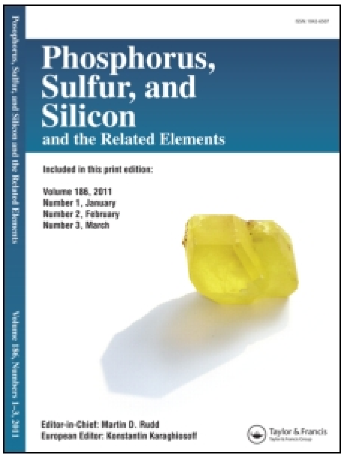

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THE REACTIONS OF SULPHUR WITH CHLORINATED PHENOLS

Bo Hortling[a]; Kari Borchers[a]; J. Johan Lindberg[a]
[a] Department of Wood and Polymer Chemistry, University of Helsinki, Helsinki

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THE REACTIONS OF SULPHUR WITH CHLORINATED PHENOLS†

BO HORTLING, KARI BORCHERS and J. JOHAN LINDBERG

Department of Wood and Polymer Chemistry, University of Helsinki, Helsinki

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Reactions of sulphur with chlorinated phenols and 2,4-dichloroanisole in open vessels under nitrogen and at high temperatures were investigated with the aim of preparing thermostable polymers. The results indicate that the chlorine atom in 4-chlorophenol is very reactive, whereas that in 2-chlorophenol is unreactive. This explains why the chlorine content of the polymers is as high as 10–15%, and also suggests that the initial reactions occur in the 4-position, after which the ortho-chlorine and the hydrogen atoms react with thermally activated sulphur.

The ratio of sulphur to monomer and the reaction time, temperature and pressure had definite effects on the reactions. The results were compared with earlier results obtained with sealed reaction ampoules.

The products were of low or high molecular weight, depending on the above conditions. The sulphur content of the products was 20–30% and the softening points varied with the molecular weight. When the products were methylated the softening points became lower.

Dimers and trimers were present in the ether-soluble fractions. Investigations by GLC-MS suggested that they were precursors for the polymers.

INTRODUCTION

This work is part of an investigation aimed at the preparation of soluble and thermoplastic substituted poly(phenylene sulfide)s which are thermally stable above 250°C. Elemental sulphur or sulphur compounds and chlorinated phenols are used as starting materials.

The necessity of removing sulphur from oil products at the refining stage has led to an overproduction of sulphur and an intensified search for new uses of this element.[1] Because of the excellent properties of the commercial poly(phenylene sulfide) Ryton,[2] it seemed worthwhile to use elemental sulphur and phenols, which are degradation products of lignin and thus potentially renewable raw materials, for the preparation of similar products.

Poly(phenylene sulfide)s (PPS) have earlier been prepared by both electrophilic and nucleophilic substitution reactions,[3] although the latter have been more thoroughly investigated.

The first synthesis of PPS by a nucleophilic substitution reaction was reported by Macallum[4] from 1,4-dichlorobenzene, sulphur and sodium carbonate. Lenz *et al.*[5,6] investigated this reaction and further developed a synthesis based on the self-condensation of metal-4-halothiophenoxides. Port and Still[7] have reported the preparation of poly(2-methylphenylene sulphide) and poly(2,6-dimethylphenylene

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†Some of these results were presented as posters at the 27th IUPAC Congress, August 27-31, 1979 and at EUCHEM Symposium on Lignin Chemistry, June 9-10, 1980 in Helsinki.

sulphide) from the respective copper(I)bromothiophenoxides under less drastic conditions than those used by Lenz *et al.*

In 1967 Edmonds and Hill[8] prepared a linear PPS from 1,4-dichlorobenzene and Na_2S, and according to this method Phillips & Co[2] has commercially produced a PPS under the trade name of Ryton. Baron and Blank[9] have reported a method of preparing PPS from aromatic dithiols and dihalo-substituted benzenes with K_2CO_3 in DMF. Similar reactions have been investigated by Haddad *et al.*[10] The reactions of sulphur and NaOH with phenols were investigated by Neale *et al.*,[11] who obtained polythiobisphenols.

Zuk *et al.*[12] and much earlier, Hilditsch[13] prepared PPS by the homopolymerization of thiophenol in concentrated H_2SO_4.

The reactions of elemental sulphur[14] with aromatic compounds are either dehydrogenation reactions in which H_2S and H_2 are formed or else oxidation reactions in which C—C and C—S bonds are formed. It is well known that sulphur is thermally activated at temperatures above 200°C and that reactive sulphur biradicals are formed.

The occurrence of chloro substituents in the aromatic compounds promotes the reactions of sulphur with aromatic compounds, because the bond strength of C—Cl bond is lower than that of the C—H bond. The occurrence of electron releasing substituents in the aromatic ring also facilitates the reactions of sulphur with aromatic compounds.[15-17]

At 350°C sulphur reacts with benzene in sealed ampoules, giving a 50% yield of PPS.[18] Sulphur reacts with mono and dichlorobenzenes to form PPS already at 200–250°C.[19]

The present authors have earlier investigated the reactions of monosubstituted chlorobenzenes and 2,4-dichlorophenol with sulphur in sealed ampoules.[17]

Because of the high pressures which develop in the ampoules the collection of reaction products is difficult. The reactions in the present work were therefore performed at atmospheric pressure, and the results for these reactions are compared with similar reactions performed earlier in sealed ampoules. The effect of the number of chloro-substituents and of the hydroxyl and methoxy substituents on the reactions and the formation of polymeric products are also investigated.

EXPERIMENTAL

Reagents Sulphur, 2,4-dichlorophenol, 4-chlorophenol, 2-chlorophenol, phenol and dimethyl sulphoxide were all commercial products and used without further purification.

2,4-dichloroanisole was prepared by methylation of 2,4-dichlorophenol with dimethyl sulphate[20] (mp. 26–27°C, litt.[21] 27–28°C).

Synthesis The syntheses were performed in the apparatus depicted in Figure 1.

The amounts of chlorine liberated were determined by argentometric titration. The sulphide ions were determined by adding excess iodine to the ZnS precipitate in the collection flasks and then titrating with $Na_2S_2O_3$.[22]

The solid crude reaction products were first fractionated by Soxhlet extraction with petroleum spirit (60–80°C), diethyl ether and ethanol. The rest of the products

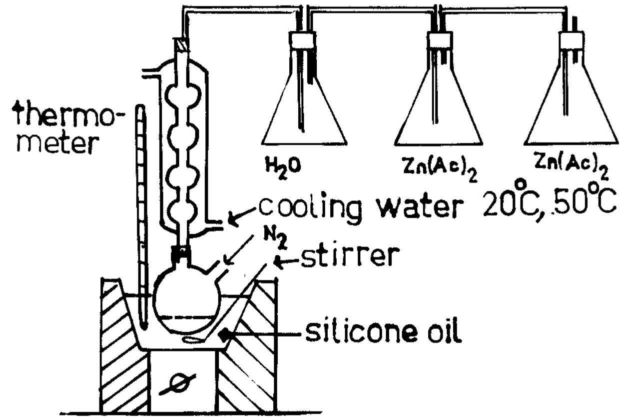


FIGURE 1 The synthesis apparatus. The cooling water was at 20 or 50°C, depending on the monomer. The gaseous products were trapped in water (HCl) and in two bottles containing 5 ml 2M $Zn(Ac)_2$ + 95 ml H_2O (for $S^=$ ion determination).

were dissolved in a mixture of DMSO—2M NaOH (1:1), precipitated with water and HCl and washed with a large excess of water.

The unreacted sulphur and monomers were determined qualitatively by thin layer chromatography.[23]

The methylations of the polymeric products obtained from 2,4-dichlorophenol and sulphur were performed with dimethyl sulphate in 2M NaOH solutions.[20] The yield of the methylated polymer was 85%.

Gas chromatography and mass spectrometry The ether-soluble compounds were investigated with a Hewlett Packard 5710A gas chromatograph on a UCC-W982 column. The heating program was 2 min at 70°C, 10°C/min from 70–270°C and finally 16 min at 270°C. The mass spectra were recorded with a Varian Aerograph model 1700 coupled to a Varian Mat CH-7 mass spectrometer, excitation energy 70 eV.

Infrared spectra A Pye Unicam SP 1100 IR-spectrophotometer and the KBr-pellet technique were used.

Gel permeation chromatography Molecular weight distributions were investigated on Sephadex G-50 gel with DMSO. Fractions of 2.5 ml were collected and the concentrations were determined with a Beckman DB spectrophotometer at 340–380 nm.

Determinations of S, Cl and OH contents in the polymers The sulphur and chlorine contents were determined by the Analytical Laboratories, Elbach, Germany.

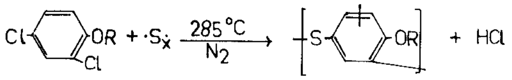
The OH content was determined by acetylation with acetic anhydride and pyridine and titration of the excess acetic acid with NaOH.[24]

Determination of thermal stability The softening points were determined visually with a melting point microscope as the temperatures at which the polymeric products softened and/or darkened.

RESULTS AND DISCUSSION

Fractionation of the Reaction Products

On the basis of earlier results,[17] the syntheses performed in the apparatus depicted in Figure 1 are assumed to occur as in Scheme (1).



(1)

Table I shows the results of both the syntheses performed earlier in sealed ampoules[17] and those performed in the present work in the apparatus in Figure 1.

The abbreviations used in Table I and later in the text are as follows: 2,4-dichlorophenol = 2,4-CP, 2,4-chloroanisole = 2,4-CA, 4-chlorophenol = 4-CP, 2-chlorophenol = 2-CP and phenol = P, PES = fraction soluble in petroleum ether (60–80°C), ES = fraction soluble in diethyl ether, EtS = fraction soluble in ethanol and DNaS = fraction soluble in DMSO—2M NaOH (1:1) and precipitated with water and HCl.

A comparison of the results of syntheses E1 and E2 performed in sealed ampoules with synthesis E3 performed at atmospheric pressure clearly indicates that only low molecular weight compounds (ether soluble) are formed at atmospheric pressure, whereas mainly polymeric products are formed in the sealed ampoules at 220°C. Syntheses E6 and E7, however, indicate that by raising the reaction temperatures from 220°C to 285°C, it is possible to prepare polymeric products at atmospheric pressure which have properties similar to those of the products prepared in sealed ampoules at lower temperatures.

The synthesis in Table I indicate that only 0–3% of the sulphur is liberated as H_2S (taking into consideration the results for heating of sulphur alone). This is in line with earlier results for reactions of sulphur with 1,4-dichlorobenzene, according to which HCl was liberated during the formation of polymeric products at 260°C.[17,19] When sulphur reacted with benzene in ampoules at 350°C, H_2S was liberated during the formation of phenyl sulphides and PPS.[18]

The amount of chlorine liberated as HCl apparently corresponds to the conversions of the present reactions, as suggested earlier.[17] The results of the reference experiments in Table I indicated that no self-condensation of 2,4-CP occurred.

Fifty-seven per cent of chlorine is liberated from 2,4-CP (E7), 78% from 4-CP (E13) and only 2% from 2-CP (E14). These differences are apparently due to the fact that the Cl substituent in the para position is reactive, and that in the ortho position is unreactive because of steric hindrance and intramolecular hydrogen bonding with the OH group.

STRUCTURES AND PROPERTIES OF THE PRODUCTS

Low Molecular Weight, Ether-soluble Products

According to TLC and GLC investigations, the fractions soluble in petroleum ether (PES) contained mostly unreacted sulphur and monomer. The fractions soluble in ether (ES) and ethanol (EtS) also contained unreacted sulphur and monomer, but the amounts decreased considerably when the conversions of the reactions increased (see Table II). Apart from unreacted starting materials, the ES fractions also contained dimers and trimers, which were considered as precursors of the polymers and were investigated by GLC-MS. Table II shows the results of these investigations for syntheses E6, E7, E8 and E10.

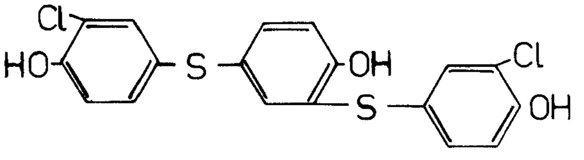
The structures of some of the ES compounds are suggested in Figures 2, 3 and 4; the masses and relative intensities of the most important fragments as determined by mass spectrometry are also suggested, together with the structures of some of the fragments.

These structures indicate the presence of monosulphide and disulphide bonds and chloro-substituents in the dimers and trimers and also suggest the presence of similar structures in the polymeric products.

Structures, Formation and Properties of the Polymeric Products

IR spectra of the polymeric products Figure 5 shows the IR spectra for the polymeric products obtained in syntheses E6, E10 and E13. The IR spectra[25] for the products in E7 are similar to the spectra of the corresponding products in E6.

The IR spectra of the polymeric products prepared from 2,4-CP (E6) and the methylated form of the products show stronger absorptions at 855 cm^{-1} than at 795



MW 411 (Occurs in the ES fractions of E7 and E8, see Table II).

m/e(intensity): 416(5), 414(22), 412(42), 410(32), 386(3), 384(8), 382(6), 360(5), 358(17) 356(30), 354(20), 320(20), 318(19), 291(7), 293(2), 257(10), 193(18), 162(100), 129(20), 97(13)

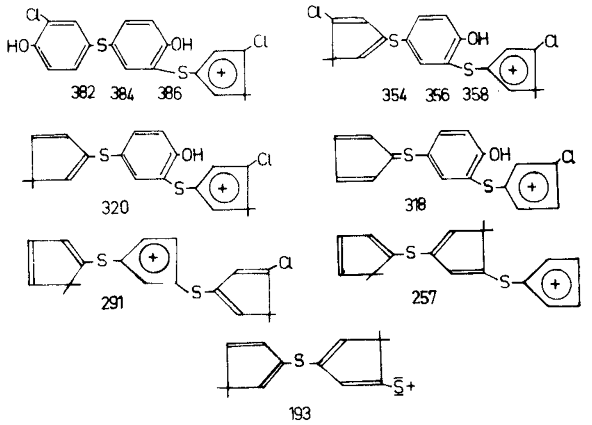


FIGURE 2 The structure of an ether soluble compound obtained in E7 and E8 (RRT = 2.56 and 2.57) according to its mass spectrum. The masses (*m/e*) and relative intensities (%) of the major peaks and the structures of a few of the corresponding fragments in the mass spectrum are also given.

TABLE I

The results of the reactions of sulphur with chlorinated phenols, phenol and 2,4-dichloroanisol under different conditions.

Synthesis number[1] (Reaction time and temperature)	Starting mat.[2]		Products soluble in[3]			Insoluble[4] products (g)	Products in gaseous[5] state	
	Monomer (mmol)	Sulfur (mmol)	Ether (ES) (g)	Ethanol (EtS) (g)	DMSO-NaOH (DNaS) (g)		Cl^-	$S^=$
E1 (in sealed ampoule) (20 h, 196°C) (1/4)	2,4-CP 40(6.5 g)	68 (2.2 g)	not det.	0.20	6.46	0.00	44%	not det.
E2 (in sealed ampoule) (20 h, 209°C) (1/4)	2,4-CP 40(6.5 g)	68 (2.2 g)	not det.	traces	1.00	6.36	60%	not det.
E3 (22 h, 222°C) (1/2)	2,4-CP 40(6.5 g)	80 (2.6 g)	8.20	0.00	0.00	0.00	not det.	not det.
E4 (1.3 h, 285°C) (1/2)	2,4-CP 40(6.5 g)	80 (2.6 g)	6.80	0.00	0.00	0.00	not det.	not det.
E5 (1.9 h, 285°C) (1/2)	2,4-CP 40(6.5 g)	80 (2.6 g)	1.00	0.34	4.58	0.50	not det.	not det.
E6 (3.0 h, 285°C)	2,4-CP 40(6.5 g)	80 (2.6 g)	1.60 (0.40)	0.67	2.57	1.43	58%	43.2%
E7 (3.0 h, 285°C)	2,4-CP 40(6.5 g)	60 (1.9 g)	1.19 (0.16)	1.54	2.95	0.16	57%	43.2%
E8 (3.0 h, 285°C)	2,4-CP 40(6.5 g)	40 (1.3 g)	7.52 (1.10)	0.00	0.00	0.00	8%	43.9%
E9 (6 h, 285°C)	2,4-CP 40(6.5 g)	40 (1.3 g)	1.74	traces	2.22	2.34	39%	43.6%
E10 (3.0 h, 285°C)	2,4-CA 40(7.1 g)	60 (1.9 g)	2.13 (0.13)	traces	3.30	0.22	54%	40.2%

E11 (in sealed ampoule) (18 h, 240°C) (1/4)	4-CP 40(5.1 g)	68 (2.2 g)	not det.	3.15	0.00	0.00	75%	not det.
E12 (in sealed ampoule) (18 h, 277°C) (1/4)	4-CP 40(5.1 g)	68 (2.2 g)	not det.	0.04	4.10	traces	98%	not det.
E13 (3.0 h, 285°C)	4-CP 40(5.1 g)	60 (1.9 g)	2.16	5.50	0.00	0.00	70%	1.9%
E14 (3.0 h, 285°C)	2-CP 40(5.1 g)	60 (1.9 g)	unreacted starting materials only traces of reaction products				2%	0.3%
E15[6] (3.0 h, 285°C)	P 40(3.8 g)	60 (1.9 g)	unreacted starting materials only traces of reaction products				00%	2.3%

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[1] The number of the synthesis and the reaction time and temperatures are given. The fractions in parentheses indicate that the synthesis was performed with 1/4 and 1/2 of the amounts in the table. The results have been calculated to make all results comparable. Unless otherwise mentioned, the reactions were performed in the apparatus in Figure 1.

[2] The following abbreviations are used: 2,4-dichlorophenol = 2,4-CP, 2,4-dichloroanisole = 2,4-CA, 4-chlorophenol = 4-CP, 2-chlorophenol = 2-CP and phenol = P.

[3] The crude reaction products were Soxhlet extracted with 75 ml of petroleum ether (60–80°C) (PE), ether (E) and ethanol (Et). The petroleum ether soluble (PES) and ether soluble (ES) fractions are added and reported together in the table. The unreacted starting materials and products were recovered by distillation of the solvents. The PES fraction contained mostly unreacted sulphur and monomer. The ES fractions contained dimeric, trimeric and probably oligomeric compounds in addition to unreacted starting materials. The amounts of dimeric and trimeric compounds were measured by GLC (peak area) and are given in parentheses under the ES fraction.

The DNaS fractions were obtained by dissolving the Et insoluble fractions in a mixture of DMSO—2M NaOH (1:1) and precipitated with $H_2O + HCl$. The precipitate was washed for several times with water. A part of this fraction is always soluble in DMSO alone. In E7 only traces was insoluble in DMSO alone.

[4] Products insoluble in the solvents used.

[5] The $S^=$ and Cl^- contents of the reaction products were determined as described in the experimental part and expressed as percentages of the S and Cl contents of the starting materials.

[6] Besides the reactions in the table, reference experiments were done by heating 0.06 mole of sulphur alone and 0.04 mole of 2,4-CP alone for 3 hrs at 285°C. From sulphur, 0.9% of the total amount was detected as H_2S. From 2,4-CP, only 0.1% of the chlorine in the monomer was detected as HCl and unreacted 2,4-CP was recovered.

TABLE II

Relative retention times (RRT) and quantities of compounds in the ether soluble (ES) fractions and the masses of assumed molecular ions.

Synthesis[1] (sulphur : monomer)		RRT (quantities as percentages of the ES fraction)[2] Mass of assumed molecular ion					
E6 (2:1)	16%[3]	3.09(2.6%) 444	2.84(18.8%) 411	2.70(3.5%)	1.34(17.7%) 224	1.00(39.7%) 163	
E7 (1.5:1)	9%	3.06(0.5%) 452	2.70(0.8%) 444	2.61(7.5%) 384	2.56(14%) 410	1.35(3.3%) 224	1.00(68.8%) 163
E8 (1:1)	100%	3.09(1.0%) 444	2.86(4.7%) 411	2.63(1.9%) 384	2.57(8.5%) 410	1.35(1.1%) 224	1.00(78.7%) 163
E10 (1.5:1)	16%	2.48(2.5%) 346	2.40(4.1%) 314	2.32(4.9%) 314	1.17(87.7%) 176(2,4-CA)	1.00(0.5%) 163(2,4-CP)	

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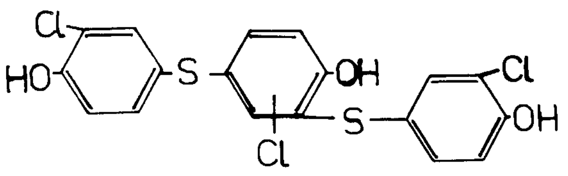
[1] The results of the syntheses are given with the proportions of the starting materials in parentheses.

[2] 1% $CHCl_3$ solutions of the samples were prepared. The retention time (RT) for 2,4-dichlorophenol (2,4-CP) = 9,90 min. The quantities of ES compounds are calculated from the peak areas in the gas chromatograms. The masses of the assumed molecular ions are given below the relative retention times (RRT).

[3] The total amount of the ES fraction as a percentage of the crude reaction product.



MW 445,5(Occurs in the ES fractions of E6 and E8, see Table II).

m/e(intensity): 448(4), 446(27), 444(50), 442(38), 416(4), 388(8), 224(35), 222(50), 196(73), 194(100), 193(88), 167(38), 165(54), 131(31), 129(46), 95(31)

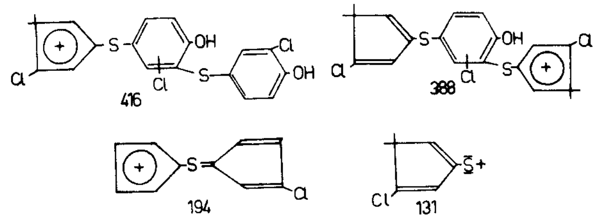
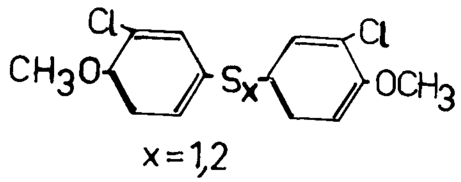
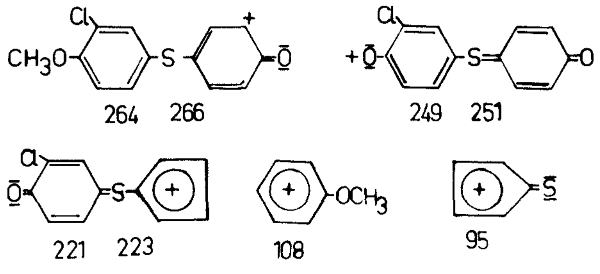


FIGURE 3 The structure of an ether soluble compound obtained in E6 and E8 (RRT = 3.09) according to its mass spectrum. The masses (*m/e*) and relative intensities (%) of the major peaks and the structure of a few of the corresponding fragments in the mass spectrum are also given.



MW 315 (x = 1) MW 347 (x = 2), Occurs in the ES fraction of E 10, see Table II.

x = 1; m/e(intensity): 318(5), 316(69), 314(100), 270(12), 268(18), 266(24), 264(62), 249(8), 251(3), 223(6), 221(15), 168(8), 132(9), 108(9), 95(14)



x = 2; m/e(intensity): 350(17), 348(74), 346(100), 315(5), 175(27), 174(51), 173(80), 161(12), 159(30), 138(76), 129(40), 127(84), 108(88), 101(17), 99(44), 95(82), 65(16)

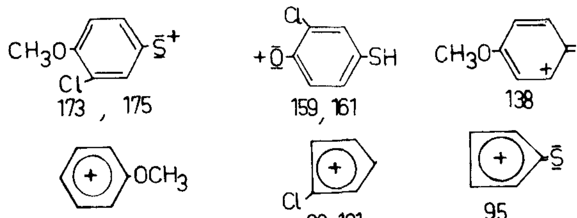


FIGURE 4 The structures of two ether soluble compounds obtained in E10 (RRT = 2.48 and 2.32) according to their mass spectra. The masses (*m/e*) and relative intensities (%) of the major peaks and the structures of a few of the corresponding fragments in the mass spectra are given.

cm^{-1}. For the products prepared from 2,4-CA (E10) and 4-CP (E13) the absorptions at 805 and 820 cm^{-1} are stronger than the absorptions at 860 and 875 cm^{-1}. This suggests a greater number of isolated ring hydrogen atoms (1,2,3,5- and 1,2,4,5-substitution) in the products obtained from 2,4-CP than in the products obtained from 2,4-CA and 4-CP, in which a 1,2,4-substitution seems to be dominant. A shift towards lower wave numbers is also observed for the products prepared from 2,4-CP

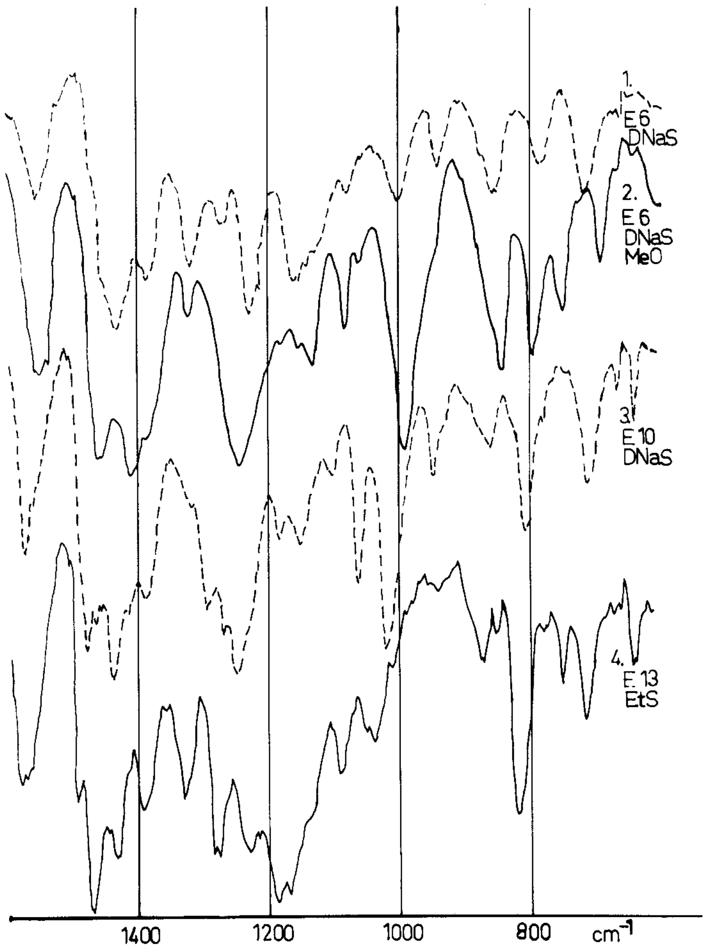


FIGURE 5 The IR spectra of the following polymeric products are given in the range 1600–600 cm^{-1}: 1. the DNaS fraction of E6 (monomer, 2,4-CP), 2. the methylated DNaS fraction of E6, 3. the DNaS fraction of E10 (monomer, 2,4-CA) and 4. the EtS fraction of E13 (monomer, 4-CP).

(855 cm^{-1} compared with 860 and 875 cm^{-1}, and 785 cm^{-1} compared with 805 and 820 cm^{-1}).

The above results indicate that the reaction products from 2,4-CP are formed differently from those from 2,4-CA and 4-CP. This could be due to intramolecular hydrogen bonding between the ortho Cl atom and the phenolic OH group, which was shown to greatly affect the conversions (% Cl liberated) of the reactions earlier in this paper.

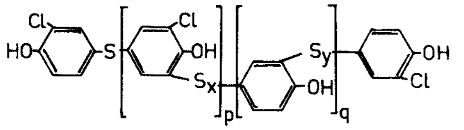
The presence of the methoxy group in the methylated product from E6 and in the product from 2,4-CA (E10) is verified by absorptions at 995 and 1025 cm^{-1} and 1250 cm^{-1}, respectively. The weak absorption at 1160 ± 10 cm^{-1} indicates that only a small number of the phenolic OH groups are present.

The absorptions at 1000 cm^{-1} in the spectra of E6 DNaS is caused by occluded DMSO.

The absorptions of the aromatic structures are seen in the region 1450–1600 cm^{-1}

and the C—Cl and C—S vibrations cause weak absorptions in the region 600–700 cm^{-1}.

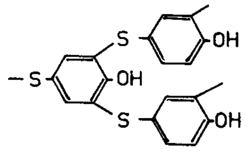
Sulphur, chlorine and hydroxyl determinations In Table III the results of the experimental S, Cl and OH determinations are compared with the corresponding calculated values for the assumed structures (2 a, b).



(2)

	M_{theor}	%S	%Cl	%OH
a) $p = q = 5$, x and $y = 1$	1700	20.7	14.6	12.0
b) $p = q = 5$, x or $y = 2$	1860	27.5	13.4	11.0

The results in Table III indicate that there is more than one sulphur atom per aromatic unit and that chlorine atoms are present as substituents in a part of the aromatic nuclei, as the structures for the low molecular weight compounds in the ES fractions suggest. The amount of hydroxyl groups determined by titration (see experimental part) decrease with increasing amounts of chlorine in the polymeric compounds. This decrease may be due to shielding of the OH group by sulphur atoms in structure (3), and should thus be related to an increase in the degree of cross-linking. In structure (4) the OH group is assumed to be unshielded because the OH group reference determinations in 2,4-CP gave values correct to within ±3%.



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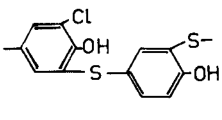

(4)

TABLE III

The S, Cl and OH contents of the DNaS and EtS fractions and of the methylated products. Visually determined softening points.

Synthesis[1] No., fraction	% S[2]	% Cl[2]	% OH[2]	Visual softening[3] points (°C)
E6 DNaS	31.1	13.9	5.4	>350
E6-MeO	not det.	not det.	not det.	290–310
E7 DNaS	29.5	17.9	10.0	110–130
E7-MeO	24.5	15.7	3.5	95–110E
E10 DNaS	28.7	10.1	5.6	>350
E13 EtS	36.7	2.7	not det.	not det.
E1 DNaS	30.9	13.7	not det.	290–300
E2 DNaS	30.8	14.7	not det.	250–260
E2 Insol	25.7	8.0	not det.	>350
E11 EtS	37.0	0.3	not det.	not det.
Structure (2)[4]				
a:	20.7	14.6	12.0	
b.	27.5	13.4	11.0	

[1] See Table 1. —MeO = methylated DNaS fraction (see experimental part).
[2] See experimental part.
[3] Temperatures at which the powder darkens and/or changes to a resinous product.
[4] Calculated values for the model structures (2 a, b).

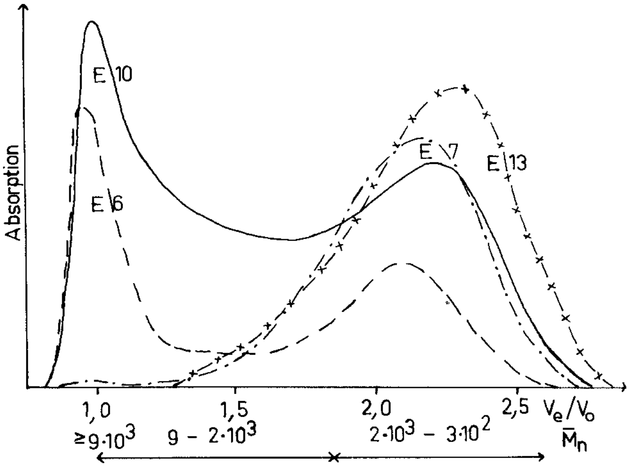

FIGURE 6 Fractionation on Sephadex G-50 gel in DMSO of the DMSO-soluble parts of the DNaS fractions of syntheses E6, E7 and E10 and of the EtS fraction of E13. The column was calibrated using the commercial polystyrenes: PS-2030 (log $\overline{M}_n = 3.31$, $V_e/V_o = 1.89$) and PS-900 (log $\overline{M}_n = 2.95$, $V_e/V_o = 2.39$), 4-hydroxyphenylsulphide (log $M = 2.34$, $V_e/V_o = 2.69$) and 2,4-CP (log $M = 2.21$, $V_e/V_o = 2.55$). The exclusion limit corresponds to $\overline{M}_n \sim 9000$ as was earlier suggested.[17]

Gel permeation chromatography measurements In order to determine the molecular weight distributions of the polymeric products, gel permeation chromatography (GPC) measurements were performed in DMSO on a Sephadex G-50 gel. The results are given in Figure 6.

The results indicate that the molecular weights of the DMSO soluble fractions increase with increasing amounts of sulphur in the starting materials (cf. E6 and E7). The products prepared from 2,4-CA have a higher molecular weight than the corresponding products prepared from 2,4-CP (cf. E7 and E10 in Figure 6).

The completely distributed DMSO soluble fraction of the E7 DNaS fraction is suggested to have $\overline{M}_n \sim 1800$, on the basis of the calibration results in Figure 6. This $\overline{M}_n$ and the experimental values of the percentages of S, Cl and OH in Table III for E7 DNaS roughly agree with the calculated values for the structure (2b).

CONCLUSIONS

The results indicate that an increase in the sulphur to monomer ratio and in the reaction time and temperature increase the yields of the polymeric products. When the reactions are performed at atmospheric pressure the reaction temperature must be considerably higher than when the reactions are performed in sealed ampoules in order to obtain high yields of the polymeric products.

The chlorine atom in the para position is much more reactive than the chlorine in the ortho position, as the reactions of sulphur with both 4- and 2-chlorophenol indicate. This is apparently due to both steric hindrance and intramolecular hydrogen bonding between the Cl and OH substituents. The high chlorine content (10–15%) of the polymers is explained by the above suggestions.

It is thus proposed that sulphur biradicals first react with the C—Cl bond in the para position, after which the propagation reactions occur with both C—Cl bonds in the ortho position and with the C—H bonds. However it has been observed that the presence of a chlorine atom in the ortho position increases the yield of polymeric products (compare E7 and E13).

The IR spectra, S, Cl and OH determinations, together with the measurements of the molecular weight distributions of the polymeric products suggest that the structures of the polymers include monosulphide bonds and disulphide bonds, and/or cross-linked structures and chlorine and hydroxyl substituents in the aromatic nuclei. Structure (2b) should be a good model for the polymeric and oligomeric products.

The methylated products were white powders, with softening points lower than the unmethylated products.

Generally, the softening points increased with increasing molecular weight (cf. E6 and E7).

The structures of the dimers and trimers in the ether soluble fraction were investigated by GLC-MS and are presented in Figures 2, 3 and 4. These compounds were considered as precursors of the polymeric products.

The products prepared from 2,4-CA had a higher molecular weight than the products prepared from 2,4-CP under similar conditions (cf. E7 and E10). The quantities of the ethanol soluble and the ether soluble fractions were less when 2,4-CA used as monomer. This suggests that use of 2,4-CA as monomer results in a greater amount of polymeric products than with 2,4-CP. The difference may be explained by the absence of stabilizing intramolecular hydrogen bonding of the ortho Cl atom in 2,4-CA, which does occur in 2,4-CP.

The products obtained from 2,4-CA were brown powders with IR spectra resembling those of the methylated products of E6 and E7. The products prepared from 2,4-CA were however, partly demethylated as can be seen from the OH determinations and IR spectra.

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