Translated from *Uspekhi Khimii*, 47, 2065-2095 (1978) U.D.C. 547.922.3

Poly(arylene Sulphides)—Preparation, Structure, and Properties

V.A.Sergeev, V.K.Shitikov, and V.I.Nedel'kin

Chemical aspects of the synthesis, structure, and properties of oligo- and poly-(arylene sulphides) are surveyed. The Review concludes with several fields of application and a list of 252 references.

CONTENTS

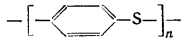
I. Introduction 1095
II. Methods of preparation of poly(arylene sulphides) 1095
III. Practical applications 1106

I. INTRODUCTION

The advantageous properties of polymers like polyphenylenes are difficult to realise practically in ready-made materials and articles, mainly because such polymers are insoluble and infusible right up to their thermal decomposition temperatures. As a consequence, vigorous research has been undertaken on the synthesis of modified polymers of this type. A great deal of experimental information has now accumulated on the synthesis and the properties of oligo- and poly-phenylenes containing functional groups[1], whose fields of practical application are continuously expanding. Polyheteroarylenes, containing in the main chain aromatic rings and various heteroatoms, e.g. oxygen[2] or sulphur[3], are being increasingly utilised in industry. Recent years have seen an especially marked increase in the number of studies aimed at developing methods of preparation, investigating the properties, and applying poly(arylene sulphides), which are distinguished by high resistance to thermal oxidation and several specific properties.

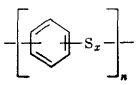
Although poly(arylene sulphides) were first synthesised in 1866, by the action of alkali-metal sulphides on bis-diazonium salts of benzidine[4], systematic investigations on their synthesis and more thorough study of their structure and properties in 1948, after Macallum's discovery[5] of a new process for obtaining poly(arylene sulphides) by the high-temperature polycondensation of polyhalogenated benzenes in the presence of mixtures of sulphur and alkali-metal carbonates.

Methods for obtaining oligo- and poly-(phenylene sulphides) of linear structure



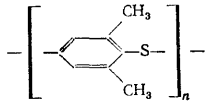
have been elaborated in the greatest detail, and their properties have been investigated most thoroughly. The enhanced heat-resistance and thermal stability of such polymers is due primarily to the comparatively high energy of rupture of the phenyl–sulphur bond (72.7 kcal mole^{-1})[6] and to their physical structure, largely determined by the strong intermolecular interaction of the polymer chains and the formation of a crystalline structure[7]. Furthermore, the presence of sulphur atoms between aromatic rings not only ensures that the polymeric molecule shall be flexible and highly resistant to thermal oxidation but also is responsible for the cross-linking of poly(phenylene sulphides) at 300–350°C.[8,9]

The term *poly(arylene sulphides)* is met more often than other names, in both Soviet and foreign literature, in relation to simple aromatic "polythioethers" or polysulphides. The Reviewers consider this name most rational and able to represent quite adequately the various chemical structures of most oligomers and polymers of simple aromatic polysulphides. For example, the name *poly(phenylene sulphides)* applies to polymers in which the repeating monomer unit is



where $x = 1$. The aromatic rings in such polymers may be combined by sulphur atoms in the relative positions 1,2, 1,3, and 1,4 (poly-(*o*-phenylene sulphide), poly-(*m*-phenylene sulphide), and poly-(*p*-phenylene sulphide) respectively). When $x \geq 2$, poly(phenylene disulphides), poly(phenylene trisulphides), poly(phenylene tetrasulphides), and poly(phenylene polysulphides) are formed.

The same principles underly the nomenclature of poly-(arylene sulphides) having a branched structure or substituents in the aromatic ring. The only difference is that the substituents and their positions are indicated before the name of the chief arylene ring. For example, a polymer based on the monomer unit



is termed *poly-(2,6-dimethyl-1,4-phenylene sulphide)*.

The present Review surveys almost all known methods for obtaining poly(arylene sulphides) of diverse structure. It gives their principal characteristic properties and several fields of application.

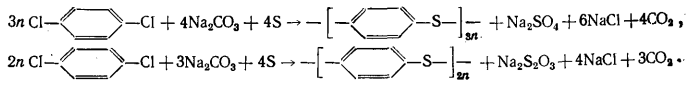
II. METHODS OF PREPARATION OF POLY(ARYLENE SULPHIDES)

1. Polycondensation of Polyhalogenated Aromatic Compounds with a Mixture of Sulphur and Various Derivatives of Alkali and Alkaline-earth Metals

One of the best known and simplest methods for obtaining poly(phenylene sulphides) is based on the high-temperature (275–360°C) polycondensation of polyhalogenated benzenes in the presence of mixtures of sulphur and alkali-metal carbonates, first accomplished in 1948 by Macallum[5]. In his view only after a first stage of formation of alkali-metal sulphides

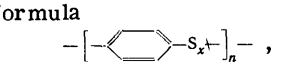
$$3M_2CO_3 + (2n+2)\,S \rightarrow 2M_2S_n + M_2S_2O_3 + 3CO_2$$
$$4M_2CO_3 + 4S \rightarrow 3M_2S + M_2SO_4 + 4CO_2$$

did polycondensation occur with the halogenobenzenes. With *p*-dichlorobenzene mixed with sulphur and sodium carbonate we can represent the process by the equations



The poly-(*p*-phenylene sulphides) thus obtained are slightly coloured powders, sparingly soluble in the usual organic solvents and softening at 250–300°C. Macallum assumed[10] that the first stage was far slower than the second, so that the reaction mass always contained a small quantity of elementary sulphur, which assists polycondensation of halogenobenzenes with metal sulphides. Indeed, it was found experimentally[5] that a slight excess of elementary sulphur not only played a part in building up the polymer chain but also catalysed the process to high degrees of conversion of the initial halogenobenzenes. In the absence of excess of sulphur halogenated aromatic compounds and alkali-metal sulphides either do not interact at all or undergo polycondensation only slowly even at high temperatures.

However, the quantity of combined sulphur depends mainly on the initial molecular ratio of the dihalogenobenzene and sulphur[10], so that the monomer unit in the resulting poly-(*p*-phenylene sulphides) can be represented by the general formula



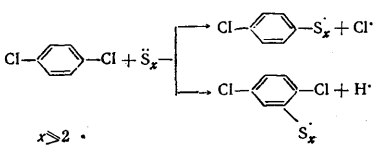
Thus the polycondensation of *p*-dichlorobenzene and sulphur taken in the molecular proportions 1.0 : 1.5 yielded solid poly-(*p*-phenylene sulphides) of m.p. 215–240°C, whose monomer unit corresponded to the above general formula with $x = 1$. When the molecular ratio was increased from 1.5 to 2–3 the melting point fell to 55–80°C, while the sulphur content corresponded to $x = 2$–5. Copolymers obtained from a mixture of *p*-di- and 1,2,4-tri-chlorobenzenes in the presence of sulphur and sodium carbonate had the analogous structure

$$-[C_6H_4S_x]\cdot[-C_6H_3S_y]_n-$$

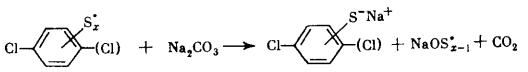
with $x = 1.15$–1.25, $y = 1.72$–1.87, and $n = 0.04$–0.25. From the above results it was concluded[10] that the main polymer molecule consisted of aromatic rings linked both by monosulphide and by polysulphide groups.

Later investigations have shown[11] that the polycondensation of dihalogenobenzenes can be accomplished also in the presence of a mixture of sulphur and an alkaline-earth metal or its carbonate, borate, or oxide. The formation of poly-(*p*-phenylene sulphides) is catalysed by *N*-halogenated derivatives, e.g. *N*-bromosuccinimide, *N*-bromoacetamide, etc. (5% based on the initial monomers)[12]. Aromatic compounds containing activated halogen atoms, e.g. di-*p*-chlorophenyl sulphide or sulphone, have been used[13] as activators of polycondensation: in their presence up to 80% yields have been obtained of poly(arylene sulphides) of molecular mass 237 000 (calculated from the chlorine content).

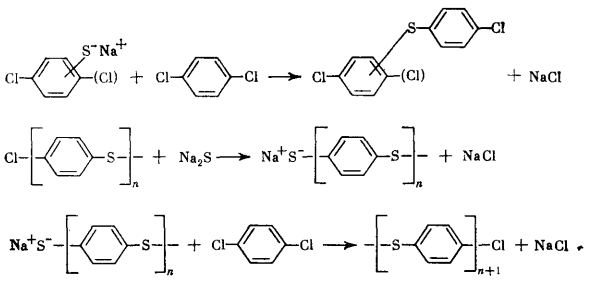
Lenz and Carrington[14] suggested an alternative mechanism, in which the first stage involves reaction between the halogenated aromatic compound and a sulphur biradical formed during heating:



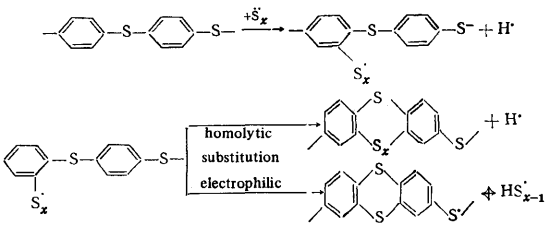
The polysulphide substituents in the aromatic ring then react with sodium carbonate to form benzenethiolate ions:



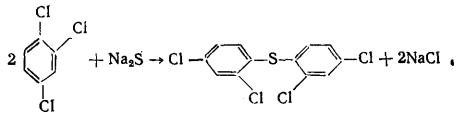
Nucleophilic substitution occurs with the dihalogenoarenes to give primary oligomeric or secondary polymeric products:



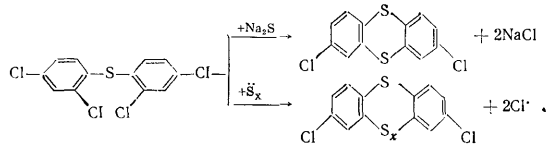
According to the above scheme sulphur biradicals are able to replace not only halogen but also hydrogen atoms in the aromatic ring, which may promote the formation both of branched and of "cross-linked" poly(arylene sulphides). Indeed, infrared spectroscopy established[15] that the polymer obtained from *p*-dichlorobenzene had a branched or partly cross-linked structure. Some ordering (detected by X-ray diffraction) was attributed[15] to the presence of linear segments comprising 6 or 7 monomer units between side-chains, able to form zones with some ordering of the spatial arrangement of the polymer chains. The increase in the sulphur content of the polymer above that calculated for a $C_6H_4.S$ monomer unit was explained[15] by intramolecular cyclisation, which may result in sulphur-containing rings:



Study of the simultaneous polycondensation of *p*-di- and 1,2,4-tri-chlorobenzenes revealed[15,16] not only that the rate of nucleophilic substitution of the latter exceeds that of the former more than fourfold but also that the 1-chlorine atom in the trichlorobenzene is the most reactive of the three in nucleophilic substitution. Therefore the first stage involves preferential formation of a dimer from 1,2,4-trichlorobenzene:



Subsequent nucleophilic or radical substitution of one of the *ortho*-chlorine atoms forms phenylthio-groups or polysulphide links, which are readily converted by intramolecular cyclisation into thianthren units:



Hence, owing to intramolecular cyclisation, 1,2,4-trichlorobenzene is actually difunctional on polycondensation in the presence of sulphur and alkali-metal carbonates. The change in functionality during copolycondensation and the considerable differences in activity between the initial monomers have a significant influence on the direction of the process and on the properties of the resulting poly(phenylene sulphides).

Table 1. Properties of homopolymer from *p*-dichlorobenzene and of copolymer from *p*-di- and 1,2,4-tri-chlorobenzenes.

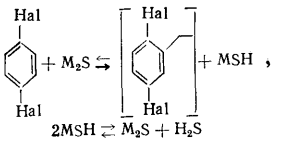
Property	Homopolymer*	Copolymer**
1	2	3
Degree of conversion (from Cl^- in aq. extract), %	99.0	99.0
Yield of toluene-soluble polymer, %	8.3	5.8
Softening point, °C	166—171	166—171
Sulphur content, %	35.1±0.4	31.5±0.3
Chlorine content, %	1.60±0.1	1.70±0.1
Yield of polymer soluble in diphenyl ether, %	63.5	77.5
Softening point, °C	193—204	171—177
Sulphur content, %	33.2±0.3	31.6±0.3
Chlorine content, %	0.50±0.1	0.6±0.1
Yield of insoluble polymer, %	20.6	11.6
Total yield, %	94.2	94.9

* Molecular proportions $C_6H_4Cl_2 : S : Na_2CO_3 = 1 : 1.73 : 1.73$ at 300°C for 20 h.
** Molecular proportions $C_6H_4Cl_2 : C_6H_3Cl_3 : S : Na_2CO_3 = 1 : 0.1 : 1.84 : 1.84$ at 300°C for 24 h.

Table 1 compares the characteristics of the homopolymer obtained from *p*-dichlorobenzene with those of the copolymer obtained from the same monomer together with 10 mole % of 1,2,4-trichlorobenzene[15]. It is evident that polycondensation gives high yields of poly(phenylene sulphides), and higher yields of soluble fractions in the case of the copolymer. However, the strength characteristics of the copolymers are somewhat inferior to those of the homopolymers. In order to improve the durability of copolymers it was suggested[16] that copolycondensation with sulphur and sodium carbonate should be conducted in the presence of alkylated aromatic hydrocarbons, e.g. toluene, xylene, methylnaphthalenes, etc., which were considered to inhibit or completely to eliminate formation of thianthren groups in the copolymer structure.

Intramolecular cyclisation can be observed especially distinctly in the high-temperature polycondensation of *o*- and *m*-dihalogenobenzenes in the presence of a mixture of sulphur with oxides or sulphides of alkali or alkaline-earth metals. . Thus under these conditions up to 75% yields of thianthren were obtained from *o*-dichlorobenzene[10], but from *m*-dichlorobenzene an insoluble product was formed and a substance was isolated (molecular mass 1120) that contained 31.5% of sulphur and was free from chlorine[17]. It was considered[17] that the polycondensation of *o*- and *m*-dihalogenobenzenes may give high yields of cyclic *ortho*- or *meta*-substituted oligomers (tetramers, pentamers, heptamers, nonamers, decamers, etc.).

The evolution of hydrogen sulphide under these conditions of the Macallum polycondensation of dihalogenobenzenes was attributed to side-reactions with the metal sulphide[14]:



This process results in formation of polymers having a branched and cross-linked structure.

Monohalogenated aromatic compounds containing various substituents in the aromatic ring can also be used for high-temperature polycondensation with sulphur and sodium carbonate[18,19]. Thus various poly(phenylene sulphides) have been obtained by heating *para*-halogenated phenols, toluene, aniline, or benzoic acid with a mixture of sulphur and sodium carbonate (molecular proportions 1 : 1.73 : 1.73) at 160–340°C for 18 h. The degree of conversion of the monomers, calculated from the quantity of chloride ions in an aqueous extract, depends on their structure and on the temperature of polycondensation; the yield of the reaction products reaches 80% or more. Experimental results are given together with the polymer structure established on the basis of infrared, ultraviolet, and nuclear magnetic resonance spectral data[18]. For comparison polymers were obtained from *p*-dichlorobenzene under the same conditions. Poly(phenylene sulphides) obtained from *para*-chlorinated phenol and aniline contain hydroxy- and amino-groups respectively, whereas the carboxyl and methyl groups of *para*-chlorinated benzoic acid and toluene undergo various changes during polycondensation. On the assumption of first- or second-order kinetics for polycondensation, with simultaneous solution of the Arrhenius and Hammett equations, it was found that the overall rate depended mainly on polar effects and on the slowest stage, i.e. electrophilic attack by the sulphur atom on the monomer. Raising the temperature of polycondensation increases the yield of polymers having a branched and cross-linked structure.

Scanning calorimetry and thermogravimetric analysis indicate[19] that poly(phenylene sulphides) containing various substituents in the aromatic ring have softening and decomposition points of 90–263 and 270–320°C respectively. The degradation of such polymers has first-order kinetics; activation energies in an atmosphere of nitrogen are 7–30 kcal $mole^{-1}$, the lowest values applying to poly(phenylene sulphides) containing amino- and hydroxy-groups.

According to a patent[20] soluble poly(phenylene sulphides) resistant to thermal oxidation at high temperatures can be obtained from a mixture of *para*-chlorinated triphenyl-1,3,5-triazines with *p*-dichlorobenzene. When such monomers undergo polycondensation in the presence of a mixture of sulphur with carbonates, sulphides, or oxides

of alkali or alkaline-earth metals at 270–360°C, triazine-containing poly(phenylene sulphides) are obtained that undergo losses in mass of 3.3% and 5.3% when heated at 300°C for 100 h and at 400°C for 20 h respectively.

Aromatic polysulphide polymers of molecular mass M_n = 2500–10 000) and general formula $[ArS_x]_n$, where x = 2–5, which form predominantly white powders soluble in oxolan and with m.p. ⩾100°C, have been obtained by the polycondensation of disulphonic, disulphinic, dithiosulphonic, and dithiosulphinic acids, and also their salts, esters, anhydrides, chlorides, and amides, with alkali-metal polysulphides formed by the action of powdered sulphur on aqueous solutions of alkali-metal sulphides[21]. Water or a lower alcohol was used as solvent, and polycondensation was effected in the presence of gaseous hydrogen together with sulphides or polysulphides of elements of the iron subgroup, as well as the finely powdered metals, under 7–350 kg cm^{-2} in an autoclave at 150–200°C.

2. Polycondensation of Polyhalogenated Aromatic Compounds with Alkali-metal Sulphides

Despite the apparent simplicity and the availability of the initial compounds, the high-temperature polycondensation of polyhalogenoarenes in the presence of a mixture of sulphur and a carbonate, sulphide, or oxide of an alkali or an alkaline-earth metal has not found wide industrial application owing to the experimental difficulties involved in isolating the poly(phenylene sulphide) from the melt containing a large quantity of impurities of low molecular weight and owing to the strongly branched and partly cross-linked character of the products. These disadvantages are to some extent avoided when polyhalogenated aromatic compounds undergo polycondensation with alkali-metal sulphides in polar organic solvents of high boiling point[22,23].

Polycondensation of polyhalogenated aromatic compounds with alkali-metal sulphides is at present the only industrial method of obtaining poly(arylene sulphides)[24], but information on this process is extremely limited. Polycondensation is continued in an inert atmosphere at 125–450°C for 17–20 h; *N*-methylpyrrolid-2-one, hexamethylphosphoramide, tetramethylurea, etc. can be used as solvents. Poly(phenylene sulphides) of highest molecular mass are obtained in *N*-methylpyrrolidone solution[22]. At moderate temperatures and pressures maximum rates can be achieved[25] by gradually adding increasing quantities of the arylene halide to the alkali-metal sulphide and varying the duration of polycondensation. The anhydrous sulphide (mainly sodium sulphide) is generally used, or else water of crystallisation is evaporated from a hydrate by preheating the reaction mass to 160°C.[22,26] Alternatively, sodium sulphide can be obtained directly in the reaction vessel by treating sodium hydroxide with hydrogen sulphide[27,28] or industrial waste gases containing it[29].

Isolation of the poly(arylene sulphides) from the reaction mixture apparently presents some difficulty. For this purpose it is proposed to treat the mixture with water vapour[30] or liquid ammonia[31] under pressure, evaporate off the solvent under adiabatic conditions[32–35], or apply filtration followed by treatment of the polymer with water and organic solvents[36]. The extractants used are acyclic or alicyclic hydrocarbons[37], dichloroethane, or benzene[38].

Yields up to 85% of poly(arylene sulphides) have been obtained in this way. The products were pale grey powders, soluble in high-boiling organic solvents, e.g. polyphenols, above 235°C.[39] Poly(arylene sulphides) obtained from *p*-dihalogenobenzenes and sodium sulphide in *N*-methylpyrrolid-2-one solution have molecular masses around $(5–14)\times10^3$. Such products probably separate from solution during polycondensation, and play no part in further growth of the polymer chain.

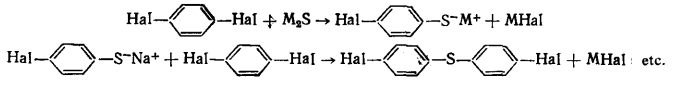
Table 2. Dependence of viscosity of poly(arylene sulphides) (melt at 303°C) on initial molecular ratio of *p*-dichlorobenzene to sodium sulphide.

Ratio	Viscosity, P	Ratio	Viscosity, P
1:1	37.3	1.04:1	4.8
1.02:1	6.4	1.05:1	7.1

The molecular mass is also influenced by the properties of the initial components[22]. Table 2 gives the viscosities of the poly(arylene sulphide) melts obtained with different initial molecular ratios of *p*-dichlorobenzene and sodium sulphide[22]. The use of purified initial compounds, including sodium sulphide with an impurity content not exceeding 1–2%, is therefore of interest[28,41]. An equimolecular mixture of purified *p*-dichlorobenzene and sodium sulphide gave poly(phenylene sulphides) having a lower melt index and a higher viscosity. With a 2:1 molecular ratio of sodium sulphide oligo(phenylene sulphides) were obtained having molecular mass 510 and softening point 125–130°C.[27] Benzenethiol separated as a byproduct in yield almost equal to that of the oligomers. If, however, a threefold excess of functional groups in the halogeno-derivative was used relative to the sodium sulphide, a product of low molecular mass was obtained[42], with a mean degree of polycondensation of 2.

Thus the above results show that equimolecular proportions of the initial components are necessary to obtain poly(arylene sulphides) of maximum molecular mass. Furthermore, there are data indicating that two measures must be taken to increase the rate of the process and the molecular mass of the products: (i) polycondensation of sodium sulphide with dihalogenated unsaturated cyclic hydrocarbons, preferably aromatic, in the presence of trihalogenobenzenes[22,28] or 3–33 wt.% of activators (a mixture of oligo(phenylene sulphides) extracted from products of a similar reaction with benzene, toluene, or *N*-methylpyrrolidone at 80–150, 110–150, or 135–150°C respectively)[43,44]; and (ii) the temperature must be raised at a specified rate during polycondensation[45].

According to infrared and n.m.r. spectral data and X-ray diffraction poly(arylene sulphides) obtained by the polycondensation of dihalogenated aromatic compounds with alkali-metal sulphides have a linear structure, in contrast to the branched polymers obtained in the presence of sulphur and alkali-metal carbonates. It follows that a mechanism of nucleophilic substitution is responsible for the appearance of the former when the process occurs in a polar organic solvent[40]:



Various halogenated aromatic compounds can be used for polycondensation with sodium sulphide in order to obtain poly(arylene sulphides) having modified properties.

Thus the copolycondensation with sodium sulphide of *p*- and *m*-dichlorobenzenes in various proportions by weight gives poly(phenylene sulphides) that are soluble in oxolan[46], a few characteristics of which are listed in Table 3. It is significant that increase in the proportion of *p*-dichlorobenzene in the reaction mixture increases the viscosity and raises the glass point of the resulting polymers. Unfortunately, however, the patent literature contains no evidence of their structure[46].

Table 3. Properties of copolymers from *p*- and *m*-dichlorobenzenes.

Isomer, %		Properties of copolymers		
para	*meta*	η	glass point, °C	solubility in oxolan, g/100 g
75	25	0.11	68	insol.
50	50	0.09	49	>20
25	75	0.05	47	42
0	100	0.01	15	<0.5

Polycondensation of a mixture of poly-(*m*- and *p*-phenylene sulphides) with sodium sulphide yields block copolymers[47] containing, according to infrared spectroscopy, *meta*- and *para*-substituted aromatic groups in proportions varying between the limits 3 : 1 and 1 : 3 for fractions of the block copolymer respectively soluble and insoluble in *N*-methylpyrrolidone.

Polymethylated and branched poly(phenylene sulphides) have been obtained respectively from dibromodurene and from a mixture of *p*-dibromobenzene and 1,3,5-tri-*p*-bromophenylbenzene in the molecular proportions 20 : 1.[40] The good solubility of the products in dimethylformamide is attributed[40] to disorder resulting from the introduction of substituents or a branching agent respectively into the polymer molecule. In contrast to the poly(phenylene sulphide) obtained from *p*-dibromobenzene and melting at 280°C, the copolymer from the 20 : 1 mixture with 1,3,5-tri-*p*-bromophenylbenzene softened at around 235°C.

Poly(arylene sulphides) containing reactive groups can be obtained by the polycondensation with alkali-metal sulphides of halogenated aromatic compounds containing various functional groups. Thus 2,5-dichloroaniline yields amino-containing polymers, which become infusible and insoluble on treatment with dicarboxylic acids[43], but the corresponding products of the simultaneous polycondensation of *p*-dichlorobenzene and *o*-chloroaniline melt at 283–286°C and have a viscosity of 52 P at 303°C.[22] Poly(arylene sulphides) from 2,4-dichlorotoluene soften below 100°C and are readily soluble in benzene, while those from 2,5-dichlorobenzenesulphonic acid are readily soluble in water[22].

The polycondensation of *p*-dichlorobenzene with sodium sulphide in the presence of copper cyanide gives oligo(phenylene sulphides) of molecular mass 500–5000, containing terminal nitrile groups[48], which may subsequently be involved in thermal or catalytic cross-linking.

Polycondensation of dichlorodinitrobenzene with sodium tetrasulphide at 70 and 110°C gives oligo(phenylene tetrasulphides) containing amino- and nitro-groups[49], the maximum yield of polymer (>90%) being obtained with the reactants in the molecular proportions 1 : 2. This is attributed mainly to secondary processes, in particular reduction of nitro- to amino-groups:

$$C_6H_2Cl_2(NO_2)_2 + 2Na_2S_4 + 2H_2O \rightarrow C_6H_2Cl_2(NH_2)_2 + 2Na_2S_2O_3 + 4S\ .$$

Since the content of so called free sulphur in the polymer is only 0.78%, while the total sulphur content is ~44.2%, it is thought[49] that all the sulphur atoms are present in the main chain of the macromolecule, while the terminal groups may be chlorine atoms or hydroxyls (analysis indicates that the latter amount to 1.93%). Apparently, therefore, the structure of the oligomer can be represented by the formula

$$Cl\,(NH_2)_2\,C_6H_2S_4 - \ldots - C_6H_2\,(NH_2)_2\,OH.$$

The maximum molecular mass is ~850 (determined cryoscopically in benzene). The resulting oligomers had softening points of 47–63°C and were readily soluble in benzene, acetone, carbon disulphide, and mineral acids.

Another monomer that has been used is di-*p*-chlorophenyl sulphone, whose chlorine atoms are activated by the electron-accepting sulphonyl group[50–52]. In dimethyl sulphoxide solution at 170°C a theoretical yield was obtained of polymers having a reduced viscosity of 0.15 in a 1% solution in this solvent at 25°C. Polycondensation of the initial sulphone with sodium sulphide can be effected also in aqueous solution or in a mixture of an organic solvent with water at 150–400°C.

Poly(quinone sulphides) of molecular mass ~3000 have been obtained by the polycondensation of tetrachloro-*p*-benzoquinone with sodium sulphide in toluene solution at 0°C.[53] They are solid powders apparently having a linear structure, with softening points of 320°C and above.

Quite recently poly(arylene sulphides) have been obtained by heating polyhalogenated aromatic compounds with thiourea and oxides (or carbonates) of alkali and alkaline-earth metals in *N*-methylpyrrolidone solution under pressure[54]. The procedure is to heat thiourea with the metal oxide (or carbonate) in *N*-methylpyrrolidone solution, and then add to the mixture the polyhalogenated aromatic compound, which probably reacts with an already formed sulphide. Yields of 41–94% are obtained of polymers that soften at 249–273°C and have reduced viscosities of 0.01–0.07.

The thiourea can be replaced by thiocarbonates of general formula R_2CS_3 (where R represents an alkali metal or a hydrocarbon radical)[55–57], thiosulphates, thiocarboxylic acids[57–59], thiols, thiolates, or sulphides containing an activating substituent in an α or β position (e.g. α-mercaptopropionic acid)[57,60], carbon disulphide and carbonyl sulphide[61], thioamides of general formula $R'(CS.NR_2)_x$ (where R is hydrogen or a radical of valency 1–4), *N*-methylpyrrolidine-2-thione[62], thiocarbamates (e.g. sodium dimethyldithiocarbamate)[63], and also phosphorus pentasulphide[64] in hexamethylphosphoramide solution.

Yields of poly(phenylene sulphides) from the polycondensation of dihalogenated aromatic compounds with alkali-metal hydrogen sulphides are only 24–45%.[65] To increase the yield the polycondensation is conducted in the presence of alkali-metal *N*-substituted ω-amino-carboxylates[66]. Similar compounds have been used also in the polycondensation of dihalogenated aromatic compounds with carbon disulphide[67]. Furthermore, up to 94% yields of poly(phenylene sulphides) are obtained from dihalogenated aromatic compounds and alkali-metal hydrogen sulphides in the presence of alkaline-earth metal hydroxides or alkali-metal carbonates[68] or of sodium hydroxide and salts of aliphatic alcohols and acids[69].

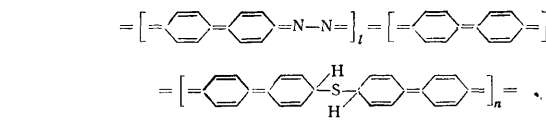
3. Decomposition of Diazonium Salts

Poly(arylene sulphides) were first obtained by Griess[4] in 1866, by the decomposition of aromatic diazonium salts in the presence of an alkali-metal sulphide. An equation has been suggested for this reaction only comparatively recently[70]:

$$n\overline{\text{Hal}}\overset{+}{\text{N}}_2\text{Ar}\overset{+}{\text{N}}_2\overline{\text{Hal}} + n\text{M}_2\text{S} \rightarrow -[-\text{ArS}-]_n- + 2n\text{MHal} + 2n\text{N}_2 .$$

Later work has shown that decomposition takes place also in the presence of hydrogen sulphide[17] or thiourea[7] and water at 0–5 °C. The products (obtained in almost theoretical yield) are brown powders, partly soluble in carbon disulphide, dioxan, and dimethylformamide. The soluble fraction of the poly(arylene sulphides) softens at 70–80 °C, but the insoluble fraction does not soften below the thermal decomposition point.

Since cryoscopic determination in diphenylamine solution and calculation from the chlorine content give molecular masses of 460–1400 and 5000–10 000 respectively for the soluble fraction, it is assumed[72] that chlorine atoms are present in the polymer molecule not only as terminal groups. Elementary analysis and the ultraviolet spectra indicate[70] that the polymer chain contains quinoid structures, azo-groups, and sulphur in semiquinoid groupings:



The presence of azo-groups is confirmed also by the evolution of gaseous nitrogen when the soluble fraction is heated to 150–200 °C, with formation of an infusible and insoluble product.

The formation of azo-groups in the polymer molecule may result from the decomposition of aromatic diazonium salts by a radical mechanism:

$$\overset{+}{\text{N}}_2\text{Ar}\overset{+}{\text{N}}_2 \xrightarrow{\text{HS}^-} {}^{\cdot}\text{N}_2\text{Ar}^{\cdot} + \ddot{\text{A}}\text{r} + {}^{\cdot}\text{N}_2\text{Ar}\overset{\cdot}{\text{N}}_2 + \ddot{\text{S}} \rightarrow -[-\text{ArN}_2-]_l - [-\text{Ar}-]_m - [-\text{ArS}-]_n -$$

However, this reaction can take place also by a mechanism of nucleophilic substitution[73,74]. In the homopolycondensation of *p*-mercaptobenzenediazonium chloride in aqueous solution at pH 7, for example, an insoluble solid product is obtained, whose colour is apparently due to the presence of azo-groups in the polymer chain[74]. The overall equation for the reaction can be written

$$2n\overset{+}{\text{H}}\overset{-}{\text{S}}\text{C}_6\text{H}_4\overset{+}{\text{N}}_2\overset{-}{\text{Cl}} \rightarrow -[-\text{S}-\text{C}_6\text{H}_4-\text{S}-\text{N}{=}\text{NC}_6\text{H}_4-]_n - + n\text{N}_2 + n\text{HCl}$$

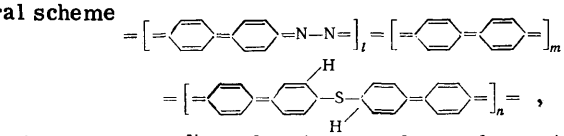
with growth of the polymer chain due to interaction of the zwitterions

$$2\overset{-}{\text{S}}\text{C}_6\text{H}_4\overset{+}{\text{N}}_2 \rightarrow -\text{S}-\text{C}_6\text{H}_4\text{SC}_6\text{H}_4\overset{+}{\text{N}}_2 + \text{N}_2 .$$

The infrared spectra of the product contain absorption bands due to diazo-sulphide groups, as well as *para*- and *meta*-disubstituted and 1,2,4-trisubstituted benzene rings, which may be centres of chain branching and cross-linking. Even after heat-treatment 150–200 °C, with evolution of nitrogen and predominant formation of poly-(*p*-phenylene sulphide) structures, nitrogen could not be completely eliminated from the polymer.

4. Polycondensation of *p*-Halogenobenzenethiolates

The homopolycondensation of metal salts of *para*-halogenated thiophenols is now one of the most promising and quite widely investigated methods for obtaining poly-(arylene sulphides). This reaction was first described in 1960 by Lenz et al.[15], and can be represented by the general scheme

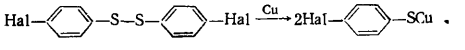


Various copper salts and amines can be used as catalysts, in amounts from 0.01 mole % to equimolecular relative to the initial thiolate[75,76].

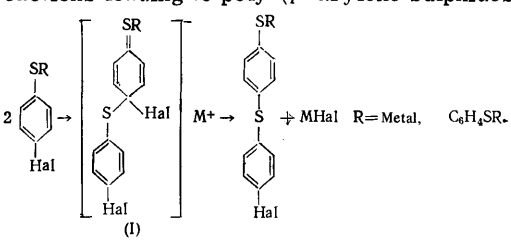
Good yields of poly(arylene sulphides) having high reduced viscosities are obtained by the homopolycondensation of *para*-halogenated thiols in the presence of catalytic quantities of dihalogenobenzenes[77]. Either soluble or infusible and insoluble polymers are obtained depending on the conditions. If the *para*-halogenated thiolate undergoes polycondensation in the mass at temperatures 10–20 deg below the melting point of the initial thiolate, for example, linear polymers are obtained; at higher temperatures infusible and insoluble products are formed under these conditions.

The rate of polycondensation in solution exceeds that in the solid state[78] by factors of 50–100. Depending on the organic solvent used—pyridine, quinoline, dimethylformamide, dimethyl sulphoxide—the process can be carried out over a wide temperature range[75]. Poly(arylene sulphides) obtained by the polycondensation of *para*-halogenated thiolates in solution had a softening point of 280 °C, and according to X-ray diffraction a linear structure.

The initial *p*-halogenobenzenethiolate can be obtained *in situ* by the action of an alkali-metal hydride or carbonate on the thiol[79,80]. An alternative is the cleavage of dihalogenated aromatic disulphides in the presence of copper powder[81]:



In a suggested[82] mechanism the resonance structure (I) formed in the first stage is responsible for the appearance of an inorganic salt and a dimer (a *p*-halogenophenyl *p'*-mercaptophenyl sulphide), the latter able to undergo further reactions leading to poly-(*p*-arylene sulphides):

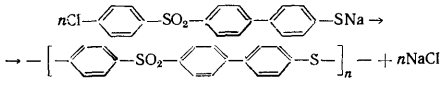


The activities of halogen atoms in the polycondensation of sodium *p*-halogenobenzenethiolates in pyridine diminish in the sequence I > Br > F ≈ Cl; and those of alkali metals in the polycondensation of a *p*-bromobenzenethiolate diminish in the sequence Li > Na > K.[82] Furthermore, the activities of iodine and bromine are little affected by the change from monomer to polymer, whereas those of chlorine and fluorine as terminal groups of the polymer molecule exceed those in the initial *p*-halogenobenzenethiolate. The nature of the halogen affects also the occurrence of secondary branching and cross-linking reactions, the probability of which decreases in the sequence I > F > Br > Cl. Such reactions disturb the balance of functional groups in the reaction mixture and lower the molecular mass of the resulting polymers. However, when monomers at least 99.6% pure are used, the occurrence of side-reactions is insignificant.

In order to obtain oligo(arylene sulphides) in which the molecular chains terminate only in chlorine atoms copper *p*-chlorobenzenethiolate was subjected to polycondensation in the presence of *p*-dichlorobenzene or di-*p*-chlorophenyl sulphide[76]. Oligomers of analogous structure have been obtained also by the copolycondensation of di-*m*(or *p*)-bromophenyl disulphide and *m*- or *p*-dibromobenzene in the presence of copper powder[83,84]. The molecular mass of the resulting oligomers varies from 186 to 2300 depending on the initial ratio of bisbromophenyl disulphide and dibromobenzene. The polycondensation of *p*-halogenobenzenethiolates in the presence of a monofunctional compound, e.g. bromobenzene or copper benzenethiolate, gives oligo(phenylene sulphides) of low molecular mass containing terminal phenyl groups[85].

Poly(arylene sulphides) containing groups other than sulphide between aromatic rings are obtained by the polycondensation of *p*-halogenobenzenethiolates containing the appropriate group in the initial structure. Thus sodium *p*-*p*'-bromophenoxybenzenethiolate in hexamethylphosphoramide solution gives poly-(*p*-phenoxyphenyl sulphides) (yield reaching 95%) having softening points of 176–188°C and a reduced viscosity of 0.09 (in the above solvent at 30°C)[79].

Linear polymers containing sulphonyl groups in the main chain have been obtained similarly from sodium 4'-*p*-chlorophenylsulphonylbiphenyl-4-thiolate[86,87]:



X-Ray diffraction indicates that the resulting polymer has a high degree of crystallinity, and it softens at ~330°C. The polycondensation of *p*-*p*'-halogenophenylsulphonylbenzenethiol and *p*-halogeno-*p*'-mercaptodiphenyl ketone in dimethylformamide solution at 140°C gives polymers of analogous structure, containing carbonyl and sulphonyl groups between two benzene rings, which are soluble in dimethylformamide, *N*-methylpyrrolidone, and sulphuric acid[88]. The reduced viscosity of their solution in dimethylformamide is 0.3.

The polycondensation of sodium and potassium 4-bromo-2-methylbenzenethiolates and 4-bromo-2,6-dimethylthiolates in dimethylformamide solution yields poly(arylene sulphides) containing methyl groups attached to the polymer chain[75]. The properties of these polymers depend on the structure of the macromolecules. Thus a polymer obtained from sodium 4-bromo-2,6-dimethylbenzenethiolate had molecular mass 740 and softening point 160–180°C, while the corresponding characteristics of poly-(2-methyl-1,4-phenylene sulphide) were 1500 and 60–100°C. The reactivity of the initial *para*-halogenated thiolate diminishes with increase in the number of substituents (methyl groups) in the benzene ring[75].

Perfluorinated poly(phenylene sulphides) have been obtained in high yield by the polycondensation of sodium pentafluorobenzenethiolate in pyridine at 50–200°C.[89-92] Completely halogenated polymers have been obtained also by the polycondensation of pentachloro- and pentabromobenzenethiolates[91,93]. Halogenated poly(phenylene sulphides) are insoluble, dark-coloured powders, which can be used to obtain materials having semiconducting properties.

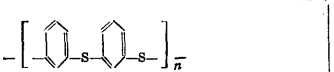
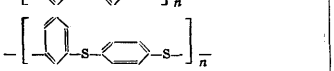
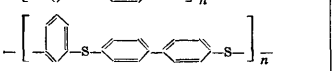
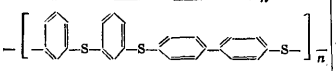
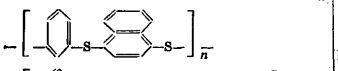
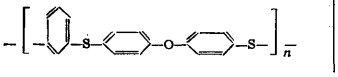
5. Polycondensation of Benzenedithiolates with Dihalogenated Aromatic Compounds

The preparation of poly(arylene sulphides) by the polycondensation of benzenedithiolates with dihalogenated aromatic compounds, which is also of practical interest, was described by Kreuchunas[94] in 1958. When sodium benzene-*p*-dithiolate and di-*p*-chlorophenyl sulphone were boiled in ethanolic solution for 4 h, poly(arylene sulphides) of not very high molecular mass were obtained.

It was proposed[95,96] that the molecular mass could be increased by carrying out the polycondensation in polar organic solvents of high boiling point, e.g. dimethyl sulphoxide, dimethylformamide, dimethylacetamide, etc., and by using dihalogenated aromatic compounds in which the halogen atoms were activated by bivalent electron-deficient groups located between aromatic rings containing halogen in the *para* position, and also by univalent electron-accepting groups present in the dihalogenobenzene as substituents. The poly(arylene sulphides) obtained in this way had specific viscosity 0.32 (in *N*-methylpyrrolidone at 20°C).

The viscosity of the poly(phenylene sulphides) obtained from benzene-*m*-dithiol and *p*-dibromobenzene in dimethylformamide in the presence of potassium carbonate initially increases[80] on polycondensation, after which it falls as the duration of the process lengthens to 96 h.

Table 4. Dependence of properties of poly(arylene sulphides) on structure of monomer unit.

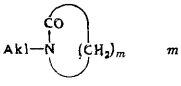
Polymer	Dihalogenoarene	Softening temp., °C	Viscosity, dl g^{-1} *
	*m*-dibromobenzene	100—120	0.1
	*p*-dibromobenzene	110—140	0.15
	4,4'-dibromobiphenyl	160—190	—
	*m*-dibromobenzene + 4,4'-dibromobiphenyl (1:1)	85—100	0.11
	1,4-dibromonaphthalene	155—195	—
	di-*p*-bromophenyl ether	55—70	0.07

* Viscosities determined for a 0.5% solution in hexamethylphosphoramide at 30°C.

Table 4 lists properties of various poly(arylene sulphides) obtained by polycondensation of benzene-*m*-dithiol with dibrominated aromatic compounds in dimethylformamide[80]. The softening points obviously depend on the structure of the macromolecules: introduction of an oxygen atom into the main chain lowers the softening temperature considerably, but biphenylylene units raise it.

However, optimum production of fibre-forming poly(arylene sulphides) of high molecular weight is achieved by the polycondensation of 25–40 wt.% of dithiolates and

bis-*p*-chlorophenyl sulphone in *N*-methylpyrrolidone at 140–160°C for 4–5 h.[97,98] Dihalogenated aromatic compounds in which the halogen atoms are inactive can also be used, e.g. *p*-dichloro- or *p*-dibromo-benzene[99], but a catalyst is then necessary—a copper compound, e.g. cupric oxide, copper acetate, a halide, etc., or *N*-bromosuccinimide (0.06–3 wt.%)—and temperatures of 200–210°C are required. In order to diminish the quantity of byproducts, whose formation is due to the high-temperature (above 140°C) decomposition and oxidation of *N*-methylpyrrolidone, cyclic lactams of general formula



$m = 5-11$,

e.g. *N*-methylcaprolactam, have also been used[100].

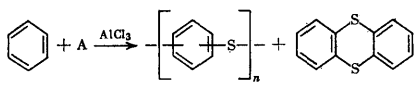
Aromatic dithiolates are usually prepared directly in the apparatus for their polycondensation with dihalogenated aromatic compounds. For this purpose the dithiol is treated with aqueous alkali[99,101], or an alkali-metal carbonate is gradually added to a solution of the dithiol in dimethylformamide[80,96,102]. The hydrogen halide evolved is removed by means of ammonia, diethylamine, morpholine, etc. introduced directly into the reaction space. This increases the rate of polycondensation and yields poly(arylene sulphides) of higher molecular mass[100].

Poly(arylene sulphides) containing functional groups have also been obtained from dithiolates and polyhalogenated aromatic compounds. Thus the reactions of aromatic dithiols with perchlorinated aromatic compounds in the presence of bases gives fusible and soluble poly(arylene sulphides) containing perchlorinated aromatic groups in the main chain[103,104]. After pressure moulding at 400°C such polymers lose their solubility in benzene.

The copolycondensation of benzene-*m*-dithiol with *p*-dibromobenzene and 2,4- or 3,5-dichlorobenzonitrile yields poly(phenylene sulphides) containing nitrile groups[80,105,106], but the action of excess of the dithiol on the dibromobenzene gives polymers having terminal mercapto-groups, treatment of which with *p*-bromobenzonitrile in dimethylformamide containing potassium carbonate gives poly(phenylene sulphides) with terminal nitrile groups. Polymers containing in the main chain sulphur, oxygen, and also various other groupings between the benzene rings are obtained by the copolycondensation of aromatic dithiols with a mixture of two dihalogenated aromatic compounds[107]. Analogous copolymers have been obtained also by using a mixture of aromatic dithiol and diol with the dihalogenated compounds[108]. Another alternative is the polycondensation of *p*-mercaptophenol with the dihalide[100,109].

6. Reaction of Aromatic Compounds and their Derivatives with Sulphur or its Chlorides

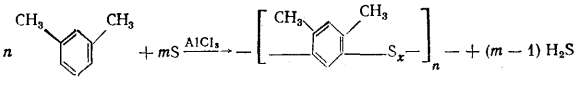
The reaction of benzene with sulphur when heated in the presence of aluminium chloride was first effected in 1888 by Friedel and Crafts[110], when relatively simple compounds—hydrogen sulphide, benzenethiol, diphenyl sulphide and disulphide, thianthren, isothianthren, etc.—were isolated. It was shown somewhat later[111,112] that under these conditions an amorphous polymer having a softening point of ~295°C can be obtained in yields up to 80%. Elementary analysis indicates that the monomer unit in the polymer is C_6H_4S, so that formation of the poly(phenylene sulphide) can be represented by the general scheme[113]



A = S, S_2Cl_2, SCl_2 .

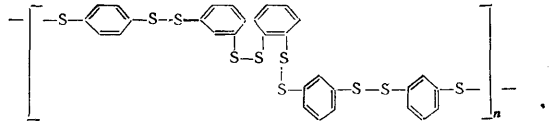
The quantity of byproducts formed—thianthren and diphenyl sulphide—depends on the initial content of aluminium chloride, increase in which increases formation of the sulphide and diminishes that of thianthren[114]. Complexes of aluminium chloride with these two compounds were also isolated[115]. The reaction between aromatic hydrocarbons and sulphur has therefore been carried out[116] in the presence of sulphuric acid under increased pressure at 220–300°C. Poly(arylene sulphides) obtained in this way from benzene, naphthalene, and anthracene softened at ~100°C. Since their sulphur content varied from 10% to 90%, it was supposed[115] that the sulphidation of aromatic rings under these conditions yields polymers containing polysulphide groups $[ArS_x]_n$.

Benzene derivatives can also be used for reaction with sulphur. Thus resinous products useful for medicinal purposes were obtained from xylene and sulphur in the presence of aluminium chloride at 80–90°C.[117] It has since been established[118] that under these conditions only *m*-xylene forms polymeric products, probably by the mechanism



The formation of polymers having a regular structure is attributed[118] to the influence of substituents in the benzene ring. With increase in the content of sulphur or the concentration of aluminium chloride in the initial mixture the quantity of combined sulphur in the polymeric product increases to a limiting maximum of 11.1%. Polymers containing >8% of sulphur solids of molecular mass 1000 and softening point 40°C. Later investigation has shown[119] that the aromatic rings in the polymer from *m*-xylene are interlinked mainly by disulphide groups.

Gaseous hydrogen chloride is evolved from the action of sulphur on chlorinated benzenes (e.g. chlorobenzene or dichlorobenzenes) at 225–350°C (and also at high pressures)[120]. The solid products are oligo(phenylene sulphides) containing 40–80 wt.% of sulphur, softening at ~100°C, and soluble in carbon disulphide. When they are decomposed by metallic sodium in liquid ammonia[121], a mixture of isomeric dithiolobenzenes is isolated in 35% yield, comprising 50% of the *para* isomer with 25% each of the *ortho* and *meta* isomers. It is thus confirmed[121] that the oligomers contain all three types of substituted aromatic rings interlinked by disulphide groups:



Black sulphur-containing polymers with improved electrical conductivity and electron-exchange properties, infusible and insoluble in organic solvents, have been obtained by the polycondensation of sulphur with chloranil, 1,4-naphthaquinone, anthraquinone, or 1,5-dihydroxyanthraquinone in the molecular proportions 4–12 : 1 at 280–400°C.[122] The polymer chains contain not only

monosulphide-linked quinoid but also thianthren groups, and may be joined by polysulphide cross-links. Excess of sulphur increases the likelihood of polysulphide bonds.

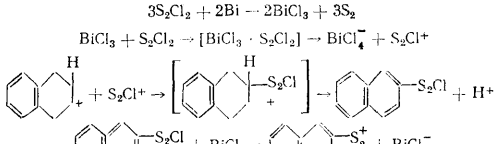
The structure of the products formed from aromatic hydrocarbons with sulphur and especially sulphur chlorides is significantly influenced by the nature of the catalyst. The reaction of benzene with sulphur dichloride in the presence of aluminium chloride yields thianthren as main product[123]. In the presence of sulphuric acid, however, sulphur dichloride acts on benzene, toluene, or xylene to give polymeric products as powders readily soluble in xylene[124].

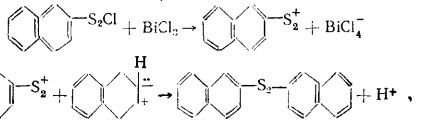
The action of sulphur chlorides on diphenyl ether and sulphide in the presence of aluminium or its salts yields cyclic compounds—phenoxatin and thianthren respectively[125,126]—intramolecular cyclisation probably being due to formation of complexes of aluminium or its salts with the initial heteroatomic products, containing oxygen and sulphur respectively. In order to obtain linear compounds of high molecular weight the reaction between diphenyl ether and sulphur chloride has been conducted in the presence of iron powder or anhydrous iron(III) chloride in chloroform solution at room temperature[125-127]. The resulting polymers (obtained in quantitative yield) had a reduced viscosity of 0.1 (in 1% solution in hexamethylphosphoramide) and a softened point at 147–156°C. Elementary analysis, X-ray diffraction, and n.m.r. spectra indicated that polymers formed from diphenyl ether and sulphur dichloride are crystalline and contain only monosulphide links between aromatic rings, whereas those obtained from the ether and sulphur monochloride are amorphous and contain not only monosulphide but also up to 15% of disulphide groups. However, it has been reported[128] that polymers obtained from diphenyl sulphide and sulphur dichloride, partly soluble solids softening at 125°C, also contain up to 10% of disulphide groups.

Poly(arylene sulphides) of diverse structure and molecular mass up to 2000 have also been obtained[129] by the polycondensation of aromatic hydrocarbons with sulphur chlorides in chloroform solution in the presence of various metals (bismuth, tin, or antimony) at ~60°C. Chlorides of the metals are probably formed in the first stage, and the overall reaction of naphthalene with sulphur dichloride in the presence of bismuth can be written

$$3S_2Cl_2 + 2Bi \rightarrow 2BiCl_3 + 3S_2$$

$$BiCl_3 + S_2Cl_2 \rightarrow [BiCl_3 \cdot S_2Cl_2] \rightarrow BiCl_4^- + S_2Cl^+$$





Further growth of the polymer molecule probably involves di-2-naphthyl disulphide formed from chlorodisulphanyl ions, polarised naphthalene, and bismuth chloride, which appear as intermediate products. However, infrared spectral data, elementary analysis, measurements of molecular mass, and the separation of elementary sulphur on prolonged storage indicate that the products are oligomers, whose molecules comprise seven or eight $\beta\beta'$-disubstituted naphthalene groups, interlinked not only by disulphide but also by polysulphide bonds. The formation of such groups can be explained by the participation in intermediate reactions of polysulphur chlorides resulting from decomposition of sulphur monochloride:

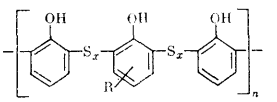
$$2S_2Cl_2 \rightarrow SCl_2 + S_3Cl_2$$

$$2S_nCl_2 \rightarrow S_{n-1}Cl_2 + S_{n+1}Cl_2 \ .$$

Oligomers obtained from anthracene or phenanthrene under the same conditions contain respectively $\beta\beta'$-substituted anthracene or 2,3- and 6,7-substituted phenanthrene groups, as well as di- and poly-sulphide groups. The yield of oligomers is 49–63% depending on the nature of the catalyst[129].

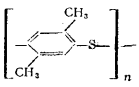
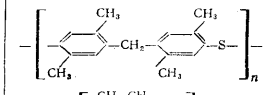
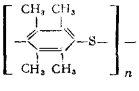
Poly(arylene sulphides) of molecular mass up to 3×10^6 are obtained[130] by reaction between various aromatic compounds and sulphur halides at a constant pH in the presence of up to 35% of an activator (an alkali or a carboxylic acid or ester). The polymer thus obtained from anthracene and sulphur chloride is a powder having a softening point of ~90°C.

Poly-(2-hydroxy-1,3-phenylene polysulphides) of general formula



where R = Alk and $x = 1-7$, are synthesised by the polycondensation of *p*-alkylphenols or their substituted derivatives with sulphur monochloride or dichloride[131,132], or of phenolic compounds with sulphur in the presence of a basic catalyst (e.g. sodium hydroxide) at 120–200°C.[133]

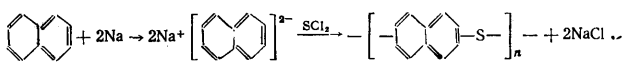
Table 5. Properties of methylated poly(arylene sulphides).

Arene	Monomer unit	Yield, %	Softening temp., °C	Mol. wt.	Cl, %
p-Xylene		60	270—285	1500	7.75
2,2',5,5'-Tetramethyl diphenylmethane		55	240—250	1300	11.88
1,2,4,5-Tetramethylbenzene		70	291	950	6.5

Methylated poly(arylene sulphides) have been obtained by the action of sulphur dichloride on methylated aromatic compounds in the presence of iron powder[128]. Table 5 gives several characteristics of such polymers. The products had a regular structure and contained up to almost 12% of chlorine. An interesting feature of this reaction is that, whereas *p*-xylene and sulphur dichloride gave methylated poly(phenylene sulphides) under these conditions, the polycondensation of *p*-xylene with sulphur in the presence of aluminium chloride does not yield polymeric products[118]. Oil-soluble chlorinated poly(phenylene sulphides) are obtained by the polycondensation of tri-, tetra-, and penta-chlorobenzenes with sulphur monochloride in the presence of aluminium chloride[134,135].

Such polymers soften above 85°C, the viscosity of the melt is 0.256 P (at 131°C), and they contain up to 50% of chlorine.

Furthermore, a process has been elaborated[136] for the preparation of poly(arylene sulphides) in high yields by the reaction of dipotassium diphenylbutane, disodium diphenylmethane, disodium naphthalene, and other dimetallated aromatic derivatives with sulphur halides in inert solvents (oxolan, n-hexane, etc.) at temperatures from −75 to +75°C. The reaction of disodium naphthalene with sulphur dichloride can be represented in general as

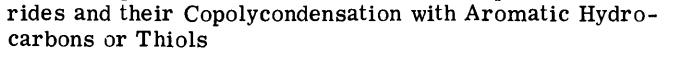


The products have softening points of ~175°C, and can be used as thermostable adhesives.

An examination of thermodynamic aspects of the formation of sulphur polymers by heating has shown[137] that polymeric phenylene polysulphides can be obtained from chlorinated aromatic compounds and polymeric sulphur.

7. Homopolycondensation of Aromatic Sulphenyl Chlorides and their Copolycondensation with Aromatic Hydrocarbons or Thiols

The first descriptions have appeared[138-140] of the preparation of poly-(*p*-phenoxyphenylene sulphides) by the copolycondensation of diphenyl and di-*p*-chlorothiophenyl ethers in the presence of metal powders or salts in an inert atmosphere away from the light at room temperature:



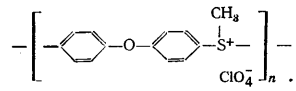
The resulting polymers dissolve readily in aromatic hydrocarbons and polar organic solvents. Table 6 gives data on the influence of the nature of the catalyst on the yield and certain properties of the products. Elementary analysis and n.m.r. spectra indicate that the polymer molecule contains *para*-substituted aromatic rings joined together by mono- and di-sulphide groups, the latter amounting to 9–10%. The formation of disulphide links is attributed[138-140] to reaction between the sulphenyl chloride groups, which is supported by the evolution of gaseous chlorine. The mechanism of polycondensation has been studied also on model compounds.

Table 6. Dependence of properties of polymers on nature of catalyst.

Catalyst	Yield, %	Softening temp., °C	Viscosity, dl g^{-1}*
Fe	75	160—170	0.12
$FeCl_3$	75	156—189	0.10
$SnCl_4$	68	153—173	0.07
$AlCl_3$	38	140—175	0.08

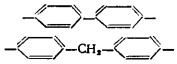
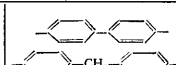
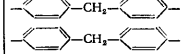
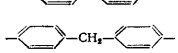
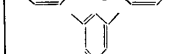
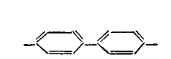
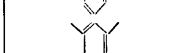
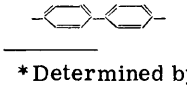
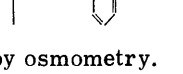
* Viscosities determined for 1% solutions in hexamethylphosphoramide at 30°C.

Polymers containing aromatic rings linked by sulphide groups are obtained[140] by the homopolycondensation of benzenesulphenyl and *p*-phenoxybenzenesulphenyl chlorides in chloroform solution in the presence of metal powders or Lewis acids. The poly-(*p*-phenoxyphenylene sulphide) was obtained in 53% yield and softened at 134–145°C. Poly(alkyl- and aryl-*p*-phenoxyphenylsulphonium) salts, with decomposition points of 165–275°C and reduced viscositities of 0.06–0.55, have been obtained[141] by the homopolycondensation of alkyl and aryl *p*-phenoxyphenyl sulphides in a mixture of 70% of perchloric acid and phosphoryl chloride in argon at 25°C for 20 h followed by heating at 50–60°C. The structure of the polymer obtained from the methyl sulphide corresponds to the formula



Such a polymer is soluble in formic acid and in aprotic polar solvents. On dealkylation by boiling in pyridine it is converted into a poly(*p*-phenoxyphenylene sulphide) of softening point ~188°C and reduced viscosity 0.27.

Table 7. Dependence of properties of polymers on structure of initial monomers.

R	R′	Molecular mass*	Sulphur, %	
			expt.	calc.
		(insol.)	29.3	29.6
		(2–4) × 10^3	27.6	27.8
		(insol.)	28.5	28.7
		(2–4) × 10^3	31.2	34.6
		(insol.)	35.1	36.0

* Determined by osmometry.

Poly(arylene sulphides) have been obtained in yields up to 90% also by the polycondensation of aromatic disulphenyl chlorides with aromatic dithiols in oxolan solution at 20°C:[142]

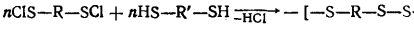


Table 7 shows that poly(arylene disulphides) containing biphenylylene groups are insoluble in the usual organic solvents, in contrast to those containing *m*-phenylene or diphenylmethane groups, and are readily soluble in oxolan and chloroform. The structure of the polymeric disulphides has been confirmed by infrared and n.m.r. spectra and by X-ray diffraction[143]. Redistribution of monomer units by interaction of the disulphide bond with the chlorothio-group does not take place, and the polymers have a regular structure.

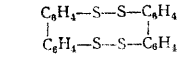
8. Preparation of Poly(arylene Disulphides) by the Oxidation of Dithiols

In 1909 Zincke and Frohnberg[144] oxidised benzene-*p*-dithiol with various oxidants (e.g. air, iron chlorides, peroxides, sulphuric and nitric acids) in acetic acid, and isolated as main product an amorphous yellow powder,

insoluble in the usual organic solvents. Analysis suggested a polymer having the monomer unit $[C_6H_4.S_2]_n$. Treatment with copper powder and heating in order to cleave the disulphide bonds gave an oil, from which a cyclic dimer, *pp'*-diphenylene bisdisulphide, was obtained[145]. When benzene-*p*-dithiol was oxidised with chlorine or bromine under the same conditions, the precipitated product passed after some time back into solution, from which benzene-*p*-disulphonyl chloride or bromide respectively was then isolated[144].

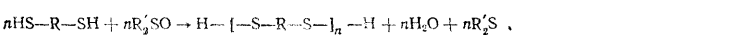
However, the oxidation of benzene-*p*-dithiol with ethanolic iodine gives an approximately 75% yield of a solid product that is partly soluble in organic solvents and softens at 198–202°C.[128] Elementary analysis (sulphur content 46.12%) and X-ray diffraction indicate that it is a linear poly-(*p*-phenylene disulphide).

Biphenyl-4,4'-diol is oxidised more slowly by air than by alkaline solutions[146], to give a cyclic tetraphenylene tetrasulphide

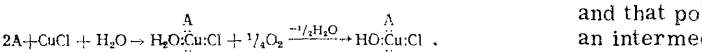


as an insoluble amorphous product.

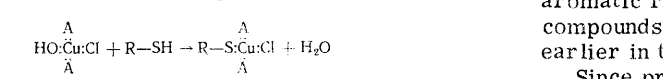
Aliphatic sulphoxides have also been used as oxidants. The oxidation of dithiols when solutions in dimethyl sulphoxide are heated at 95–170°C can be represented by the general scheme[147]



More detailed investigation of the action of various oxidants on aromatic dithiols has established[148] that iodine and hydrogen peroxide tend to increase not only the rate of formation but also the yield of poly(arylene disulphides), while the use of catalysts (e.g. a mixture of a copper salt and an amine, acid, or alkali) dissolved in an inorganic solvent (e.g. water) at temperatures of 0 to 38°C promotes the formation of poly(arylene disulphides) of higher molecular mass. An intermediate complex is probably formed in the inorganic solvent, according to the general scheme (for a mixture of copper(I) chloride and an amine A)



Its reaction with a mercapto-group can then be written



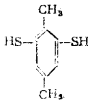
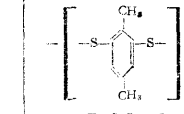
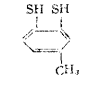
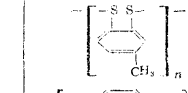
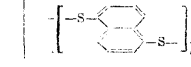
This reaction results in regeneration of the amine complex of the copper salt and formation of organic disulphides. It is noteworthy that the polycondensation of dithiols also occurs in conformity with the mechanism suggested for the oxidation of thiols.

Table 8 gives the structural formulae of the initial dithiols subjected to oxidation together with characteristics of the poly(arylene disulphides) obtained in quantitative yield. The polymer from 4-methylbenzene-1,2-dithiol dissolves readily in chloroform, whereas that from naphthalene-1,5-dithiol is insoluble in the usual organic solvents.

9. Polytransarylation of Aromatic Sulphides

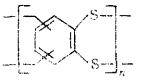
A process suggested comparatively recently[149] for obtaining poly(arylene sulphides) by the polycondensation of aromatic sulphides is to heat them in the presence of Friedel–Crafts catalysts to 160–350°C. Either insoluble or solvent-soluble products can be obtained depending on the conditions. Thus when diphenyl sulphide is heated with 6 mole % of aluminium chloride at 200°C for 4 h, benzene distils off and an 85.2% yield is obtained of a powder containing 85.6% of a benzene-soluble product of molecular mass 450 (determined cryoscopically in benzene) and softening temperature 110–120°C. Elementary analysis indicates a 37.53% sulphur content, exceeding by 8% the content for the monomer unit $[C_6H_4.S]_n$. Furthermore, preparative thin-layer chromatography has revealed thianthren among the reaction products[150].

Table 8. Structure of polymers obtained from initial dithiols.

Dithiol	Monomer unit	Softening point, °C
		~190
		~118
		>250

From the results it is considered[150] that the mechanism of the polycondensation of diphenyl sulphide is analogous to that of the well known transarylation of diarylalkanes[151] and that polycondensation is accompanied by formation of an intermediate complex of diphenyl sulphide with aluminium chloride. The appearance of cyclic products is attributed to the greater activity of the *ortho* position in the aromatic ring relative to the sulphur substituent. Cyclic compounds containing *ortho* substituents had been isolated earlier in the transarylation of diarylalkanes[152].

Since products of the transarylation of diphenyl sulphide contain neither thiol nor disulphide groups according to the infrared spectra and chemical analysis, the structure of the oligomers may contain predominantly polythianthren groupings.

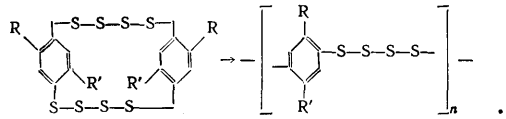


The presence of such structures among the reaction products is confirmed by mass spectrometry and also by the polymerlike conversion of these products into the corresponding sulphones followed by analysis of thermal decomposition products of the polymer analogues.

10. Polymerisation of Cyclic Sulphides

Poly(arylene tetrasulphides) have been obtained by the thermal polymerisation of cyclic diarylene bistetrasulphides in the mass or in solution in a stream of an inert

gas at 150–220°C:[153-155]



R=R′=OC_2H_5 (I); R=R′=OCH_3 (II); R=OCH_3, R′=Cl (III).

Table 9 gives conditions of preparation, reduced viscosity, and molecular mass for a few poly(arylene tetrasulphides). The products are stable under normal conditions and possess satisfactory adhesion to metals.

Table 9. Reaction conditions and properties of poly(arylene tetrasulphides).

Monomer	Conditions	Reduced viscosity, 0.4 g/100 ml $CHCl_3$	Mol. wt. (number-av.)
(I)	in mass, 195°C, 1 h	0.21	15 781
(I)	in bromobenzene, 150°C, 3 days	0.08	7 129
(I)	in bromobenzene, 150°C, 16 h	0.06	4 653
(II)	in mass, 220°C, 1 h	0.08	—
(III)	in mass, 195°C, 1 h	0.04	—

11. Polycondensation of Dihalogenated Aromatic Compounds with Alkali Metals

Application of the Wurtz–Fittig reaction to di-*o*(and *p*)-chlorophenyl sulphides with metallic sodium has recently[156] yielded soluble poly-(*o*(and *p*)-diphenyl sulphides), respectively plastic at room temperature and solids passing into a state of viscous flow at 170–200°C.

III. PRACTICAL APPLICATIONS

A previous review[3] has examined in sufficient detail the properties of various poly(arylene sulphides), the changes undergone under processing conditions, and the properties of articles made from them. Below, therefore, we give only general information on properties and practical applications, noting primarily the main lines of development in the light of recent work.

Poly(arylene sulphides) are distinguished by high thermal[8,92,95,157-163], thermo-oxidative[15,113,157-159,164,165] and chemical[17,157,162,166-168] stability, fire resistance[157,166,187-192], non-toxicity[24,183,193,194], and several other specific properties[24,103,164,195-201]. They can be readily oxidised by various oxidants (hydrogen peroxide[95-97,162,202-206], nitric acid[207], etc.) to poly(arylene sulphoxides or sulphones), a process that should be applied to the ready-made materials and articles[208]. Heat-treatment has been used to diminish the fluidity and raise the softening point[184,192,209-214]: thus heating at 320°C for 300 h raised the working range of a poly(arylene sulphide) to higher temperatures (from 100 to 200°C and above)[211]. The maximum operating temperature at which films retain their strength for a long time (>10 weeks) has been regarded[157,158,164,166,187,214] as 260°C, but the temperature of prolonged operation of the polymer has been restricted[188] to 180°C.

Poly(arylene sulphides) surpass polysulphones and polyimides in many physicochemical indices[164]. They are used as adhesives for glass-fibre laminates[164,166,180,182,215-223], which have better mechanical strength at 204°C than has polyethylene at room temperature[166].

Poly(arylene sulphides) provide good electrically insulating materials[187-189,224-228]. Thus the dielectric constant of poly(phenylene sulphide) has been given as 3.1 (10^6 Hz), the dielectric loss angle as 0.0007 (10^6 Hz), the dielectric strength as 23.8 kV mm^{-1}, and the bulk resistance as 10^{16} ohms cm.[157,166]

Great attention has been paid to studying the properties of films based on poly(phenylene sulphides)[7,157,162,164,166,168,171,172,184,187-189,229-244], which show good adhesion to various supports[24,82,164,195-199].

Compositions of poly(arylene sulphides) with various fillers can be processed into articles by injection moulding, extrusion, pressure moulding, etc.[214,215,223,229,245-251]. Articles made of such compositions can be ground, milled, drilled, welded ultrasonically, metallised with chromium and other metals, and also threaded[252]. This explains the widespread use of poly(arylene sulphides) and articles made from them in mechanical and electrical engineering, aircraft construction, chemical industry, and other technologies.

REFERENCES

1. V.A. Sergeev, V.K. Shitikov, and L.G. Grigor'eva, Uspekhi Khim., 45, 1842 (1976) [Russ. Chem. Rev., No. 10 (1976)].
2. V.V. Kopylov, Uspekhi Khim., 39, 471 (1970) [Russ. Chem. Rev., No. 3 (1970)].
3. V.A. Sergeev, V.K. Shitikov, and V.I. Nedel'kin, in "Itogi Nauki i Tekhniki, Seriya, Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii" (Summaries of Science and Technology—Chemistry and Technology of High Polymers Series), Izd. VINITI, Moscow, 1977, Vol. 11, p. 53.
4. P. Griess, Annalen, **137**, 74 (1866).
5. A.D. Macallum, J. Org. Chem., **13**, 154 (1948).
6. V.N. Kondrat'ev (Editor), "Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu, Spravochnik" (Handbook of Chemical Bond Energies, Ionisation Potentials, and Electron Affinities), Nauka, Moscow, 1974, p. 93.
7. B.J. Tabor, E.P. Magre, and J. Boon, European Polymer J., 7, 1127 (1971).
8. V.A. Sergeev, V.K. Shitikov, V.I. Nedel'kin, N.V. Batenina, and V.V. Korshak, Vysokomol. Soed., **17B**, 710 (1975).
9. R.T. Hawkins, Macromolecules, 9, 189 (1976).
10. US P. 2 538 941 (1951); Chem. Abs., 45, 5193 (1951).
11. US P. 2 513 188 (1950); Chem. Abs., 44, 8165 (1950).
12. US P. 3 285 882 (1966); Chem. Abs., 63, 13 440 (1965).
13. US P. 3 268 504 (1966); Chem. Abs., 65, 16 902 (1966).
14. R.W. Lenz and W.K. Carrington, J. Polymer Sci., 41, 333 (1959).
15. R.W. Lenz and C.E. Hadlovits, J. Polymer Sci., 43, 167 (1960).
16. US P. 3 375 232 (1968).
17. N.G. Galylord, "Polyethers", in High Polymers Series, Vol. 13, Part 3, Interscience, New York, 1962, p. 11.

18. B. Horting and I. I. Lindberg, Chem. Scripta, **2**, 179 (1972).
19. B. Hortin, International Symposium on Macromolecules, Helsinki, 1972, Vol. 5, p. 37.
20. US P. 3 303 170 (1967); Chem. Abs., **63**, 13 515 (1965).
21. US P. 3 843 614 (1974);
22. US P. 3 354 129 (1967); Chem. Abs., **68**, 13 598 (1968).
23. US P. 3 524 835 (1970); Chem. Abs., **73**, 121 201 (1970).
24. I. N. Short and H. W. Hill, Chem. Tech., 481 (1972).
25. US P. 3 790 536 (1974).
26. Jap. P. 123 799 (1975); Chem. Abs., **84**, 45 908 (1976).
27. US P. 3 415 889 (1968).
28. US P. 3 786 035 (1974).
29. US P. 3 783 138 (1974); Chem. Abs., **80**, 121 518 (1974).
30. US P. 3 839 302 (1974); Chem. Abs., **82**, 17 894 (1975).
31. US P. 3 407 182 (1968).
32. US P. 3 707 528 (1972); Chem. Abs., **73**, 73 100 (1973).
33. US P. 3 478 000 (1969).
34. US P. 3 800 845 (1974).
35. US P. 3 941 664 (1976); Chem. Abs., **84**, 151 227 (1976).
36. US P. 3 687 907 (1972).
37. US P. 3 457 242 (1969).
38. US P. 3 697 487 (1972); Chem. Abs., **78**, 4942 (1973).
39. US P. 3 380 951 (1968).
40. V. A. Sergeev, V. K. Shitikov, V. I. Nedel'kin, and V. V. Korshak, Vysokomol. Soed., **11A**, 2420 (1975).
41. US P. 3 763 124 (1973).
42. US P. 3 429 932 (1969).
43. BRD P. 2 026 655 (1973).
44. US P. 3 607 843 (1971).
45. US P. 3 756 993 (1973).
46. US P. 3 869 434 (1975).
47. US P. 3 966 688 (1976); Chem. Abs., **85**, 94 921 (1976).
48. V. A. Sergeev, V. K. Shitikov, V. I. Nedel'kin, and V. V. Korshak, USSR P. 532 609 (1976); Byull. Izobr., No. 39 (1976).
49. A. A. Shutov and E. Ya. Vaiman, Ser. Khimiya i Khim. Tekhnol., **16**, 1736 (1973).
50. USSR P. 410 594 (1974); Byull. Izobr., No. 1 (1974).
51. Bulg. P. 13 958 (1972); Ref. Zhur. Khim., 3S331 (1973).
52. B. P. 1 153 035 (1969).
53. BRD P. 1 179 715 (1965).
54. US P. 3 862 095 (1975); Chem. Abs., **82**, 141 002 (1975).
55. US P. 3 865 795 (1975); Chem. Abs., **82**, 157 012 (1975).
56. US P. 3 884 883 (1975); Chem. Abs., **83**, 115 382 (1975).
57. US P. 3 919 177 (1975).
58. US P. 3 865 794 (1975); Chem. Abs., **83**, 12 389 (1975).
59. US P. 3 870 687 (1975); Chem. Abs., **82**, 171 717 (1975).
60. US P. 3 870 686 (1975); Chem. Abs., **82**, 171 718 (1975).
61. US P. 3 880 815 (1975); Chem. Abs., **83**, 115 369 (1975).
62. US P. 3 867 357 (1975); Chem. Abs., **82**, 157 020 (1975).
63. US P. 3 882 092 (1975); Chem. Abs., **83**, 115 376 (1975).
64. US P. 3 876 592 (1975); Chem. Abs., **83**, 44 029 (1975).
65. US P. 3 876 591 (1975); Chem. Abs., **83**, 44 030 (1975).
66. US P. 3 867 356 (1975); Chem. Abs., **82**, 171 704 (1975).
67. US P. 3 884 884 (1975); Chem. Abs., **83**, 115 384 (1975).
68. US P. 3 869 433 (1975); Chem. Abs., **82**, 171 719 (1975).
69. BRD P. Appln. 2 453 749 (1975); Chem. Abs., **83**, 115 380 (1975).
70. M. Poninski and M. Kryszewski, Roczniki Chem., **39**, 1523 (1965).
71. M. Poninski and M. Kryszewski, Roczniki Chem., **39**, 505 (1965).
72. M. Poninski and M. Kryszewski, Bull. Acad. polon. Sci., **13**, 49 (1965).
73. R. Leukart and P. Holzapfel, J. prakt. Chem., **41**, 213 (1890).
74. C. C. Price and S. Tsunawaki, J. Org. Chem., **28**, 1867 (1963).
75. S. Tsunawaki and C. C. Price, J. Polymer Sci., **2**, 1511 (1964).
76. US P. 3 098 103 (1963).
77. US P. 3 940 375 (1976); Chem. Abs., **84**, 165 391 (1976).
78. Belg. P. 613 003 (1962); Chem. Abs., **57**, 15 356 (1962).
79. Jap. P. 42 157 (1972); Chem. Abs., **80**, 83 896 (1974).
80. I. Haddad, S. Harley, and C. S. Marvel, J. Polymer Sci., Polymer Chem., **11**, 2793 (1973).
81. US P. 3 291 779 (1966); Chem. Abs., **66**, 29 346 (1967).
82. R. W. Lenz, C. E. Handlovits, and H. A. Smith, J. Polymer Sci., **58**, 351 (1962).
83. USSR P. 376 412 (1973); Byull. Izobr., No. 17, 80 (1973).
84. BRD P. 1 275 535 (1969):
85. BRD P. Appln. 61 859 (1968); Chem. Abs., **70**, 38 311 (1969).
86. US P. 3 780 000 (1973).
87. B. P. 1 355 059 (1974).
88. US P. 3 819 582 (1974).
89. Jap. P. 36 299 (1973); Chem. Abs., **79**, 126 927 (1973).
90. P. Robson, M. Stacey, R. Stephens, and J. C. Tatlow, J. Chem. Soc., 4754 (1960).
91. H. Kawazura and T. Taketomi, J. Polymer Sci., **B10**, 265 (1972).
92. N. S. J. Christopher, J. L. Cotter, G. J. Knight, and W. W. Wright, J. Appl. Polymer Sci., **2**, 863 (1968).
93. E. A. Aroskar, M. T. Chandhry, R. Stephens, and J. C. Tatlow, J. Chem. Soc., 2975 (1964).
94. US P. 2 822 351 (1958); Chem. Abs., **52**, 7778 (1958).
95. Swiss P. 464 538 (1968); Chem. Abs., **69**, 97 357 (1968).
96. A. L. Baron and D. R. Blank, Makromol. Chem., **140**, 83 (1970).
97. L. N. Slesareva, E. P. Perepechkina, F. M. Mandrosova, M. I. Bogdanov, and A. V. Volokhina, International Symposium on Chemical Fibres, Kalinin, 1974, Section 4, Preprints, p. 45.

98. USSR P. 479 789 (1975); Byull. Izobr., No. 52, 82 (1975).
99. Swiss P. 478 866 (1969); Chem. Abs., 71, 81 923 (1969).
100. Swiss P. 555 382 (1974); Chem. Abs., 78, 44 219 (1973).
101. US P. 3 730 949 (1973).
102. G. Montaudo, G. Bruno, P. Maravigna, and P. Finocchiaro, J. Polymer Sci., Polymer Chem., 11, 65 (1973).
103. US P. 3 736 293 (1973); Chem. Abs., 75, 64 615 (1971).
104. US P. 3 740 375 (1973).
105. I. Haddad and C. S. Marvel, J. Polymer Sci., Polymer Chem., 12, 1301 (1974).
106. US P. Appln. 541 489 (1975); Chem. Abs., 85, 124 992 (1976).
107. Swiss P. 503 066 (1971); Chem. Abs., 73, 110 311 (1970).
108. Swiss P. 486 517 (1970); Chem. Abs., 72, 32 479 (1970).
109. Swiss P. 521 407 (1972).
110. M. C. Friedel and J. M. Crafts, Ann. Chim. Phys., 14, 433 (1888).
111. M. P. Genvresse, Bull. Soc. chim. France, 15, 1038 (1896).
112. M. P. Genvresse, Bull. Soc. chim. France, 17, 599 (1897).
113. H. A. Smith, "Encyclopedia of Polymer Science and Technology", 10, 653 (1969).
114. G. Dougherty and P. D. Hammond, J. Chem. Soc., 57, 117 (1935).
115. O. Böeseken, Rec. Trav. chim., 24, 221 (1905).
116. Neth. P. Appln. 6 507 380 (1965); Chem. Abs., 64, 16 016 (1966).
117. DRP. 365 129 (1922); see Ref. 118.
118. I. I. Yukel'son, V. S. Glukhovskoi, and L. V. Fedotova, Vysokomol. Soed., 10B, 116 (1968).
119. V. S. Glukhovskoi, E. S. Kostin, and I. I. Yukel'son, Vysokomol. Soed., 12B, 136 (1970).
120. B. P. 1 100 273 (1968).
121. US P. 3 578 718 (1971); Chem. Abs., 71, 49 563 (1969).
122. I. Gal, R. Vallot, T. J. Liang, and R. Buvet, Compt. rend., 280C, 53 (1975).
123. M. C. Friedel and J. M. Crafts, Ann. Chim. Phys., 6, 530 (1884).
124. USSR P. 33 299 (1933); Chem. Zbl., 34, 2454 (1934).
125. T. Fujisawa and M. Kakutani, J. Polymer Sci., B8, 19 (1970).
126. T. Fujisawa, N. Ohtsuka, T. Kobori, and G. Tsuchinachi, Tetrahedron Letters, 4533 (1968).
127. Jap. P. 27 255 (1971).
128. G. Montaudo, G. Bruno, P. Maravigna, and F. Bottino, J. Polymer Sci., Polymer Chem., 12, 2881 (1974).
129. Z. Binenfeld and A. F. Damanski, Bull. Soc. chim. France, 679 (1961).
130. Yugosl. P. 26 519 (1969).
131. US P. 3 843 600 (1974).
132. US P. 3 845 013 (1974).
133. US P. 3 494 966 (1970).
134. French P. 1 335 514 (1963); Chem. Abs., 61, 13 110 (1964).
135. USSR P. 176 533 (1965); Chem. Abs., 64, 12 604 (1966).
136. US P. 3 119 795 (1964); Chem. Abs., 60, 12 136 (1964).
137. M. Schmidt, Inorg. Macromol. Rev., 1, 101 (1970).
138. T. Fujisawa and M. Kakutani, J. Polymer Sci., B8, 511 (1970).
139. T. Fujisawa, T. Kobori, N. Ohtsuka, and G. Tsuchihashi, Tetrahedron Letters, 5071 (1968).
140. Jap. P. 39 960 (1972); Chem. Abs., 80, 15 467 (1974).
141. T. Fujisawa, M. Kakutani, and N. Kobayashi, J. Polymer Sci., Polymer Letters, 11, 721 (1973).
142. G. G. Cameron, D. R. Hogg, and S. A. Stachowiak, Makromol. Chem., 176, 9 (1975).
143. G. G. Cameron and S. A. Stachowiak, Makromol. Chem., 176, 1523 (1975).
144. T. Zincke and W. Frohnberg, Ber., 42, 2721 (1909).
145. V. C. Parekh and P. C. Guna, J. Indian Chem. Soc., 11, 95 (1934).
146. T. Zincke and A. Dahm, Ber., 45, 3457 (1912).
147. US P. 3 522 312 (1970).
148. US P. 3 294 760 (1966); Chem. Abs., 66, 46 785 (1967).
149. V. A. Sergeev, V. K. Shitikov, V. I. Nedel'kin, S. A. Nenashev, and V. V. Korshak, USSR P. 509 619 (1976); Byull. Izobr., No. 13 (1976).
150. V. A. Sergeev, V. K. Shitikov, and V. I. Nedel'kin, Vysokomol. Soed., 19A, 2754 (1977).
151. V. V. Korshak and G. S. Kolesnikov, Dokl. Akad. Nauk SSSR, 70, 625 (1950).
152. V. V. Korshak and G. S. Kolesnikov, Dokl. Akad. Nauk SSSR, 76, 69 (1951).
153. N. A. Hiatt, Amer. Chem. Soc. Polymer Preprints, 13, 594 (1972).
154. N. A. Hiatt, "Polymerization Reactivity and New Polymers", Washington, 1973, p. 92.
155. US P. 3 719 645 (1973).
156. M. G. Voronkov, A. K. Khaliullin, V. Z. Annenkova, L. M. Antonik, L. M. Kamkina, E. N. Deryagina, and T. I. Vakul'skaya, Dokl. Akad. Nauk SSSR, 228, 1341 (1976).
157. R. V. Jones, Hydrocarbon Processing, 51, No. 11 89 (1972).
158. N. A. Smith, Rubber Plastics Age, 44, 1048 (1963).
159. R. M. Black, C. F. List, and R. J. Wells, J. Appl. Chem., 17, 269 (1967).
160. G. Montaudo, M. Przybylski, and H. Ringsdorf, Makromol. Chem., 176, 1763 (1975).
161. G. Montaudo, M. Przybylski, and H. Ringsdorf, Makromol. Chem., 176, 1753 (1975).
162. R. Gabler and J. Studinka, Chimia, 28, 567 (1974).
163. Plastverarbeiter, 25, 733 (1974); Chem. Abs., 85, 6847h (1976).
164. Plastvärlden, 2, 44 (1973).
165. US P. 3 575 819 (1971).
166. H. W. Hill and I. T. Edmonds, Amer. Chem. Soc., Polymer Preprints, 13, 603 (1972).
167. H. Domininghaus, Feinwerktech. Micron., 77, 289 (1973).
168. E. Heitz, Gummi—Asbest—Kunstst., 28, 578 (1975); Chem. Abs., 84, 19 262 (1976).
169. B. G. Kimmel, Mater. 16th Nat. Symp. and Exhib., Vol. 16, Azusa, Calif., 1971, p. 266.
170. Tekn. Ukebl., 120, No. 42, 35 (1973).
171. H. W. Hill and J. T. Edmonds, "Polymerization Reactivity and New Polymers", Washington, 1973, p. 80.
172. G. De Callatay, Muanyages Gumi, 14, 129 (1977).
173. E. Meckelburg, Gummi—Asbest—Kunstst., 27, 414 (1974).
174. Chem. Tech., 20, No. 9, 40 (1974).
175. R. V. Jones, Polymer Age, 5, 166 (1974).

176. R. V. Jones and H. W. Hill, Adv. Chem. Ser., **140**, 174 (1975).
177. D. C. Raia, Plast. World, **31**, No. 9, 74 (1973).
178. Plastics, **34**, 283 (1969).
179. G. C. Bailey and H. W. Hill, Amer. Chem. Soc. Symp. Ser., 4, Symposium on New Industrial Polymers, 83,(1974); Chem. Abs., 82, 157 848 (1975).
180. C. W. Osborn and I. H. Walker, Proc. Ann. Conf. Reinf. Plast. Compos. (Inst. Soc. Plast. Ind.), **30**, No. 12A, p. 3 (1975).
181. R. V. Jones and P. I. Boeke, Proc. Ann. Conf. Reinf. Plast. Compos. (Inst. Soc. Plast. Ind.), **30**, No. 12B, p. 5 (1975).
182. I. Theberge, A. Barry, and P. Could, Soc. Plast. Eng., Tech. Papers, 1975, p. 164.
183. Kobunsi Kako, Polymer Appl., **24**, No. 10, 334 (1975).
184. H. W. Hill and I. T. Edmonds, Adv. Chem. Ser., **129**, 80 (1973).
185. A. M. Houston, Mater. Eng., **84**, 36 (1976).
186. I. N. Murray, Soc. Plast. Eng., Tech. Papers, 1976, No. 22, p. 259.
187. R. V. Jones, Soc. Plast. Eng., Tech. Papers, 1972, No. 8, p. 12.
188. A. M. Houston, Mater. Eng., **81**, No. 6, 28 (1975).
189. Poliplasti, **21**, 188 (1973); Chem. Abs., 80, 122 465 (1974).
190. Ing. Chim. (Ital.), **22**, No. 2, 14 (1973).
191. G. De Callatay and I. Autin, Plast. Mod. Elastomers, 28, No. 3, 40 (1976).
192. Jap. P. 59 952 (1976); Chem. Abs., 85, 109 356 (1976).
193. BRD P. Appln. 2 703 918 (1977); Chem. Abs., 87, 136 871 (1977).
194. US P. 3 492 125 (1970).
195. Europlast. Mon., **46**, No. 7, 77 (1973).
196. US P. 3 744 530 (1973).
197. US P. 3 819 407 (1974); Chem. Abs., 81, 123 009 (1974).
198. BRD P. Appln. 2 443 296 (1975); Chem. Abs., 83, 14 926 (1975).
199. BRD P. Appln. 2 321 404 (1976); Chem. Abs., 84, 152 408 (1976).
200. BRD P. Appln. 2 537 155 (1976); Chem. Abs., 85, 6584 (1976).
201. M. L. Hallensleben, Makromol. Chem., **177**, 3213 (1976).
202. Swiss P. 491 981 (1970); Chem. Abs., **73**, 99 414 (1970).
203. US P. 3 948 865 (1976); Chem. Abs., 85, 22 890 (1976).
204. B.P. 1 234 008 (1971); Chem. Abs., 72, 91 416 (1970).
205. US P. Appln. 911 007 (1973); Chem. Abs., 79, 54 779 (1973).
206. T. Fujisawa, M. Kakutani, and H. Kobayashi, J. Polymer Sci., B9, 91 (1971).
207. BRD P. 1 211 399 (1966); Chem. Abs., **63**, 7182 (1965).
208. Swiss P. 501 028 (1971).
209. US P. 3 793 256 (1974); Chem. Abs., 81, 14 277 (1974).
210. US P. 3 562 199 (1971).
211. V. A. Sergeev, V. K. Shitikov, V. I. Nedel'kin, A. A. Askadskii, K. A. Bychko, G. L. Slonimskii, and V. V. Korshak, Vysokomol. Soed., **19A**, 1298 (1977).
212. US P. 3 317 487 (1967).
213. B. P. 1 014 158 (1965); Chem. Abs., **63**, 5841 (1965).
214. I. Penczek and J. Bialy, Polymery-Tworz. wielko-czasteczk, **21**, 197 (1976).
215. US P. 3 716 609 (1973).
216. Plast. Eng., **29**, No. 9, 48 (1973).
217. French P. 2 109 838 (1972); Chem. Abs., 78, 112 352 (1973).
218. J. D. Graham and G. H. West, Wear, **36**, No. 1, 111 (1976).
219. Jap. P. 11 844 (1976); Chem. Abs., 84, 165 562 (1976).
220. Jap. P. 142 697 (1975); Chem. Abs., 84, 152 405 (1976).
221. G. De Callatay and J. Autin, Rev. Plast. mod., **30**, No. 234, 841 (1975).
222. US P. 3 954 932 (1976); Chem. Abs., 85, 79 213 (1976).
223. Jap. P. 36 255 (1976); Chem. Abs., 85, 47 635 (1976).
224. H. W. Hill and R. T. Werkman, Modern Plastics Encycl., 48, 10A, 89 (1971–1972).
225. H. Batzer and F. Lohse, Chemische Rundschau, **26**, No. 20, 1 (1973).
226. Engineering, **213**, 411 (1973).
227. R. F. Craig, Soc. Plast. Eng., Tech. Papers, 1976, No. 22, p. 141.
228. R. F. Craig, Soc. Plast. Eng., Tech. Papers, 1976, No. 89, p. 105.
229. D. G. Brady and H. W. Hill, Mod. Plast. Int., **4**, No. 5, 86 (1974).
230. A. A. Conte, Chem. Technol., **4**, No. 2, 99 (1974).
231. Mater. Eng., **69**, No. 2, 34 (1969).
232. W. Baerecke, Muanyag es Gumi, **11**, No. 2, 53 (1974).
233. Plastnytt, No. 5, 12 (1973).
234. K. K. Korpati, Paint Technol., **45**, No. 580, 49 (1973).
235. S. Iwata, Purasuchikkusa, **24**, No. 11, 25 (1973).
236. I. U. Short and H. W. Hill, Plasticos, **20**, No. 123, 50 (1973).
237. Mater. Plast. ed elast., **35**, 946 (1969).
238. US P. 3 634 125 (1972).
239. US P. 3 622 376 (1971).
240. US P. 3 652 327 (1972).
241. US P. 3 948 865 (1976).
242. US P. 3 658 753 (1972).
243. US P. 3 931 419 (1976).
244. US P. 3 925 530 (1975).
245. H. W. Hill, R. T. Wekman, and G. E. Carrow, Adv. Chem. Ser., 134, 149 (1974).
246. Jap. P. 28 145 (1976); Chem. Abs., 85, 34 019 (1976).
247. Jap. P. 119 040 (1975); Chem. Abs., 84, 18 497 (1976).
248. US P. 3 935 347 (1976); Chem. Abs., 84, 152 393 (1976).
249. Europlast. Mon., **46**, No. 9, 49 (1973).
250. BRD P. Appln. 2 503 336 (1976); Chem. Abs., 85, 125 154 (1976).
251. US P. 3 969 307 (1976); Chem. Abs., 85, 125 277 (1976).
252. S. Yanaguti, H. Amano, T. Katase, F. Sato, and S. Isiwatari, Plastics, **21**, No. 9, 12 (1975).

Institute of Hetero-organic Compounds,
USSR Academy of Sciences,
Moscow