*-oligomers respectively. The mass spectra of several of the oligomers have also been investigated[78].

The high radiation stability of the oligomers is especially interesting. According to various workers oligo(phenylene oxides) withstand, without appreciable change in viscosity, irradiation with γ-rays and neutrons of total dosages up to 10^8 rad at temperatures up to 140°C.[79-81] The addition of 1–10% of an acylate, dialkyldithiocarbamate, or a dialkyl phosphorodithioate of an alkaline-earth metal, mercaptobenzothiazole, or a dithiol enables the stability of the oligomers to be raised to 10^9–10^{10} rad.[81-85]

The mechanical properties of the oligomers have been discussed in a review[86].

4. Chemical Properties of Oligo(phenylene Oxides)

As has been stated above, the ether bond in oligo(phenylene oxides) is very inert chemically. It is cleaved only by the action of alkali-metal amides in liquid ammonia[87] or (by a radical-anion mechanism) by interaction with alkali metals in an aprotic solvent in an inert atmosphere[88-90]. In the former case a phenol and an amine are formed, and in the latter case a phenol and biphenyl.

Substitutions in the benzene ring of the oligomers are almost identical with the corresponding reactions in the aromatic series. The ether bridges in the oligomers are able to form complexes with aluminium bromide and several other electron acceptors; the heat of formation of the complex depends on the structure of the oligomer[91,92].

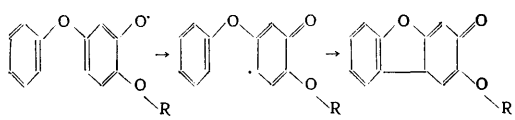
The great resistance of the oligomers to the action of oxidising agents at high temperatures is especially interesting. In air oxidation begins only above 300°C. This stability is responsible for several special applications of oligo(phenylene oxides) (see below). The standard method for testing the oligomers for thermo-oxidative degradation consists[93-95] in bubbling air or oxygen at different rates through a portion of the molten oligomer at a constant temperature, preferably 315°C, for 24 and 48 h. This method is used to determine the relative stability of different oligo(phenylene oxides), the stabilising effect of additives, the influence of contact with various metals on the course of the process and on the corrosive power of the oligomers under these conditions.

Results obtained by different workers indicate that oligo(phenylene oxides) are thermally stable up to 300–450°C and withstand oxidation up to 200–300°C. Wilson and Smith[96] investigated the thermo-oxidative degradation of the oligomers labelled with deuterium and tritium, and found the process to be accompanied by the detachment of hydrogen atoms, predominantly from terminal groups, with the participation of phenyl and hydroxyl radicals, the formation of new C–C bonds, and in the later stages new C–O–C bonds, as a consequence of which macromolecular compounds of phenylene oxide structure are observed among the products of oxidative degradation.

The thermal and thermo-oxidative degradation of unsubstituted, neutral oligo(phenylene oxides) has been investigated systematically by Archer and Bozer[97]. They found the *meta*-oligomers to be considerably less stable than the corresponding *para*-isomers: the latter exhibit self-stabilisation, evidently as a consequence of the formation of dibenzofuran structures in the early stages of oxidation. The tetrameric and pentameric oligo(*m*-phenylene oxides) are thermally stable up to 420°C; after 336 h in air at 315°C the *para*-isomers have absorbed one-tenth of the oxygen absorbed by the *meta*-isomers during 150 h under the same conditions. Mass-spectroscopic and chromatographic examination of the products of thermo-oxidative degradation has shown them to include a bisphenoxyphenyl ether (in the case of the pentamers), a diphenoxybenzene, *o*- and *p*-phenoxyphenol, diphenoxide, phenol, benzoquinone, benzofuran, dibenzofuran, 2-phenoxybenzofuran, and traces of benzenediols, carbon dioxide, and water. Monomeric products constituted 34–48% of the total organic products; the yields of carbon dioxide and water were respectively 0.0003 and 0.0006 mole per gramme of the initial oligomer.

The authors suggested a mechanism of oxidative degradation of oligo(phenylene oxides) initiated by the oxidation by oxygen of an *ortho*- or *para*-position in a terminal benzene ring to a hydroperoxide, which then breaks down into hydroxyl and aryloxyl radicals. The former radical abstracts a hydrogen atom from the next molecule, and the resulting phenyl radical undergoes recombination or adds oxygen; the peroxy-radical thus formed detaches a hydrogen atom from another molecule, and then breaks down into a hydroxy-radical and a new aryloxy-radical, which results in branching of the kinetic chain. Termination of this chain by the coupling of phenyl and hydroxyl radicals will give phenols containing a hydroxyl end-group.

Initial attack by oxygen on an inner benzene ring in the oligo(phenylene oxide) by a somewhat different mechanism yields the same final situation: the initial ether is converted into a number of phenoxyl radicals and substituted phenols. Thus the role of oxygen in this process reduces to the formation of phenoxy-radicals. According to the authors the subsequent course of degradation is determined solely by these radicals. In the case of the *para*-isomers there are two possibilities: if the initial attack takes place *ortho* to the ether bond, the molecule undergoes a quinonoid rearrangement, and then a dibenzofuran structure is formed which stabilises the system:



when the initial attack occurs at the *para*-position, elimination of *p*-benzoquinone followed by chain growth is more probable. Furthermore, the authors accept the possibility of the formation of *o*-benzoquinone, without detailing the mechanism.

Much attention has been paid to the problem of improving the thermo-oxidative stability of oligo(phenylene oxides) by means of various additives or special treatments. As noted above, the stability of the oligomers is substantially influenced by their purity. Further treatment of the oligomers with alkali[98] or alkaline-earth[99] metals, or their oxides or hydroxides[100,101], lengthens the period of service of the oligomers at 300–350°C. A favourable effect is produced by the addition of aryltin halides, trifluoroacetates, or thiocyanates[102-109], arylhalogenoplumbanes and lead acylates[110,111], or triphenylphosphine oxide and tri-*p*-chlorophenylphosphine oxide[112,113]. Among organic compounds the best stabilisers for the oligomers were compounds containing at least one sulphur or halogen atom in the molecule[114], including halogenophenols[115,116], and also phthalimide, anthraquinone, phenyl benzoate, diphenyl phthalate, benzanilide, acenaphtho[1,2-*a*]acenaphthylene, or Schiff bases from 3-aminorhodamine[117-123]. However, organic salts and complexes of metals have proved to be more effective, such as the benzoates and naphthenates[112,124],

dithiocarbamates[125], acetylacetonates[108,126,127], and bis-2-*N*-phenylformimidoyl-5-nitrophenoxides[128] of nickel and cobalt, tricarbonyltristriphenylphosphinyliron[129], and aryl-ferrocenes or -titanocenes[130,131]. The standard mixture of oligo(phenylene oxides) for testing the stabilising action of additives comprised 65% of *mm'm"*-, 30% of *mm'p"*-, and 5% of *pm'p"*-pentaphenylene tetroxide. The same mixture is most widely employed in industry when oligo(phenylene oxides) are used as hydraulic liquids, heat-transfer agents, coolants in atomic reactors, high-temperature lubricants, etc.

5. Uses of Oligo(phenylene Oxides)

Oligo(phenylene oxides) are used either alone or with various additives in many fields besides those mentioned above. Oligomers containing 4–6 benzene rings enable heat transfer to be effected by direct contact between a gas stream and the heat-transfer agent[132]. A study has been made[133] of the dependence of heat transfer on the composition of the oligomer, the character of the surface, the properties of the flow, etc.

In No. 102 diffusion pumps the *meta*-pentamer ensures that a vacuum down to 10^{-9} torr can be obtained[134,135].

Oligo(phenylene oxides) can be used as operating liquids in hydraulic systems at 400°C for up to 600 h, and at 480°C for 80 min[136,137], withstanding loads up to 30 kbar[138]. This has enabled them to be used as fireproof hydraulic liquids for submarines[139].

Elastodynamic film lubricants, greases for gas turbines, and other lubricants based on the oligomers are able to function at 315°C for more than 100 h. Partial fluorination of the oligomers, or the addition of polyphenylenes or chloroperfluoroacylates of heavy metals, enhances the fire-resistance and the oxidative stability of these lubricants, and also improves their properties at high pressures[140–148].

Lubricating greases based on the oligomers, suitable for operating at speeds up to 20 000 rev/min and temperatures up to 300°C, are obtained by introducing into the oligo(phenylene oxide) 5–40% of an acylate of an alkali or an alkaline-earth metal[149,150], 1–2% of a polymethacryate containing C_{22-24} alkyl groups[151], a mixture of 30% of silica gel with 0.5% of asbestos[152,153], 25–50% of esters of polyols with higher fatty acids[154], or a mixture of oligomeric poly(phenylene sulphides)[155].

Oligo(phenylene oxides) are used as lubricants in the machining of thin aluminium sheet and foil at 350–450°C.[156] In several cases their application is determined by their specific chemical properties. It has been noted earlier that sulphonic acids based on the oligomers are surface-active agents[53]. Hydroxy-derivatives of the oligomers are used as strong antiseptics and herbicides[157], and alkylthio-derivatives as pesticides[158]. In combination with substituted phenols and compounds of Group IVa metals oligo(phenylene oxides) stabilise polypropylene to the action of ultraviolet rays[159]. An oligomer can be used as cocatalyst for the Ziegler polymerisation of alkenes[160]. Functional derivatives of the oligomers have been used to obtain polymers of enhanced thermal stability[161].

III. MESO(PHENYLENE OXIDES)

Meso(phenylene oxides) have acquired hardly any intrinsic value in technology. However, considerable experience has been gained in the course of studying their synthesis and properties, and this has subsequently led to the successful synthesis of poly(phenylene oxides).

1. Syntheses from Halogenated Phenols

The first person to obtain a synthetic meso(phenylene oxide) was probably Benedict, who in 1879 investigated the decomposition of 2,4,6-tribromophenol at 130°C, and obtained an amorphous powder whose composition corresponded to the formula $C_6H_2Br_2O$.[162] As Hunter showed later, this was undoubtedly a polymeric product of not very high molecular weight. A similar result was obtained by Castle[163].

The polycondensation of halogenated phenoxides was investigated later by a group of chemists under the direction of Hunter[164]. They found that britle amorphous polymers were formed when suspensions of the 2,3,6-trichloro-, 2,4,6-tribromo-, and 2,4,6-tri-iodophenoxides, 2,4,6-tribromo-3-methoxyphenoxide, and other halogenated phenoxides of silver were heated in benzene or in ethyl iodide at 60°C or in the form of the dry powders. Silver 2,4,6-tribromophenoxide reacted with ethyl iodide to form a dark blue solution, which gradually became brownish yellow, and then deposited silver bromide; alcohol precipitated from the solution an amorphous product of molecular weight 6600 and empirical formula $C_6H_2Br_2O$. A systematic study of the process revealed the following rules: (*a*) in the case of the trihalogenated compounds the reaction took place predominantly in the *para*-position; (*b*) the activity of the halogens diminished in the sequence iodine–bromine–chlorine; and (*c*) only those halogen atoms which were attached directly to a hydroxylated benzene ring reacted under the conditions investigated.

Conclusions (*b*) and (*c*) are confirmed by the dehalogenation by mercury of 2,6-dibromo-4-(4-chloro-2,6-di-iodophenoxy)phenol and 4-(4-chloro-2,6-di-iodophenoxy) phenol: only bromine is abstracted from the former compound, whereas the latter does not react at all. The colour of the meso(phenylene oxides) obtained is probably due to the formation of biphenylquinonoid units in the chain, for it disappears on reduction of the polymer. Additional confirmation has been obtained by means of infrared spectroscopy.

"Mesomeric" phenylene oxides of the same type are formed also by (i) the action of mercury on 2,4,4,6-tetrabromocyclohexa-2,5-dienone, (ii) the action of iodine on potassium trichlorophenoxide in aqueous or benzene medium, and (iii) the electrolysis of silver halogenophenoxides.

Golden[165] has prepared several meso(phenylene oxides) of this type using a modification of Hunter's method. The properties of the products are listed in Table 2. From solutions they all yield only brittle films, as was to be expected for polymers of low molecular weight. The possibility of the formation of dibenzodioxan was also noted in the course of this work; with pentachlorophenol the reaction could be controlled to give mainly polymers in which the unit was either C_6Cl_4O or 2,3,4,5,7,8,9,10-octachlorodibenzodioxan.

Rainford and LeRosen[166] obtained a dark blue meso(phenylene oxide) of molecular weight 1800 by heating sodium 2,4,6-tribromo-3-fluorophenoxide. Blanchard and his coworkers[167] developed Hunter's work further, and found that 2,4,6-tribromo-3-methoxyphenol in the

presence of iodine in benzene, and 2,4,4,6-tetrabromocyclohexa-2,5-dienone in the presence of metallic mercury, give initially a green polymer, which when subsequently dissolved in benzene and allowed to stand became decolourised. At the same time the molecular weight of the polymer doubled, probably as a result of coupling and the formation of dienone structures.

Table 2. Meso(phenylene oxides) synthesised by Golden[165].

Phenoxide substituents	metal	Polymer yield, %	softening point, °C	mol. wt.
p-Chloro-	K	4	356—260	2800
2,4-Dichloro-	Na	45	270—273	—
2,4-Dibromo-	Na	81	240—245	—
2,4,5-Trichloro-	Na	37	215—220	—
2,4,6-Trichloro-	Na	90	185—186	4800
2,4,6-Trichloro-	Ag	79	185—188	9600
2,4,6-Tribromo-	K	60	244—246	3200
2,3,4,6-Tetrachloro-	Na	78	219—222	—
2,3,4,6-Tetrachloro-	Ag	80	213—235	—
Pentachloro-	Ag	73	192—194	1500
Pentabromo-	Na	63	300—310	—

The free-radical mechanism of the condensation of halogenated phenols to meso(phenylene oxides) has been proved by work on the oxidation of these phenols by aryloxy-radicals[168], benzoyl peroxide[169-171], lead tetraacetate or dioxide[172], or copper(II) acylates[173], in which trichloro-, tribromo-, tri-iodo-, and pentabromo-phenols gave meso(phenylene oxides) having molecular weights of 2000–5000, melting points from 165° to 265°C, and cyclohexadienone terminal groups; potassium pentafluorophenoxide in the presence of copper(II) oxide yielded the corresponding polymer of molecular weight 1700–4300.[174]

The formation of meso(phenylene oxides) from *m*-halogenophenols has been investigated by Brown and his coworkers[175-180]. They find that the Ullmann polycondensation of *m*-bromophenol takes place at 150–220°C to give the corresponding meso(phenylene oxide). Catalysis by copper salts results in branched products. In the presence of polar solvents secondary reactions involving C–C coupling predominate. The exothermic character of the reaction results in cross-linked products when the process is accomplished in the mass. Optimum results are obtained in a system formally analogous to suspension polymerisation, with high-boiling aliphatic hydrocarbons used as reaction medium. With appropriate preparation and purification of the catalyst (metallic copper) it is possible to obtain by this method meso(phenylene oxides) having molecular weights from 4000 to 10000 in the form of solid powders suitable for the production of filled plastics which are thermostable up to 500°C.[175,176].

2. Synthesis of Meso(phenylene Oxides) by the Decomposition of 4-Diazocyclohexadienones

The second general method used in attempts to synthesise meso(phenylene oxides) was the decomposition of "*p*-benzenediazo-oxides" [4-diazocyclohexadienones]. It was assumed that such decomposition would involve the intermediate formation of a biradical



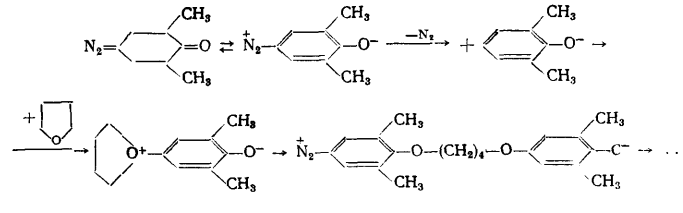
which would probably polymerise to a poly(phenylene oxide). Süs and his coworkers[181] studied the decomposition of 4-diazocyclohexadienone in various solvents under the influence of ultraviolet radiation. In all cases products containing solvent molecules were obtained. Similar results have been found by Wang[182]. In methanolic solution the main product was *p*-methoxyphenol. In boiling benzene *p*-phenylphenol was formed in almost theoretical yield. At room temperature a small quantity of a phenolic resin melting at 300°C could be isolated together with a phenylphenol from benzene solution.

An elastomer having good thermal stability could be obtained by decomposing a fluorinated "diazo-oxide"[183].

Dewar[184] investigated the thermal decomposition of 2,6-dibromo-4-diazocyclohexadienone in chlorobenzene. He hoped that blocking the oxygen by means of adjacent bromine atoms would diminish secondary reactions, including those in the *ortho*-position relative to the oxygen. This method yielded only polymers of low molecular weight (1600–6600) soluble in chloroform, with softening points of 200–220°C. Elementary analysis showed that the polymer contained chlorine as well as bromine, indicating that the solvent had taken part in the reaction. Conducting the same reaction in chlorobenzene containing 1% of methanol or water diminishes the yield of polymer, several benzene derivatives of low molecular weight being formed. The author regards these results as confirming the intermediate formation of a biradical similar to the above.

Kunitake and Price[185] studied the decomposition of 4-diazo-2,6-dimethylcyclohexadienone in a series of solvents under the influence of heating and ultraviolet irradiation. The diazonium salt, prepared by the usual method, was extracted from aqueous solution in an organic solvent, in which it was then decomposed. In benzene solution only 2,6-dimethyl-4-phenylphenol is formed by the action of light and heat. From chlorobenzene solution unchanged diazonium salt and *o*- and *p*-chlorohydroxybiphenyls were isolated, which was taken as evidence that an intermediate biradical was involved in the reaction.

The heating or ultraviolet irradiation of 4-diazocyclohexadienone in oxolan or dioxan yields semi-solid products of molecular weight 1400 or a powder of melting point 60–70°C. The ratio of the areas of the peaks for aliphatic and aromatic protons in the nuclear magnetic resonance spectrum of these products indicates a structure in which the ratio of tetramethylene oxide and phenylene oxide units is about 1 : 1. This is supported by elementary analysis. The facts that the polymers have the same composition independently of the conditions of this reaction and that some of the polymers are shown by X-ray diffraction to be crystalline indicate a structure with a regular alternation of aliphatic and aromatic units. The mechanism suggested for the reaction is



It is interesting that the "diazo-oxide" reacts to form either a biradical or an ionic intermediate compound depending on the solvent.

A similar formation of alternant copolymers has been observed by Stille et al.[186] when diazocyclohexadienone

reacts with 1,4-epoxycyclohexane or with 2,2-bischloromethyloxetan. No copolymer could be obtained with methyloxiran[187].

Dimerisation and ring-closure have also been observed in several experiments on the decomposition of 4-diazocyclohexadienones.

With the exception of the work of Wall[183], in which the intermediate biradical may have been stabilised by the electron-acceptor effect of fluorine, and work by Price and Stille on copolymers, the use of diazo-compounds to prepare poly(phenylene oxides) has proved to be on the whole unsuccessful.

3. Other Methods for the Synthesis of Meso(phenylene Oxides)

Several other routes to the synthesis of meso(phenylene oxides) have been tried by various workers. Golden[165] and Briner[188] were unsuccessful in attempting to synthesise poly(phenylene oxides) by the dehydration of polyhydric phenols. Paushkin and his coworkers[189,190] conducted this reaction in the presence of zinc chloride at 200°C, but obtained only oligomers of molecular weight exceeding 1000 and softening points of 310–330°C. Treatment of phenols with iron(III) chloride gave similar results[191]. Although a polyphenylene structure was attributed to the products, their properties, especially the infrared spectra, were closer to those of known meso(phenylene oxides), not those of polyphenylenes.

Price[192] prepared a cross-linked polymer, in the form of a powder containing 12% of a soluble oligomeric fraction, by the decomposition of 4-acetoxymercuri-2,6-dimethylphenol.

An interesting method for synthesising a polymer containing alternating poly-*p*-phenylene and poly-(*p*-phenylene oxide) units was found by Stille and his coworkers[25], who accomplished a Diels–Alder polycondensation between 3,3-(oxydi-*p*-phenylene)-2,4-bistriphenylcyclopentadienone and *m*- and *p*-diethynylbenzene in toluene solution at 200°C.

A series of meso(phenylene oxides) were synthesised as insoluble, infusible powders of molecular weight 4000–7000 (from end-group analysis) or soluble resins of molecular weight 1000–2000 by Cox et al.[193], who subjected alkali-metal halogenophenoxides to thermal decomposition in the absence of a catalyst.

Meso(phenylene oxides) have been prepared also by the radiolysis of diphenyl ether[81] and by the Williamson polycondensation of dihydric phenols with bis-*p*-chloromethylphenyl ether[23,194,195]. In neither case was the structure of the products proved, and the molecular weight did not exceed 2000. Molecular weights up to 2300 have been obtained[196] by the condensation of oligo(phenylene oxides) with arenedisulphonyl chlorides. Several meso(phenylene oxides) have been synthesised by the oxidative polycoupling of phenols. Since this reaction is discussed in the following Section, information on these compounds will be given there.

Almost all meso(phenylene oxides) are dark coloured, friable powders which, although exhibiting certain properties characteristic of polymers, have not yet found practical application.

IV. POLY(PHENYLENE OXIDES)

As has been indicated in the preceding Section, the history of the synthesis of poly(phenylene oxides) of high molecular weight has been characterised by perennial unsuccessful attempts. The best results were obtained when the intermediate formation of radicals of phenoxyl type was possible under the conditions of polycondensation of halogenated phenols. The approach to catalysts for the process was therefore reviewed: metallic copper was replaced by oxides and complex salts of the metal, as a result of which polymers of high molecular weight could be obtained in good yield not only from halogenated phenols but also from phenols containing no *ortho*- or *para*-substituents.

The early failures are explained by the inadequate mobility of the halogen in these monomers, as is confirmed by the relatively easy preparation of polymers containing arylene oxide units by the polycondensation of diphenoxides with aromatic dihalides activated by a strongly electron-acceptor nuclear substituent, such as sulphonyl, nitro, or fluorine. For example, a polymer prepared from the disodium salt of bisphenol A and bis-*p*-chlorophenyl sulphone has already become available commercially[19,197,198]. This reaction is accomplished in a dipolar aprotic solvent by heating in the absence of oxygen and moisture at 130–140°C for 4–5 h. Several polymers of this type are listed in Table 3.

Table 3. Poly(arylene oxides) synthesised by nucleophilic substitution of halogen.

Diol	Dihalide	Glass point T_{gl}, °C
2,2-Diphenylpropane-*pp'*-diol	di-*p*-chlorophenyl sulphone	19
1,1-Diphenylethane-*pp'*-diol	ditto	200
Diphenylmethane-*pp'*-diol	"	180
Quinol	"	1
1,3-Diphenylethylcyclohexane-*pp'*-diol	"	230
1,1-Diphenylisopropylethane-*pp'*-diol	"	200
pp'-Dihydroxybenzophenone	"	205
Tetraphenylmethane-*pp'*-diol	"	230
Di-*p*-hydroxyphenyl sulphone	"	*
Di-*p*-hydroxyphenyl ether	"	180
2,2-Diphenylpropane-*pp'*-diol	*pp'*-difluorobenzophenone	155
2,2-Diphenylpropane-*pp'*-diol	2,4-dichloronitrobenzene	150
2,2-Diphenylhexafluoropropane-*pp'*-diol	di-*p*-fluorophenyl sulphone	205
2,2-Diphenylhexafluoropropane-*pp'*-diol	*pp'*-difluorobenzophenone	175

* Softening point 310°C.

A similar result is obtained by treating pentafluorophenol with caustic soda in pyridine[199]:

$$C_6F_6 + NaOH \rightarrow C_6F_5ONa \rightarrow [-C_6F_4O-]_n .$$

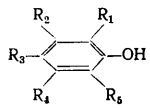
Heterolytic nucleophilic substitution is usually difficult in the aromatic series. Poly(phenylene oxides) can be successfully synthesised probably only by homolytic substitution of halogen, as is confirmed both by the coloration noted by Hunter and by Blanchard and by the sequence of activity of the halogens—I > Br > Cl—observed by Hunter, for the opposite sequence—F > Cl > Br > I—is found with heterolytic substitution[200].

An unexpected result has been found by Bolton and his coworkers[201,202], who have obtained insoluble films of poly(phenylene oxides) by the prolonged heating of *p*-phenoxyphenols in air at 330°C. This method of synthesis is an example of oxidative coupling.

During the past 10–15 years, in the course of work on the oxidation of phenols under various conditions, in particular in the synthesis of biphenylquinones by this

method, formation of a certain amount of an amorphous polymeric byproduct has been observed[203-207]. More careful study and development of this line of research led Hay[208] and Price[192] to the almost simultaneous discovery in 1959–1960 of a new method of synthesising poly(phenylene oxides) of high molecular weight by the oxidative polycoupling of phenols and halogenated phenols. Poly-(2,6-dimethyl-1,4-phenylene oxide) was synthesised from 2,6-xylenol by the action of oxygen in the presence of a copper–pyridine catalyst or interfacially from 4-bromo-2,6-xylenol in the presence of potassium hexacyanoferrate(III) in the benzene–aqueous alkali system. Poly-(phenylene oxides) have since been obtained by the same and similar methods from several dozen other phenols.

Table 4. Poly(phenylene oxides) obtained by oxidative coupling of phenols of the type.

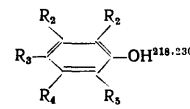


Substituents					Yield, %	Intrinsic viscosity, dl g^{-1}	Mol. wt.	Ref.
R_1	R_2	R_3	R_4	R_5				
Me	H	H	H	Me	85	0.72	31000	213
Me	H	H	H	Et	82	0.40	25400	213
Me	H	H	H	OMe	60	0.27	13000	213
Me	H	H	H	Pr^i	62	0.24	15350	213
Me	H	H	H	Ph	60	oil	—	213
Ph	H	H	H	Ph	46	0.05	—	213
Et	H	H	H	Et	81	0.53	32000	213
Me	H	H	H	All	—	oil	—	213
All	H	H	H	All	—	oil	—	213
OMe	H	H	H	OMe	30	—	2450	214
Me	H	H	H	H	22	oil	—	218
Me	H	H	H	H	82	—	15000	219
H	Me	H	H	H	35	—	800	220
H	Me	H	Me	H	10	—	1000	220
Me	H	Me	H	Me	79	—	1800	221
Me	Me	H (Br)	Me	Me	0	—	—	192
Me	H	H	H	Cl	88	0.47	71000	213
Me	H	H	H	Br	18	0.03	—	213
Cl	H	H	H	Cl	70	0.16	4000	222
Br	H	H	H	Br	—	—	3800	223
Cl	H	H	H	H	30	—	4750	224
Br	H	H	H	H	60	—	5500	224
Me	H	Cl	H	Me	92	1.20	65000	224
Me	H	Br	H	Me	85	0.40	14000	225
Cl	H	Cl	H	Cl	75	—	13000	226
Br	H	Cl	H	Br	—	0.01	—	225
Cl	H	Br	H	Cl	90	0.07	11000	225
Br	H	Br	H	Br	90	0.02	2300	225
Cl	Cl	Cl	Cl	Cl	87	0.02	—	225
Br	Br	Br	Br	Br	0	—	—	192
H	Cl	H	Cl	H	20	—	1900	227
OR	H	H	H	H	34	0.26	—	228
Me	H	H	H	Ph	55	0.88	—	229
Ph	H	H	H	Ph	75	0.80	—	229

The results are summarised in Tables 4–6. An emulsion method of synthesis has been patented[209]. Complex compounds of almost all metals of variable valency were used as catalysts. Electrochemical synthesis has also been tried[210-212]. Replacement of pyridine by its derivatives and the introduction of platinum black into the system have enabled the poly(phenylene oxides) to be obtained from phenols which do not polymerise under ordinary conditions (Table 5).

Only the two original methods of synthesising poly-(phenylene oxides)—the hexacyanoferrate(III) and copper–amine processes—have been investigated in any detail. Though sharing many common features, they have several individual characteristics, and will therefore be discussed separately.

Table 5. Synthesis of poly(phenylene oxides), on an activated copper–amine catalyst, from phenols of the type.



Substituents					Intrinsic viscosity, dl g^{-1}	Cocatalyst
R_1	R_2	R_3	R_4	R_5		
CH_3	H	H	H	H	0.10	2-benzylpyridine
H	H	H	H	H	0.20	2-methyl-6-undecylpyridine
CH_3	H	H	H	H	0.39	2-ion-5′-ylpyridine
C_6H_5	H	H	H	H	0.11	2-benzylpyridine
H	C_6H_5	H	H	H	0.66	2,4,6-trimethylpyridine
CH_3	CH_3	H	CH_3	CH_3	0.92	platinum on carbon

1. Polymerisation initiated by Potassium Hexacyanoferrate(III)

Staffin and Price[192] found that poly(phenylene oxides) of molecular weight 4000–7000 are formed from 4-bromo-2,6-dimethylphenol in the presence of oxidants of the type potassium hexacyanoferrate(III), lead dioxide, etc. The reaction is initiated by ultraviolet irradiation, iodine, and phenoxy-radicals. The correctness of the 1,4-chain structure was confirmed by the nuclear magnetic resonance, infrared, and ultraviolet spectra. When polymerisation is initiated by phenoxy-radicals, excess of alkali is required: otherwise the polymerisation slows down[231,232]. This suggests that initiation consists in oxidation of the phenoxide anion to the phenoxy-radical.

Since the bromide ion is quantitatively precipitated during the process, chain growth may be supposed to occur by replacement of the *para*-bromine atom, probably with the formation of some intermediate state, i.e. that on the whole the process is a classic case of oxidative coupling. In an inert atmosphere polymerisation ceases soon after introduction of the catalyst, and the "frozen" process is revived by a fresh portion of catalyst; the molecular weight of the poly(phenylene oxide) does not exceed 10 000.[233] In air polymerisation continues until the monomer is completely converted, and the molecular weight reaches 40 000–50 000. In neither case is a direct relation between molecular weight and degree of conversion observed. The authors therefore regard this process as similar to the free-radical polymerisation of vinyl monomers. The mechanism of the action of oxygen consists in chain transfer by means of the hydroperoxy-radical.

End-group analysis combined with osmometry showed that 0.1 phenolic hydroxyl and 4 bromine atoms were associated with each macromolecule. This was explained either by the formation of ethers of quinol similar to those obtained by Dimroth[234] or by branching of the polymer chain resulting from attack by a phenoxylic macroradical at the middle of a neighbouring chain.

Considerable attention has been paid to the effect of substituents in the phenols. In the view of Staffin and Price[192] 4-bromodurenol and pentabromophenol do not polymerise because of steric hindrance to the approach of a phenoxy-radical to a bromine atom. Poly(phenylene oxides) from 2,6-disubstituted 4-bromophenols are listed in Table 6.[235,236]

Table 6. Effect of substituents on the polymerisation of 2,6-disubstituted 4-bromophenols[235,236].

R_3	R_4	Intrinsic viscosity	Product
$-CH_3$	$n\text{-}C_3H_7$	0.15	polymer
$-CH_3$	$-CH_2CH=CH_2$	0.17	polymer
$-CH_2CH=CH_2$	$-CH_2CH=CH_2$	0.15	polymer
$n\text{-}C_3H_7$	$-CH_2CH=CH_2$	0.11	polymer
$n\text{-}C_3H_7$	$-C_6H_5$	0.10	polymer
$-CH_2CH=CH_2$	$-C_6H_5$	0.11	polymer
$-H$	$-H$	—	biphenylquinone and oligomers
$-CH_3$	$-COOCH_3$	—	polymer
$-CH_3$	F	—	minute amounts of semi-solid products
$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	—	no polymer

Table 6 shows that introducing a phenyl, allyl, or n-propyl group into an *ortho*-position yields poly(phenylene oxides) of low molecular weight. The allylic double bond is then inactive towards the growing radical and the catalyst: such great liability of phenolic hydroxyl to oxidation in comparison with an ethylenic double bond has been observed previously[237]. An attempt to polymerise 4-bromo-2-vinylphenol by this method resulted in an amorphous powder containing 80–90% of bromine based on the amount calculated for the monomer, probably as a consequence of a complicated growth reaction involving the double bond.

Polymerisation does not take place with bulky substituents such as t-butyl or strong electron acceptors such as $COOCH_3$ or fluorine.

A polymer containing reactive groups in its framework is interesting as a basis for several polymerlike reactions. Allylphenols themselves do not polymerise readily, but with xylenol they give various copolymers having molecular weights up to 50 000.[238-241]

2. Polymerisation initiated by Amine Complexes of Copper Salts

Although the interfacial polycondensation of halogenated phenols does enable copolymers to be obtained, the low molecular weight of the poly(phenylene oxides), the complicated technology, and the use of expensive monomers restrict its application. The homogeneous oxidative coupling of phenols is free from these defects and permits delicate control of the activity of the catalyst (Table 5). The use of a copper–amine catalyst for synthesising poly(phenylene oxides) from *p*-halogenophenols in the absence of oxygen revealed the necessity of using stoichiometric or even greater quantities of catalyst relative to the monomer[219], which is consistent with results for the catalytic activity of basic copper salts alone[242,243]. 4-Bromo-2,6-dinitrophenol and 4-bromo-2,6-dichlorophenol did not yield polymers by this method, and only an oil of low molecular weight was obtained from a 2-aryl-4-bromo-6-methylphenol.

The secondary formation of biphenylquinones during the synthesis of poly(phenylene oxides) had already been noticed in Hay's early work[213]. Further investigations established that polymerisation (C–O coupling) and the formation of the quinones (C–C coupling) are competitive reactions, depending on the substituents and the amine : copper (N/Cu) ratio. The larger the substituent the more readily is a biphenylquinone formed (Table 7).

Table 7. Formation of biphenylquinones.

R_3	R_4	Yield, %	M.p., °C
$-CH_3$	$t\text{-}C_4H_9$	45	217
$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	97	246
$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	53	255
$-OCH_3$	$-OCH_3$	74	>300

Interesting results have been obtained for the oxidation of 2,6-xylenol. The highest rate of absorption of oxygen by the reaction mixture was observed at a ratio N/Cu ≃ 100, whereas formation of biphenylquinones was noted only at N/Cu < 10.[244] The specific rates of C–O and C–C coupling were calculated by means of the equations

$$R_{C-O} = f_P \cdot R; \quad R_{C-C} = f_Q \cdot \frac{R}{2}$$

where f_P and f_Q are the yields of poly(phenylene oxides) and biphenylquinones respectively, while R is the actual rate of absorption of oxygen. Table 8 shows that both R_{C-O} and R_{C-C} increase with increase in N/Cu, with the former increasing more rapidly, so that polymerisation predominates.

Table 8. Specific rates of C–C and C–O coupling of 2,6-dimethylphenol under the influence of oxygen on a copper–pyridine catalyst.

N/Cu	$10^4 \cdot R_{C-O}$	$10^3 \cdot R_{C-C}$
0.67	0.0065	0.0256
1.0	0.0338	0.0505
2.0	0.267	0.112
3.0	0.639	0.162
10.0	3.90	0.270

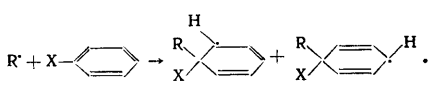
Later Blanchard et al.[245,246] have shown that the polymers and the quinones are formed on catalysts differing in structure, which are present together in the reaction system.

A study of the relation between degree of conversion (from the absorption of oxygen) and the molecular weight of the poly(phenylene oxide) established[244] that the latter was not very high up to 80–90% of the theoretical absorption of oxygen, but increased rapidly as the stoichiometric quantity was approached. In view of this it was at first assumed that this was a process of step-by-step increase

in molecular weight, akin to polycondensation, as was supported indirectly by the ability of dimers and trimers to give a polymer identical with that obtained from the monomer. Since neutral oligo(phenylene oxides) are inert solvents for the process [247,248], a mechanism was suggested in which oxidation of an oligomeric phenoxide anion to the phenoxy-radical is followed by migration of the unpaired electron along the polymer chain from its "tail" to its "head", so that the "head" again becomes anionic, and the "tail" a radical-ion. Addition of the radical "head" of a monomer or an oligomer to such a "tail" makes the number of electrons in the system even, after which the process is repeated [249]. An alternative mechanism was proposed by Cooper, who used trimethylchlorosilane to terminate the polymerisation of dimers at an early stage, and observed considerable quantities of monomer and trimer among the products [55-57]. On the basis of these results a new scheme—of quinol ether equilibrium disproportionation—was set up. The use of labelled atoms [250,251] revealed that exchange of protons in *meta*- and *para*-positions occurred during polymerisation, which was explained by a fresh scheme involving a phenonium intermediate compound (Scheme 2). It was suggested that the hexacyanoferrate(III) and copper–amine methods of synthesising poly(phenylene oxides) occurred by different mechanisms. It was found, however, that the dimeric 4-(4-bromo-2,6-dimethylphenoxy)-2,6-dimethylphenol polymerised in the same way by both methods [252], which could be explained only by the same mechanism—quinol ether equilibrium disproportionation—operating in both cases.

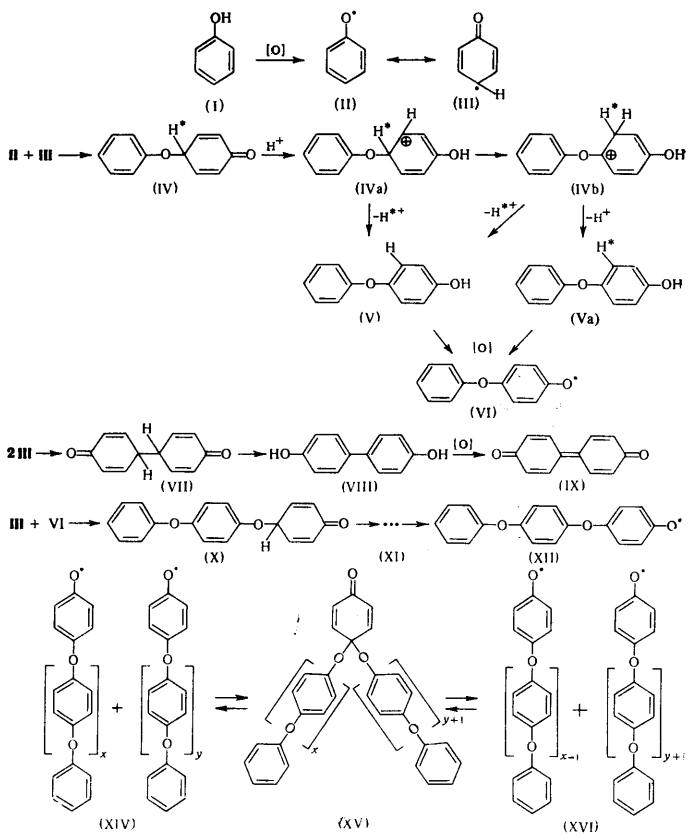
Taking this into account, McNelis [268] represented his own and published experimental results by a fundamentally different general scheme of oxidative polycoupling of phenols to form poly(phenylene oxides) and biphenylquinones (Scheme 1). Analysis of this scheme reveals several defects:

1. The formation of biphenyldiols (VIII) and biphenylquinones (IX) is in no way related to the composition or the structure of the catalyst.
2. The scheme is applicable only to phenols in which the *para*-position is unsubstituted.
3. The stage of conversion of quinol ether (IV) into aryloxyphenol (V) and aryloxyphenoxyl (VI) involves hydrogen ions and should depend on the pH of the medium. In practice, however, replacement of pyridine by trihexylamine and other amines has hardly any effect on the results [24], and the acceleration of the reaction in the presence of caustic alkalis [269-271] is inconsistent with such a mechanism.
4. Coupling of the isomeric radicals (II) and (III) was presented as probability processes. According to this scheme no biphenylquinone is formed if the system contains very little or no radical (III), but in such case nor could a polymer be formed. Moreover, this scheme takes no account of the work of Milyutinskaya [272], de Tar [273], or Grashey [274], who showed that the addition of free radicals to a benzene ring resembles their addition at a C=C bond:

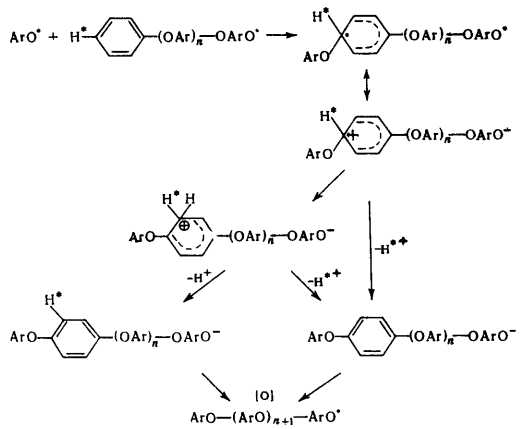


Kopylov and Pravednikov [275] were the first to show experimentally that the synthesis of poly(phenylene oxides) by this method involves free radicals of phenoxyl type, and this was soon confirmed by Waters [276]. Conversion of the monomer, formation of the polymer, and the variation in content of e.p.r. detectable species in the reaction system

Scheme 1 (Ref.268)



Scheme 2



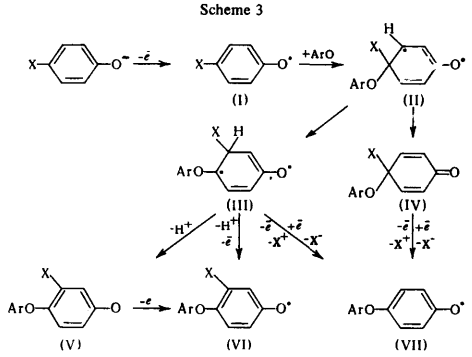
(where H* = H, D, T).

were used to investigate the kinetics of the process, and a new generalised scheme was suggested [277] in which the process consisted of a series of consecutive reactions of the first order with respect to the monomer and having activation energies of 16–17 kcal mole^{-1} (Scheme 3). On the whole the mechanism of the oxidative polycoupling of phenols to poly(phenylene oxides) is ambiguous, being determined by the oxidisability of the phenol and the nature of the *para*-substituents and also by the oxidant used. The former group of factors can be assessed quantitatively from the distribution of electron density in the phenoxyl radical,

which can be estimated from the critical oxidation potentials, the pK of the phenols, or the Hammett constants.

Only certain empirical rules can be derived for the latter group of factors. The catalysts used for the synthesis of poly(phenylene oxides) have been various salts and complex compounds of silver [268,278], cupric and cuprous copper [252-267], and lead [208,214-216], oxides, chelates, and halides of cobalt and manganese [279-285], manganese dioxide [217,221], potassium permanganate [286], nickel peroxide [287,288], iron complexes [192], persulphates [289], organic and inorganic peroxides [169-171], compounds of mercury [290], chromium, iodine, and many compounds of Groups IV – VI elements [291,292], and tri-t-butylphenoxyl radicals [293]. It has also been shown that poly(phenylene oxides) are formed by the oxidation of *p*-phenoxyphenols by air in the absence of a catalyst [201], by their oxidation with chlorine in the presence of copper salts [294], and by the electrolytic oxidation of phenols [211].

Scheme 3



and then as XIV-XV-XVI in Scheme 1, where X = H, D, T, Hal, etc.

It was found here that phenols of low pK yield a polymer only when catalysts of high oxidation potential are used, and conversely. Furthermore, it was definitely established that the activity of the catalyst could be controlled by varying the coordinated ligands. Thus poly(phenylene oxides) of high molecular weights are obtained by the polycondensation of sodium *p*-halogenophenoxides in the presence of complexes of copper(I) chloride with organic compounds containing a tertiary nitrogen atom. The yield and the molecular weight of the polymer vary with the ligand used [295,296]. A similar rule has been noted in the oxidative coupling of amines to give azo-polymers [297].

3. Secondary Processes

Besides the formation of biphenylquinones, several other secondary processes, especially oxidation of the skeleton, complicate the oxidative polycoupling of phenols to form poly(phenylene oxides). Many workers have noted that the resulting polymer is yellowish or reddish, the colour not being removed or even weakened by repeated reprecipitation or purification by Soxhlet extraction. The presence of an absorption band in the region of 1660 cm^{-1} in the infrared spectra of such polymers and the weakening of the colour under the influence of reducing agents indicate that the colour is due to quinonoid groups entering the polymer chain [298]. Peroxy- and hydroperoxy-groups are probably present in poly(phenylene oxides) [192,299-301]. Up to one carboxyl per twenty chain units has been found in the polymer [219,298], its formation being explained by the presence of peroxides in the reaction system. In several cases cross-linked, insoluble, or thermosetting polymers are formed during the synthesis, which can be explained by the production and interaction of functional groups in the skeleton of the polymer chain. The occurrence of such "defects" is due to replacement of the catalyst—of copper halides by acylates—or to a rise in the temperature of the synthesis above a critical value.

When 2,6-xylenol is polymerised in a mixture of chlorobenzene and methanol, the molecular weight of the resulting poly(phenylene oxide) is inversely proportional to the mole fraction of methanol, this being due to precipitation of the polymer when it reaches a certain molecular weight [302].

4. Properties of Poly(phenylene Oxides)

Published information on the properties of poly(phenylene oxides) is extensive and varied—from advertising matter to special reviews and references in textbooks and monographs [303-310]. Only general technical and working properties will be discussed here: questions of the mechanism of synthesis and thermal degradation are discussed elsewhere.

At the present time only poly-(2,6-dimethyl-1,4-phenylene oxide) (2,6-p.ph.o.) is produced on an industrial scale, being manufactured by the General Electric Company in the USA, by A. K. U. in Holland, and by Hodgson-Thomson [*sic*] in France. It is a thermoplastic, non-crystalline linear polyether. The material can be welded by means of ultrasonic vibrations and cemented with organic solvents. Injection moulding and extrusion are effected in standard equipment at 288 – 343°C, the duration of the casting cycle being 15 – 30 s and the pressure employed 850 – 1400 atm. The mould should first have been heated to 120 – 150°C to improve filling; the mould is emptied at 190°C. Preliminary mastication on worm machines is recommended to shorten the casting cycle. This process is used to make tubes, profiled articles, rods, insulation for wire, parts for mechanical and electrical equipment, wood screws, etc. The resistance to heat and moisture and their great chemical stability enable 2,6-p.ph.o. to compete with alloy steel and fluorinated plastics for operation in corrosive media at high temperatures. The high resistance to arcing and the low dielectric loss angle of 2,6-p.ph.o. enable it to be used for the manufacture of parts for electronic equipment. The good dielectric properties permit the employment of this polymer for the electrical insulation of high-voltage lines.

Two brands of 2,6-p.ph.o. —C-1001 pure polymer and Noryl modified polymer—are manufactured on an industrial scale. Furthermore, foam plastics are also obtained from C-1001. [311,312].

The chief characteristics of these materials are listed in Table 9. Goods made of C-1001 withstand 200 treatments in a sterilisation autoclave without change in appearance or mechanical properties. The polymer resists the action of mineral acids and alkalis, salt solutions, organic acids, and aliphatic hydrocarbons and alcohols, swells slightly in ketones, and dissolves in aromatic hydrocarbons, halogenated hydrocarbons, and certain cyclic ethers. Although 2,6-p.ph.o. is usually amorphous, it crystallises on the prolonged heating of a 2-pinene solution [313]. The parameters of the unit cell are a = 8.45 Å, b = 6.02 Å, and γ = 91°1′. The dielectric characteristics of the polymer do not vary by more than 20% over the temperature range from –80° to +160°C and

the frequency range $10-10^8$ c/s.[314] The dependence of certain properties of 2,6-p.ph.o. on molecular weight is given in Table 10.

Such almost unique combination of properties with simplicity of production and processing ensure for 2,6-p.ph.o. wide practical applications—from high-frequency insulation to parts of chemical equipment, from surgical instruments to units in the construction of sputniks. Information is available on the production from it of films and fibres by spinning from solutions and melts[315-317].

Table 9. General characteristics of poly(phenylene oxides).

Property	Units	C-1001	Noryl
Tensile strength at 23°C	kgf cm^{-2}	750	675
Tensile strength at 125°C	ditto	420	—
Modulus of elasticity at 23°C	»	26000	24500
Modulus of elasticity at 125°C	»	23000	—
Relative extension on rupture at 23°C	%	80	20
	%	9	8
Residual extension at 23°C	%	0.75	—
Cold flow at 23°C under 200 kgf load after 300 h	kgf cm^{-2}	1000	—
Bending strength at 23°C	kgf cm cm^{-2}	750—970	—
Impact strength	—	118	119
Rockwell hardness	g/1000 rev	0.017	—
Abrasion	—	0.18—0.23	—
Coefficient of friction to rotation on the material	—	beige	black
Colour	g cm^{-3}	1.06	—
Density	—	opal	opaque
Optical properties	—	none	none
Odour	%	0.1	—
Absorption of moisture at 23°C during 7 days	%	0.3	—
Absorption of moisture at 100°C during 7 days	10^{-5}/°C	5.2	6.7
Coefficient of linear expansion	%	0.8	0.5—0.7
Moulding shrinkage	°C	191	—
Deformation temperature under 19 kgf cm^{-2} load	—	—	self-extinguished
Rate of burning	°C	—170	—
Temperature of loss of flexibility	V mm^{-1}	16000—20000	—
Breakdown voltage	ohm cm	10^{17}	—
Volume resistivity	—	2.58	—
Dielectric constant at 60 c/s	—	0.00035	—
Dispersion factor at 60 c/s	—	0.00090	—
Dispersion factor at 10^6 c/s			

The characteristics of poly(phenylene oxides) obtained by other methods or having a different structure from 2,6-p.ph.o. can be briefly summarised as follows: (1) all poly(phenylene oxides) possess high thermal stability (this will be discussed in greater detail in the following subsection); (2) all poly(phenylene oxides) possess good hydrolytic and chemical stability and good electrical properties; and (3) various polymers having specific properties can be prepared from poly(phenylene oxides) by various polymerlike transformations.

A base for high-temperature adhesives has been obtained by the epoxidation of copolymers of 2,6-xylenol and 2-allyl-6-methylphenol[240].

A series of papers has been published on the preparation of ion-exchange resins having a poly(phenylene oxide) matrix. An anion-exchange resin has been prepared by the dimethylamination of chloromethylated 2,6-p.ph.o.[318-321]. Treatment of 2,6-p.ph.o. or chlorinated 2,6-p.ph.o. with chlorosulphuric acid, oleum, trialkyl phosphites, potassium cyanide, and other reagents followed by hydrolysis or reduction gives cation exchangers and anion exchangers based on poly(phenylene oxides) and having exchange capacities up to 4.0 m-equiv. g^{-1}.[322-339] Most of these ion exchangers are soluble in organic solvents, and from the solutions yield durable elastic films of electrical resistance 4 ohm cm and above, which can be used as membranes in fuel cells and for other purposes. The conductivity of these membranes is determined by the degree of sulphonation, which depends on the reaction conditions[335]. Electron-exchange resins and semiconductors have been based on poly(phenylene oxides)[324]. The ion-exchange resins are used for the coagulation of photographic emulsions[339], for the production of antistatic coatings[329,331], etc. The action of *N*-bromosuccinimide on 2,6-p. ph.o. in the presence of benzoyl peroxide results in bromination of the methyl groups. By choosing different catalysts it is possible to control the chlorination of 2,6-p.ph.o. to produce substitution in the benzene ring or in the methyl groups[319,321]. As analogue of benzyl halides the products are highly reactive, are easily hydrolysed, form quaternary ammonium salts with amines[318,329], and can be reduced to the original polymer[340].

Table 10. Properties of poly-(2,6-dimethylphenylene oxides) of different molecular weights.

Property	Units	Specimens		
		No. 1	No. 2	No. 3
Intrinsic viscosity [η]	dl g^{-1}	0.635	0.780	0.920
Dispersion factor tanδ	—	0.00245	0.00200	0.00146
Dielectric constant ε	—	2.54	2.2—2.4	2.50
Volume resistivity $10^{-16}\rho_v$	ohms	7.41	2.8—3.8	—
Tensile strength σ	kgf cm^{-2}	—	775.4	705
Relative extension ε	%	—	8.3	8.7
Vicat thermal stability	°C	225	222	—
Vickers hardness	—	18.9	17.2	—
Dinstat impact resistance	—	—	7.7	—

Under mild conditions poly-(2,6-diallylphenylene oxide) is oxidised to the corresponding carboxylic acid, with incidental degradation of the polymer chain and considerable decrease in the molecular weight[235].

The infrared spectra of poly-(2,6-dimethylphenylene oxides) have been investigated in some detail. All authors agree in asigning the absorption bands at 835 and 855 cm^{-1} to a tetrasubstituted benzene ring, at 1180–1190 cm^{-1} to an ether bond, at 1232 cm^{-1} to a *para*-substituted benzene ring, at 1300 and 1380 cm^{-1} to aliphatic C–H bonds, and at 1490 and 1600 cm^{-1} to C=C bonds in the benzene ring. Some divergence appears in the asignment of bands at 3400–3500 cm^{-1}, in the region of vibrations of the hydroxy-group. Hay[213] considers this band as due to the presence of traces of water. Endres[244] explains it as originating in terminal phenolic hydroxyls, the content of which per macromolecule is calculated as 1.5 group. Laborie-Gardaix[223] also attributes this band to hydroxy-groups in the polymer, without specifying their position. Kopylov and Pravednikov regard this band as due to the presence of carboxy-groups in the polymer[298]. The most debatable are the bands at 1660, 1690, and 1720 cm^{-1}, which have been ascribed to residual catalyst[213], overtones of out-of-plane C–H vibrations[213], a C=O group of undefined position[135], a tetrasubstituted benzene ring[224], and a carboxylic or quinonoid C=O group[219,220,298].

The molecular weight of the poly(phenylene oxides) also proved to be a quite complicated problem, since large discrepancies were observed depending on the method of

determination. From an analysis of end-groups Price[192] derived for 2,6-p.ph.o. the equation

$$[\eta] = 8.7 \cdot 10^{-5} M^{0.675}$$

linking the intrinsic viscosity in benzene at 30°C with the molecular weight. Tsou[238] compared viscometric and osmometric data in benzene at 25°C, and suggested the equation

$$[\eta] = 1.5 \cdot 10^{-7} M^{1.44} .$$

Hay and his coworkers[341,342] determined the molecular weights of a series of poly(phenylene oxides) by osmometry and light scattering, and obtained the values given in Table 11. A systematic investigation of the viscosity, osmotic pressure, and light scattering of dilute solutions of fractionally precipitated 2,6-p.ph.o. led Pepper et al.[343,344] to establish the following formulae at 25°C:

in toluene $[\eta] = 2.85 \cdot 10^{-4} M^{0.68 \pm 0.02}$,

in chlorobenzene $[\eta] = 3.78 \cdot 10^{-4} M^{0.66 \pm 0.02}$,

in chloroform $[\eta] = 4.83 \cdot 10^{-4} M^{0.64 \pm 0.02}$.

Table 11. Viscosity and molecular weight of some poly(phenylene oxides) obtained by the oxidative polycoupling of phenols.

Monomer	$[\eta]$ in $CHCl_3$ at 25°C, $dl\,g^{-1}$	Mol. wt. of polymer from	
		osmometry	light scattering
Phenol	0.070	18500	66000
	0.085	28000	—
	0.095	41000	710000
	0.115	58000	—
	0.200	80000	6100000
o-Cresol	0.190	44000	382000
	0.450	63000	2150000
2,6-Xylenol	0.185	16500	114000
	2.140	165000	6780000
o-Phenylphenol	0.150	47700	1220000
o-Chlorophenol	0.240	82000	5400000

The size of the undisturbed molecular tangle in the same solvents was calculated as (883 ± 10), (830 ± 5), and (845 ± 20) × 10^{-11} cm $mole^{0.5}$ $g^{-0.5}$ respectively.

5. Thermal Properties of Poly(phenylene Oxides)

Two aspects of the thermal degradation of aromatic polyethers must be distinguished. The degradation of the phenylene oxide chain itself has been studied in sufficient detail on oligo(phenylene oxides). This case is hardly ever met in poly(phenylene oxides) of high molecular weight, since these polyethers begin to break down at lower temperatures under the influence of end-groups, chain defects, and functional groups in the framework. The phenylene oxide chain itself is stable in an inert atmosphere and in air at least up to 500°C, as Stille and his coworkers[25] showed, for example for poly(penta-*p*-phenylene oxide) prepared by Diels–Alder condensation. It was also shown that the thermal stability of polymers containing aromatic hydrocarbon or heterocyclic rings joined by carbonyl, sulphonyl, and/or oxygen bridges equals or exceeds that of polyphenylenes[345]. It was found that, in the case of poly-(*p*-phenyleneethylene-*p'*-phenylene oxide) in air for 2 h, loss in weight, beginning at 375°, reaches 50% by 425° and 80% at 450°C, the activation energy of this process being 40 kcal $mole^{-1}$. The polymer specimen investigated had a molecular weight of 5000 and a softening point of 150°C, and was soluble in chloroform. Neither the mechanism of degradation nor the composition of the products was examined.

Cox and his coworkers[193] made a kinetic study of the thermal degradation of a large number of poly(arylene oxides) prepared by the polycondensation of halogenated phenols and containing 3–70 monomer units in the polymer chain. The structure of these units and the properties of some of the polymers are given in Table 12.

Table 12. Properties of some poly(phenylene oxides) obtained by polycondensation[193].

Polymeric	Mol. wt.	Solubility	Softening temp.	$T_{50\%}$*
m-Phenylene oxide	1800/A	—	465	610 (40%)
o-Chloro-*p*-phenyl oxide	—	+	270	590
p-Phenylene oxide (I)	7700/A	—	315	515 (31%)
p-Bromo-*o*-phenylene oxide–*p'*-phenylene oxide	4000	—	500	550
2,6-Dichloro-1,4-phenylene oxide	9600/B	+	190	480
p-Phenylene oxide (II)	2800/B	+	285	480
o-Bromo-*p*-phenylene oxide	—	+	240	510
2-Bromo-6-*p*- chlorophenyl-1,4-phenylene oxide	—	+	310	470
2,6-Dibromo-1,4-phenylene oxide	3150/B	+	240	445
pp'-Biphenylylene oxide	2000	+	155	470 (48%)
o-Fluoro-*p*-phenylene oxide–*p'*-phenylene oxide	4200	+	210	445
2,3,6-Trichloro-1,4-phenylene oxide	—	+	210	425
6-Bromo-4-phenyl-1,2-phenylene oxide	1400/B	+	265	445
2,6-Dibromo-1,4-phenylene oxide–4,6-dibromo-1,2-phenylene oxide	2800/B	+	210	425
2,3,5,6-Tetrabromo-1,4-phenylene oxide	—	+	300	380
2,3,5,6-Tetrachloro-1,4-phenylene oxide	1450/B	+	195	370
2,5-Dichloro-1,4-phenylene oxide	—	+	215	135

Notes: A = analysis of end-groups; B = cryoscopic measurements. Solubility in organic solvents in the cold and on heating.

* Temperature at which 50% loss in weight is achieved in 2 h. In the second column a minus sign means insoluble, and a plus sign soluble.

It was established that degradation of most of the polymers investigated took place in two stages. There was a considerable loss in weight during the first stage. After this, the losses diminished sharply, owing to stabilisation of the polymer probably caused by the formation of a system of fused aromatic rings after the loss of substituents, X-ray examination showed that, at a pyrolysis temperature of 400°C, the non-volatile residue was almost identical with the initial polymer. With a pyrolysis temperature of 600°C the rings were randomly arranged in the residue, and after 1000°C the residue contained structures comprising 3–4 fused rings. After degradation at 400°C the elementary composition of the residue was close to that of the original polymer, but at higher temperatures the carbon content of the residue increased, and the hydrogen content decreased.

The relative stability of the polymers investigated was expressed in terms of the temperature at which heating the polymer for 2 h results in half-decomposition (50% loss in weight). These values are also included in Table 12. With increase in the number of substituents in the aromatic ring the thermal stability diminishes. The anomaly observed with poly-(2,5-dichlorophenylene oxide) is probably due to 2,3,7,8-tetrachlorodibenzo-*p*-dioxan

structures, either present in the specimen or formed during degradation. With the exception of the tetra-substituted poly(phenylene oxides), the chlorinated polymers are more stable than the brominated derivatives. Polymers in which rotation about the oxygen atom is difficult are the least stable. Poly(phenylene oxides) having the same structure but obtained by different methods differ in thermal stability. The rate constants of the initial stage of degradation can be represented by the equations $k = 10^{12} \exp(-52\,000/RT)$ and $k = 10^{10} \exp(-43\,000/RT)$ for poly-(2,3,6-trichloro-1,4-phenylene oxide) and poly-(2,3,5,6-tetrabromo-1,4-phenylene oxide) respectively.

Most of the degradation products of poly(phenylene oxides) consisted of compounds which were volatile at the pyrolysis temperature but not volatile at room temperature. Compounds volatile at room temperature constituted not more than 4% of the total products. An attempt at a mass-spectroscopic analysis of the composition of the thermal degradation products was unsuccessful because of the complexity of the mass spectra, and therefore the authors refrained from expressing any ideas on the mechanism of degradation.

Thermogravimetric data indicate that the degradation of 2,6-p.ph.o of molecular weight ~10 000 begins in an atmosphere of nitrogen at 350°, goes most rapidly at about 400°, reaching 65% in extent, and then slows down markedly, the loss in weight reaching 70% by 900°C.[240] Other results indicate weight losses of 1%, 13%, and 69% at 320°, 370°, and 420°C.[192] After degradation at 320° and 370°C no products which condense out in a liquid nitrogen trap are observed, and after degradation at 420°C most of the products condense out at room temperature.

Heating 2,6-p.ph.o. with an equimolecular amount of phenol in the presence of a free-radical type of catalyst at 150–250°C results in the formation of 4-aryloxy-2,6-dimethylphenols and the corresponding trimers[42]. In the electrolytic oxidation of 2,6-p.ph.o. of molecular weight 20 000 at potentials up to 1.6 V only a portion of the polymer is converted into 2,6-dimethylbenzoquinone and 3,3′,5,5′-tetramethylbiphenylquinone; the unoxidised residue was not investigated[346].

Investigation of the thermal properties of 2,6-p.ph.o. of molecular weight about 40 000 in a differential adiabatic calorimeter showed[347] that its melting point was 267°C (540°K), its glass point 221°C (498°K), and its specific heat of fusion 16.4 J g^{-1}. The abnormally high T_{gl}/T_m ratio was attributed to the residual entropy of the amorphous polymer. Degradation of the polymer in an atmosphere of nitrogen began at about 460°C with a strongly exothermic process. The discrepancy in the temperature at which degradation begins, in comparison with the results of other workers, was explained by differences in the molecular weight and the method of preparation of the polymer.

Petris used a thermomechanical method and obtained different values for the glass point[348]. He found temperatures of 600°, 480°, and 400°K respectively for poly-(1,4-phenylene oxide), poly-(2,6-dimethylphenylene oxide), and poly(diphenylenepropane–diphenylene sulphone oxide).

The thermo-oxidative degradation of poly-(2,6-dimethylphenylene oxide) of molecular weight 40 000 and of the corresponding 2-isopropyl-6-methyl polymer of molecular weight 10 000 was investigated at temperatures up to 500°C by Conley and Alvino[349]. In an inert atmosphere thermogravimetric results were consistent with those of other investigators, but in air loss in weight began at 150°C with the dimethyl polymer, some increase was then observed at about 250°C, after which degradation rapidly reached 100% by 400°C. In argon the isopropyl methyl polymer behaved in the same way as the dimethyl polymer, but this behaviour did not change in air. Differential thermal analysis of the dimethyl polymer showed a strong exothermic effect at 210°C, overlapped by a still stronger endothermic effect in the range 250–270°C. Infrared spectroscopy indicated the appearance and increase in intensity of absorption bands in the range 1660–1720 cm^{-1}, which were attributed to a carboxy-group and to quinonoid structures. The mass spectra of the volatile degradation products were too complicated to be deciphered; with the dimethyl polymer the mass spectra were almost identical for degradation in inert and oxidising atmospheres. In both cases chromatography showed the presence of sixteen products, three of which, constituting up to 40% of the total quantity, could be identified as substituted phenols and quinones. With the isopropyl polymer the main products were water and acetone. No viscometric results could be obtained for the residues because of gel formation.

The scheme suggested for degradation of the isopropyl polymer involves attack on a tertiary hydrogen atom by oxygen followed by the cumene hydroperoxide type of decomposition into acetone and phenol with further cross-linking of the polymer of the ether, dioxan, or biphenyl type.

Oxidation of the methyl group is assumed to involve the successive formation of CH_2OOH, CH_2OH, CHO, and COOH groups with decarboxylation of this last group and parallel processes of cross-linking of the polymer by interaction of the groups. In both cases cleavage of the polymer chain was probably due to attack by aryloxy-radicals, but the mechanism was not specified. Kelleher and his coworkers[299–301] have studied the oxidative degradation, initiated by heat and by light, of poly-(2,6-dimethylphenylene oxide) at 100° and 125°C. The experiments were made on films of the polymer 0.025 and 0.15 mm thick, of intrinsic viscosity 0.32. The films were heated in air in the dark or in ultraviolet radiation for up to 10 000 h. Elementary analysis of the initial polymer indicated excess of oxygen—13.51% in comparison with 13.32% calculated for the formula C_8H_8O—and traces (0.14%) of nitrogen, which was regarded as indicating some oxidation of the polymer even during preparation and contamination by the catalyst. However, an alternative interpretation can be given for this fact, for the experiment was made on industrial specimens of the polymer which had been carefully purified, so that the retention of traces of catalyst in the polymer was doubtful. On the other hand, picric acid is a good initiator for synthesis of this polymer[341], and calculation based on Pepper's formula[343] gives a value of 55 000 for the molecular weight of the polymer. Accepting a bimolecular mechanism of termination during polymerisation, i.e. assuming the macromolecule to contain two $C_6H_2(NO_2)_3O$ end-groups, we obtain calculated oxygen and nitrogen contents of 13.67% and 0.153%.

As the polymer specimens aged under the above conditions their oxygen content increased from 13.51% to 17.95%. At the same time the intensity of absorption increased in the region of the hydroxy-group and at 1695 cm^{-1} (carboxyl C=O group), while a weak absorption band appeared at 1660 cm^{-1}. The mass spectrum of the volatile degradation products shows the formation of carbon dioxide and traces of hydrogen. Losses in weight reached 2% during the first 200–500 h, and increased to 4% by 10 000 h. Up

to 10% of a gel fraction was formed on ultraviolet irradiation, and up to 80% in the dark. The intrinsic viscosity of the soluble fraction fell to 0.49, compared with an initial value of 0.52. The authors regard this as indicating that the molecular weight of the polymer does not change, which can hardly be correct, for the appearance of a large quantity of functional groups in the framework should result in a change in the rigidity of the macromolecule and a decrease in the viscosity of the solution. The maintenance of the viscosity in this case indicates an increase in the molecular weight of the polymer, i.e. the first stage of cross-linking. The 0.15-mm film after exposure in air to ultraviolet radiation for 2 min gives an electron spin resonance signal with $g = 2.0065$, probably due to radicals of phenoxyl type; exposure in a vacuum doubles the intensity of the signal.

The mechanism suggested for the process involves formation of phenoxy-radicals in the polymer as the first stage. There are three sources—decomposition of hydroperoxides present in the initial polymer, photolysis of an Ar–O–Ar bond, or breakdown of hydroperoxides formed during the experiment—for such radicals. The radical chain grows by the attack of an aryloxy-radical on the methyl groups, formation of phenol and a benzyl radical following addition of oxygen, etc. by a branching kinetic chain, terminated by cross-linking of the polymer or the formation of hydroxymethyl, oxomethyl, carboxyl, and other groups in the framework.

A systematic study of the thermal degradation of a series of poly(phenylene oxides) made by Kopylov and Pravednikov[350,351] established the following generalisations:

1. At 175–300°C quinol ether groups in the polymer dissociate by a first-order reaction having an activation energy of 22–23 kcal mole^{-1}, with the formation of terminal radicals of phenoxyl type.

2. At 350–450°C these radicals initiate degradation of the polymer chain, which under their influence undergoes random breakdown into a mixture of fragments, mainly hexamers of phenylene oxide structure containing hydroxy- and oxo-groups.

3. Increasing the molecular weight of the poly(phenylene oxide) and blocking the end-groups tends to improve the thermal stability of the polymer and increase the activation energy of degradation from 15–20 to 30–40 kcal mole^{-1}.

These authors suggested a general scheme for the thermal degradation of alkylated poly(phenylene oxides) involving radicals of phenyl, phenoxyl, and benzyl types as well as quinone methides. The conclusions reached in this work are confirmed by the effective stabilisation of poly(phenylene oxides) by blocking their end-groups by arylation, alkylation, alkoxylation, acylation, or the action of isocyanates, thiols[352–359], phosphites, or borates[360,361].

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Oligo-, meso-, and poly-(phenylene oxides) constitute a separate class of organic compounds. They exhibit several identical chemical properties—high resistance to acid and alkaline hydrolysis, stability towards oxidants, ability to form complexes, and readiness to undergo substitution rather than addition and cleavage—besides having the same chemical structure. On the other hand, all these compounds are equally inclined to interact with free-radical species, which results in breakdown of the phenylene oxide chain, except in rare cases of self-stabilisation. With regard to practical application phenylene oxides are of greatest value as materials stable to heat and radiation and as a durable basis for several polymerlike transformations.

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