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Poly(Hydroxiphenylene Sulfide)s from Sulfur and Phenols by Activation with Halogens

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SUMMARY

The activating effect of halogens on the reactions of sulfur with phenol, guaiacol and o-cresol is investigated. As expected bromine has a stronger effect than chlorine, but in both cases oligomeric and polymeric poly(hydroxiphenylene sulfides) containing halogens are formed. When o-cresol is used as monomer, CH_2-S-CH_2 bonds are apparently formed when the reaction time is increased. The products are investigated by IR-spectroscopy, gel permeation chromatography, elementary analyses and the temperature at which the material turns to a resinous product is given.

INTRODUCTION

The favourable chemical and physical properties of linear poly(phenylene sulfide)s are well known[1]. They are prepared by nucleophilic substitution reactions both in the solid state and in solution. Phenolic sulfides are used as antioxidants and have been investigated by Pospisil[2]. Weichan-Judek et al.[3] have investigated the reactions of S_2Cl_2 with resorcinol and the resultant poly(hydroxiphenylene sulfide)s.

The present investigation is a continuation of our attempts to prepare poly(hydroxiphenylene sulfide)s using phenols and elemental sulfur as starting materials. Earlier experiments have been performed in sealed ampoules where 4-substituted chlorobenzenes have reacted with sulfur with or without sodium carbonate.[4]

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In a continuation of these investigations sulfur was reacted with chlorinated phenols at 280 °C under N_2 at atmospheric pressure.[5] In both cases polymeric products with good thermal properties were obtained. However it was noticed that o-chlorophenol and phenol alone did not react with sulfur: intramolecular hydrogen-bondings (-OH.....Cl), were the suggested reason. From the literature it is known that 4,4'-dihydroxidiphenyl sulfide is formed from a reaction between S_2Cl_2 and phenol.[6]

It is known that S_2Cl_2 is formed when sulfur reacts with chlorine.[7] The corresponding bromine derivative is apparently also formed and the S-Br bond is known to be very unstable.[7] The formation of halophenols from phenols in reactions with halogens is very wellknown. As was mentioned above the chlorophenols react with sulfur to polymers and thus a similar reaction is expected for bromophenols.

Thus it seemed natural that addition of chlorine to a melt of sulfur and phenol should cause polymerization. It was also expected that bromine should be more reactive than chlorine. We therefore investigated the reactions of phenol, guaiacol and o-cresol with sulfur by adding chlorine and bromine to the reaction mixture under nitrogen at atmospheric pressure. This avoids high pressures and the use of halogenated phenols, and facilitates the performance of the experiments.

EXPERIMENTAL

Reagents: Sulfur, halogens, phenol, guaiacol and o-cresol were all commercial products used without further purification.

Syntheses: The reactions were performed under nitrogen in a 3-necked glass bottle containing sulfur and the phenol. The chlorine was added over a period of 1.3 h at the reaction temperature (250°C) and this time was included in the reaction time.

The bromine was added at 125°C and the reaction temperature was increased to 220°C over a period of 0.8h. The reaction time is given as the time of the reaction at 220°C.

The amounts of chlorine and bromine liberated as HX were collected in water and determined by argentometric titrations. The sulfur liberated as H_2S was collected in a $Zn(Ac)_2$ solution and determined by iodometric titrations.[8]

The crude reaction products were fractionated with ether, ethanol and DMF in this order. The fractions of syntheses II, III and IX, soluble in DMF, were further fractionated by precipitating the high molecular weight fraction with ethanol (+ 0.1M HCl), and then precipitating the lower molecular weight fraction (A) from the DMF-ethanol solution by adding water (+0.1M HCl).

The amounts of unreacted sulfur and monmomer were determined qualitatively using TLC. Only small (<3%) amounts were detected in the ethanol and DMF soluble fractions.

Molecular weight determinations: The molecular weight distributions of the fractions soluble in DMF were investigated by gel permeation chromatography on a Sephadex LH-60 gel in DMF. The column was calibrated with commercial monodisperse polystyrene samples (M_n=20,000, 10,400, 4,000, 2,030 and 900) and with 4,4'-dihyroxidiphenyl sulfide.

Elemental analyses: The sulfur, chlorine and bromine contents were determined at the Analytical Laboratories, Elbach, Germany.

RESULTS AND DISCUSSIONS

The results of the reactions of the phenols with sulfur and chlorine or bromine are given in Table 1. The results show that bromine reduces the reaction temperature and time in comparison with chlorine. It has also been observed that longer reaction times and a greater amount of halogen increase the DMFs fractions, except in synthesis VI which apparently depends on demethylation and, therefore, formation of o-dihydroxibenzene units. When halogen is added, three reaction steps probably occur simultaneously, (1) - (3). When $x \geq 2$ in reaction (3) the formation of sulfenylchlorides is also possible (4).[9)] These reactions may be regarded as initiation reactions. The propagation steps are apparently a continuation of reaction (3) and the reactions given in (5).

TABLE 1

The reactions of 0.08 mole of phenol (7.52 g) (I-IV), guaiacol (9.92 g) (V,VI) and o-cresol (8,64 g) (VII-IX) with 0.16 mole of sulfur and chlorine or bromine.

No. of synthesis,[1] Reaction temp.(°C) and time(h)			Halogen[2] (mole)	Fractionated reaction products[3] (g)			Gaseous products[4] (%)	
				Ether sol(Ets)	Ethanol sol(EtOHs)	DMF sol(DMFs)	S	X
I	250	2.0	0.16 Cl_2	8.2	0.7	0.7	-	62
II	"	5.3	" "	2.5	3.0	4.2[5]	0.2	61
III	220	0.1	" Br_2	7.6	1.4	8.2[5]	-	70
IV	"	3.0	0.08 "	1.5	9.8	0.5	2.7	87
V	250	1.3	0.16 Cl_2	0.1	0.5	10.4	0.4	76
VI	"	5.5	" "	7.7	5.6	0.3	15.9	51
VII	"	1.3	0.13 "	4.7	0.7	7.1	2.9	63
VIII	"	5.5	" "	0.5	0.5	10.0	15.7	50
IX	220	0.1	0.16 Br_2	4.7	0.3	11.5[6]	1.7	69

1) The number of the synthesis and the reaction time and temperature are given.

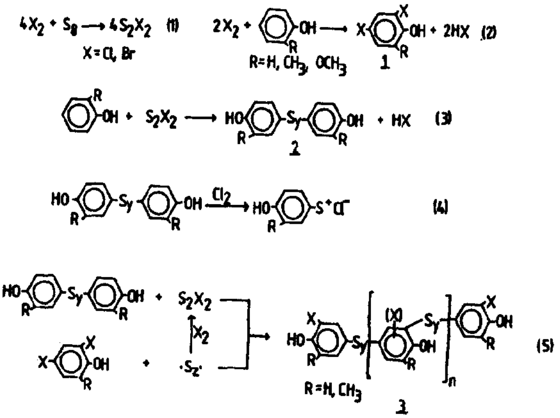
2) Amount of the specific halogen used in mole.

3) The crude reaction products were fractionated in three different fractions as described in the experimental section (sol=soluble). The DMFs fractions were partially soluble in ethanol after drying.

4) The %S of total sulfur liberated as H_2S and the %X of total halogen liberated as HX in the reaction.

5) 18 % in II and 14 % in III of the DMFs fraction precipitates with ethanol(+0.1M HCl) and the residue precipitates with water (+0.1M HCl).

6) 31 % of the DMF fraction precipitates with ethanol (+0.1M HCl) and the residue precipitates with water (+0.1M HCl)



The degree of substitution of the polymers can be seen from the IR-spectra in Fig. 1. The effect of bromine is clear when the spectra of IIIDMFs are compared, in that the relative intensity of the absorption band at 875 ± 10 cm $^{-1}$ (suggesting one isolated H atom in the benzene ring) is much stronger for IIIDMFs than for IIDMFs. This indicates a more cross-linked and/or substituted structure for IIIDMFs, which may partly depend on the higher quantity of bromine than chlorine in the polymer.

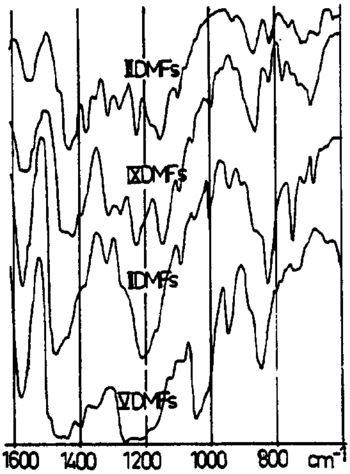


Fig. 1. IR-spectra of the polymer fractions IIDMFs, IIIDMFs, IXDMFs and VDMFs (The KBr pellet technique was used)

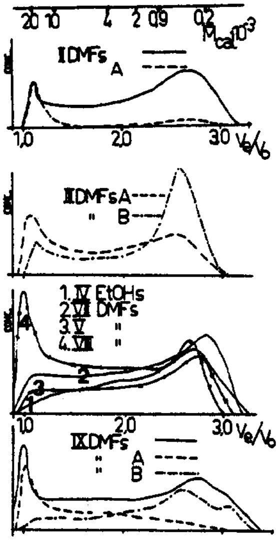


Fig. 2. Molecular weight distribution curves for some of the polymers. The DMF soluble part of the polymers II, III and IX are precipitated first with ethanol (curve B) and then with water (curve A). The solid lines represent the corresponding unfractionated polymer. M_{cal} signifies the molecular weights of the monodisperse polystyrene samples

IR-spectra also show that fraction (B) precipitated with ethanol has a spectrum similar to that of fraction (A) precipitated with water.

Table 2 shows that the B fraction contains only slightly less bromine than the A fraction. These results strongly suggest that the fraction precipitated with ethanol is not more cross-linked than the fraction precipitated with water and that the decreased solubility depends on an increase in molecular weight, as is seen from the GPC meassurements in Fig. 2.

TABLE 2

The results of the elemental analyses, molecular-weight and softening point determinations of the polymers

Polymer (color)[1]	%S[2]	%Cl[2]	%Br[2]	Amounts of fractions(in%)[3] precipitated with water(A) and ethanol (B)	Calculated molecular[4] weights		Softening points[5] (°C)
					<2000	>2000	
IIDMFs (grey) A	26.8	9.4		82	54	46	90 - 110
B				18			170 - 270
IIIDMFs(yellow) A	34.6		24.7	86			
B	35.6		22.0	14			
IVDMFs "	-	-			63	37	
VDMFs(dark gray)	36.4	3.7			48	52	130 - 190
VIIDMFs (brown)	20.8	5.4					75 - 100
VIIIDMFs "	24.7	4.3			31	69	150 - 200
IXDMFs " A	35.4		21.9	69	37	63	110 - 130
B	26.8		18.9	31			300

1) The same numeration is used as in Table 1. The colors of the polymers are given in parentheses. B refers to the DMFs fraction precipitated with ethanol and A to the fraction precipitated with water (see the experimental section).

2) The elemental analyses were performed at the Analytical Laboratories, Elbach, Germany. Calculated values for IIDMFs(prepared from phenol) if $n=4$ and $y=2$ in formula $\underline{3}$: %S=31.6 and %Cl=7.8; and for IIIDMFs(prepared form phenol) if $n=4$ and $y=2$: %S=28.8 and %Br=16.0.

3) The relative amounts of the fractions A and B.

4) The calculated amounts of polymer with $\bar{M}_w < 2000$ and $\bar{M}_w > 2000$ for the unfractionated DMF soluble polymers, using the results of the calibration polystyrene samples.

5) The softening points were determined visually (using a conventional melting point apparatus) as the temperature at which the material became resinous.

The molecular weight distributions given in Fig. 2 and Table 2 show that, depending on the amount of halogen and the reaction conditions, a low and a high molecular weight fraction are formed. These fractions have been separated by precipitation from the DMF solution.

The volumes of the fractions precipitated with ethanol are considerably smaller than the calculated volumes of polymer with a molecular weight >2000, suggesting that fraction B has a high molecular weight, which is also seen from the GPC curves in Fig. 2.

The softening points for the two fractions of IIDMFs and IXDMFs, which were precipitated with ethanol and water, differed from each other and indicated that it is possible to prepare polymers with high molecular weights and thermal stabilities above 300 °C in this way.

Preliminary experiments show that 2,5-xylenol and p-xylene react in a similar way to the phenols above.

The oligomers, and also the polymeric products, can be acetylated and they also react with terephthaloylchloride forming cross-linked polyesters.

CONCLUSIONS

The results indicate that it is possible to prepare poly(hydroxiphenylene sulfide)s using chlorine or bromine as activating reagents in the reactions of sulfur with phenol, guaiacol and o-cresol. The increase in the DMF soluble fractions and thus in the higher molecular weight with time (compare syntheses I with II, and VII with VIII) and the formation of polymeric products by the gradual addition of halogen suggest that a step-wise reaction occurs. When bromine is used the main part of the reaction occurs already during the addition of bromine (syntheses III and IX).

The products obtained from phenol are linear and contain halosubstituents. With longer reaction times the formation of H_2S is increased when guaiacol and o-cresol are used as monomers. In the case of o-cresol the formation of H_2S is accompanied by an increase in DMF soluble products: this is explained by the formation of CH_2-S-CH_2 bonds and the simultaneous increase in the molecular weight.

For guaiacol the increase in the ethanol soluble fraction is explained by the formation of o-dihydroxibenzene units as a result of demethylation reactions.

The lower quantity of sulfur in the polymers prepared with chlorine is explained by the higher reaction temperature, which favors the cleavage of sulfur-sulfur bonds.

The rather high "softening points" of the DMF soluble fractions obtained on precipitation with ethanol show that there is potential for preparing thermostabile poly(hydroxiphenylene sulfide)s in this way. By optimizing the reaction conditions the amount of the high molecular weight fraction can apparently be increased.

The investigations into these reactions and products are being continued.

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