+ Cl) atomic ratio (2.45) (Table II) was very similar to that of *p*-polyphenyl, except for a broad band at 1585 cm.$^{-1}$.

3. **Solubility.**—The polymer is essentially insoluble in boiling ethanol, ether, chloroform, xylene, and *o*-dichlorobenzene; 0.35% dissolved in xylene, and 0.4% in chloroform. The soluble material consisted partly of tar.

4. **Pyrolysis.**—The thermal decomposition was carried out *in vacuo* as previously described.[3,4] Infrared, ultraviolet, and gas chromatographic analyses were used in the identification of biphenyl, m.p. 69–70°, m.m.p. 69–70°; *p*-terphenyl, m.p. 209–210°, m.m.p. 209–210°; and 4-chlorobiphenyl ($\lambda_{\max}^{\text{CHCl}_3}$ 256.5 mμ). *p*-Quaterphenyl melted at 304–305°, authentic material, m.p. 306–307°, m.m.p. 304–305°. The infrared and ultraviolet spectra ($\lambda_{\max}^{\text{CHCl}_3}$ 299 mμ) were identical with those of authentic *p*-quaterphenyl. *p*-Quinquephenyl was characterized by the infrared and ultraviolet spectra ($\lambda_{\max}^{\text{CHCl}_3}$ 309 mμ), and by m.p. 385–390°; authentic material, m.p. 382–386°; lit.[7] m.p. 395°. In addition, higher molecular weight sublimate was obtained whose infrared and ultraviolet spectra indicated a *p*-polyphenyl structure.

5. **Oxidation.**—An earlier procedure was followed.[4] Dimethyl terephthalate melted at 139–140°, m.m.p. with authentic material, 139–140°. The gas chromatogram and infrared spectrum indicated the absence of the 1,2- and 1,3-isomers in the unpurified dimethyl terephthalate. Dimethyl-4,4′-biphenyldicarboxylate was identified by the infrared spectrum and m.p. 210–212°; the mixture melting point with authentic ester was undepressed. The infrared spectrum, melting point (237°), and mixture melting point were used to characterize 4-chlorobenzoic acid.

6. **Thermal and Oxidative Stability.**—Three types of benzene polymer (1 g. each) were placed in porcelain vessels and heated for 30-min. periods at temperatures which were increased by 50° increments in the 350–600° range. The data obtained are shown in Table II.

***p*-Polyphenyl–Ferric Chloride.**—A mixture of *p*-polyphenyl[3] (4 g.), ferric chloride (81.1 g.), and an appropriate solvent was stirred at 80 ± 5°. Work-up was by the standard procedure. The data are summarized in Table III.

***p*-Polyphenyl–Benzene–Ferric Chloride.**—A mixture of *p*-polyphenyl[3] (4 g., C/H atomic ratio 1.47), ferric chloride (162.2 g.), and benzene (156.2 g.) was stirred at the reflux temperature under nitrogen. Precautions were taken (weighing in a dry box, dry apparatus, etc.) to minimize the water content of the system. The reaction mixture was worked up by the usual procedure. The results are shown in Table IV. Table V contains the data for control experiments carried out under the same conditions, but with no added *p*-polyphenyl.

Dehydrogenation of 1,4-cyclohexadiene with Ferric Chloride.—Ferric chloride (1.62 g.) was added in portions with shaking to 1,4-cyclohexadiene (2 g.) while the temperature was kept at 1–43° by cooling. The liquid was decanted and subjected to gas chromatographic analysis. Benzene was identified by retention time and infrared spectrum. Also present were additional products possessing higher retention times.

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Polycondensation of Mercaptobenzenediazonium Salts

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Both 4- and 3-mercaptobenzenediazonium salts have been polymerized under various conditions to give red, insoluble infusible solids containing sulfide and diazosulfide bonds in equal amounts. On heating to 150–250°, about 80% of the nitrogen was lost. In order to characterize further the diazosulfide bond, several new diazosulfides have been synthesized.

One of the most useful procedures for the preparation of alkyl aryl sulfides is the reaction of aryl diazonium salts with alkyl mercaptide ions. It has, however, been long known that aryl mercaptide ions react with aryl diazonium salts to give diazosulfides.[1,2]

$$\text{ArN}_2^{\oplus} \xrightarrow{\text{RS}^{\ominus}} \text{ArSR} + \text{N}_2$$

$$\xrightarrow{\text{Ar}'\text{S}^{\ominus}} \text{Ar}'\text{SN{=}NAr}$$

We wish to report here on an investigation of the polymerization of mercaptodiazonium salts, an extension of recent work on polymerization of diazooxides.[3]

When 3- or 4-mercaptoanilines were diazotized and then buffered to neutrality by sodium acetate, red-brown polymer was obtained in each case. The insoluble polymers were found to contain about half the original nitrogen of the diazonium salt. The reaction apparently corresponds to the following stoichiometry.

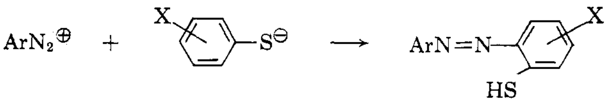
$$\underset{\substack{\text{I}\\(p\text{- and } m\text{-})}}{2n\ {}^{\ominus}\text{SC}_6\text{H}_4\text{N}_2{}^{\oplus}} \longrightarrow \underset{\text{II}}{\left(\text{SC}_6\text{H}_4\text{SN{=}NC}_6\text{H}_4\right)_n} + n\text{N}_2$$

The presence of the azo link is indicated by the color, by the infrared spectra bands at 1465 and 1580 cm.$^{-1}$ (diazosulfide), at 810 cm.$^{-1}$ (1,4-disubstituted benzene[4]) for *p*-II, and at 770 cm.$^{-1}$ (1,3-disubstituted benzene) for *m*-II, and by the substantial loss of nitrogen which occurred on heating at 150–250°.

$$\underset{p\text{-II}}{\left(\text{SC}_6\text{H}_4\right)\left(\text{SN}_2\text{C}_6\text{H}_4\right)} \xrightarrow{250^\circ} \underset{p\text{-III}}{\left(\text{SC}_6\text{H}_4\right)_5\left(\text{SN}_2\text{C}_6\text{H}_4\right)} + \text{N}_2$$

The resulting polymer (*p*-III) showed the characteristic infrared peaks of poly(*p*-phenylene sulfide).[5]

The insolubility of the polymers, a weak infrared band at 870 cm.$^{-1}$ (1,2,4-trisubstituted benzene) for *p*-II, and the failure to evolve all nitrogen on heating is consistent with some azo coupling on carbon.



Such coupling would produce the trifunctional centers necessary for insoluble cross-linked polymer.

Of the three possible structures from self-condensation, diazo coupling on sulfur, diazo coupling on carbon, and diazo displacement by sulfur, it thus appears that

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(1) A. Hantsch and H. Freese, *Ber.*, **28**, 3237 (1895).

(2) P. Jacobson, *ibid.*, **21**, 3104 (1888).

(3) J. K. Stille, P. Cassidy, and L. Plummer, *J. Am. Chem. Soc.*, **85**, 1318 (1963); T. Kunitake and C. C. Price, **85**, 761 *ibid.*, (1963).

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 64.

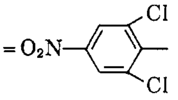
(5) S. Tsunawaki and C. C. Price, *J. Polymer Sci.*, in press.

all three are involved in the formation of the polymer. There remains the interesting question as to why the ratio of diazo coupling on sulfur and diazo displacement by sulfur proceed at a ratio so nearly equal to one.

Experiment indicated that three different diazonium salts couple with thiophenol to give the diazosulfide as the only isolated product, although in yields of only about 50%.

$$ArN_2^{\oplus} + C_6H_5S^{\ominus} \longrightarrow ArN{=}NSC_6H_5 \xrightarrow[\text{2. oxidation}]{\text{1. reduction}} C_6H_5SSC_6H_5$$

IV. Ar = p-$NO_2C_6H_4$—
V. Ar = p-$NO_2C_6H_4SC_6H_4$—

VI. Ar =


VII. Ar = p-$C_6H_5SC_6H_4$

In the case of VII, the diazosulfide was isolated only as an oil in 33% yield.

The data suggest to us that the diazo displacement reaction may be favored by electron-donating groups, a view proposed earlier from kinetic studies.[6] Thus dimerization of the initial zwitterion may occur by diazo displacement while subsequent reaction must then occur principally by coupling on sulfur.

$$2\ {}^{\ominus}SC_6H_4N_2^{\oplus} \longrightarrow [{}^{\ominus}SC_6H_4SC_6H_4N_2^{\oplus}) + N_2$$
$$\downarrow$$
$$\text{II}$$

Experimental

Polymerization of Sulfhydrylbenzene Diazonium Salts.—4-Aminothiophenol (3.13 g.) was diazotized, using 15 ml. of concentrated hydrochloric acid, 1.80 g. of sodium nitrite, 130 ml. of water, and 0.3 g. of urea. After neutralizing by addition of 30 ml. of 25% aqueous sodium acetate and 40 ml. of 4% aqueous sodium hydroxide, the mixture was stirred an additional 5 hr. and heated to 90°. The brown solid was collected by filtration, washed with hot water, and extracted with hot benzene. The red residue weighed 2.4 g. (82%), gradually darkened at 140°, but did not melt up to 300°. The infrared spectrum (KBr) showed absorptions at 670 (w), 810 (s), 870 (vw), 1000 (m), 1060 (m), 1080 (m), 1090 (w), 1160 (s), 1185 (m), 1230 (s), 1270 (w), 1290 (w), 1330 (w), 1380 (w), 1425 (m), 1465 (s), 1490 (m), 1580 (s), 1620 (w), and 3060 (w) cm.$^{-1}$. The residue did not dissolve in hot dimethylformamide, diphenyl ether, or nitrobenzene, although the solvents turned red.

Anal. Calcd. for C_6H_4SN: C, 58.98; H, 3.28; S, 26.24; N, 11.50. Found: C, 58.71; H, 3.82; S, 25.95; N, 11.51.

The red, benzene solution was concentrated and freeze dried to give 0.32 g. of red powder, m.p. 70–80°, mol. wt., 720. The infrared spectrum showed the same absorptions as that of the previous residue.

About 0.1 g. of the residue was heated in a vacuum sublimation flask with a finger type condenser at a fixed temperature for 1 hr. *in vacuo*. After heating at 250°, the residue was a red powder weighing 80.8% of the original weight.

Anal. Calcd. for $(C_6H_4S)_5\,(C_6H_4SN_2)$: C, 63.87; H, 3.58; S, 23.42; N, 4.13. Found: C, 64.56; H, 3.14; S, 27.93; N, 4.37.

After heating at 150°, the residue was also a red powder weighing 84.2% of the original weight.

Anal. Calcd. for $(C_6H_4S)_4\,(C_6H_4SN_2)$: C, 63.35; H, 3.57; S, 28.18; N, 4.90. Found: C, 63.80; H, 4.11; S, 27.43; N, 4.65.

The infrared spectra of these residues as potassium bromide disks were poorly resolved but showed absorption at 800, 1000, 1060, 1080, 1170, 1380, and 1460 cm.$^{-1}$, which were all observed in the spectra of poly(phenylene sulfide).[5]

3-Aminothiophenol (3.13 g.) was diazotized and polymerized by the same procedure as described in the previous experiment. The red residue weighed 1.8 g. (67%), gradually darkened above 120°, and softened at 250–290°. The infrared spectrum of this residue as a potassium bromide disk was poorly resolved but the characteristic absorption of 1,3-disubstituted benzenes was observed at 770 cm.$^{-1}$.

Anal. Calcd. for C_6H_4SN: C, 58.98; H, 3.78; S, 26.24; N, 11.50. Found: C, 58.83; H, 3.30; S, 26.19; N, 11.64.

The red extract was concentrated and freeze dried but gave only 0.01 g. of red paste.

Preparation of Diazosulfides. (a) **4-Nitrophenyldiazothiobenzene.**—4-Nitroaniline (13.8 g.) was diazotized, using 30 ml. of concentrated hydrochloric acid, 300 ml. of water, and 7.6 g. of sodium nitrite. After adding to a solution of 12.1 g. of thiophenol in 120 ml. of 5% sodium hydroxide, the yellow solid was collected by filtration and recrystallized twice from ethanol to give pink leaflets (12.2 g., 48%), m.p. 94–95° (lit.[1] m.p. 96–97°); $\lambda_{max}^{ethanol}$ (log ϵ); 223 mμ (4.00), 267 mμ (3.97), and 348 mμ (3.96).

Anal. Calcd. for $C_{12}H_9N_3O_2S$: C, 55.60; H, 3.49; S, 12.37; N, 16.20; mol. wt., 259.2. Found: C, 55.66; H, 3.73; S, 12.18; N, 15.89; mol. wt., 247.

The infrared spectrum (in KBr) showed peaks at 630 (w), 680 (s), 695 (w), 840 (vs), 860 (m), 975 (s), 1010 (w), 1060 (w), 1090 (m), 1100 (m), 1140 (w), 1305 (m), 1340 (vs), 1360 (w), 1390 (m), 1420 (s), 1430 (m), 1465 (m), 1510 (vs), 1575 (m), 1590 (m), and 3100 (w) cm.$^{-1}$.

Treating an alcoholic solution of the compound with sodium dithionate and then oxidizing with hydrogen peroxide gave a yellow solid which, after recrystallization from methanol, yielded white needles, m.p. 60–61°, undepressed on admixture with authentic diphenyl disulfide (m.p. 60–61°).

(b) **4-(4-Nitrophenylthio)phenyldiazothiobenzene,** m.p. 102° (dec.), was prepared in 49% (1.8 g.) yield, from 4-amino-4′-nitrodiphenyl sulfide (2.46 g.) by the same procedure as described.

Anal. Calcd. for $C_{18}H_{13}N_3O_2S_2$: C, 58.82; H, 3.57; N, 11.44; S, 17.46; mol. wt., 367.4. Found: C, 58.90; H, 3.62; N, 11.29; S, 17.41; mol. wt., 381.

The ultraviolet spectrum in ethanol solution showed λ_{max} (log ϵ) 213 (3.15), 238 (4.15) and 344 mμ (4.14). The infrared spectrum (in KBr) showed peaks at 685 (m), 700 (w), 740 (s), 760 (m), 830 (s), 845 (s), 1000 (m), 1020 (w), 1060 (w), 1075 (s), 1090 (w), 1110 (s), 1155 (w), 1170 (w), 1270 (w), 1330 (vs), 1360 (w), 1390 (w), 1420 (w), 1435 (m), 1470 (m), 1500 (s), 1570 (s), and 1585 (m) cm.$^{-1}$.

Reduction with sodium dithionate and then oxidation gave diphenyl disulfide.

(c) **4-Phenylthiophenyldiazothiobenzene,** a pink oil at 0°, mol. wt., 330 (theory 322.5), was prepared in 33% (5.2 g.) yield from 10.0 g. of 4-aminodiphenyl sulfide, keeping always under 0°. The ultraviolet spectrum in ethanol solution showed λ_{max} (log ϵ) 210 (4.47), 243 (4.42), and 354 mμ (4.25).

(d) **2,6-Dichloro-4-nitrophenyldiazothiobenzene.**—2,6-Dichloro-4-nitroaniline (2.07 g.) was diazotized, according to the procedure of Schoutissen[7] and added to a cold solution of thiophenol (1.2 g.) in 200 ml. of 4% aqueous sodium hydroxide. The mixture was extracted with cold ether. The ether was added to methanol and cooled in Dry Ice to give a yellow precipitate. After reprecipitating in the same way, recrystallization from ethanol gave pink needles (1.8 g., 55%), m.p. 75–76°.

Anal. Calcd. for $C_{12}H_7Cl_2N_3O_2S$: C, 43.93; H, 2.11; Cl, 21.61; N, 12.82; S, 9.77; mol. wt., 328.2. Found: C, 43.85; H, 2.12; Cl, 21.51; N, 12.70; S, 9.75; mol. wt., 330.

The ultraviolet spectrum in ethanol solution showed λ_{max} (log ϵ) 223 (4.10) and 317 mμ (3.91). The infrared spectrum (in KBr) had peaks at 680 (m), 695 (w), 705 (w), 735 (m), 740 (vw), 775 (s), 800 (m), 860 (w), 885 (m), 910 (m), 1015 (w), 1060 (m), 1140 (m), 1150 (m), 1180 (m), 1200 (m), 1270 (w), 1340 (vs), 1355 (w), 1380 (m), 1430 (m), 1440 (s), 1465 (m), 1500 (m), 1520 (s), 1570 (m), and 3090 (m) cm.$^{-1}$.

Treatment with sodium dithionate and then hydrogen peroxide also gave diphenyl disulfide.

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[6] M. L. Crossley, R. H. Kienle, and C. H. Benbrook, *J. Am. Chem. Soc.*, **62**, 1400 (1940).

[7] H. A. J. Schoutissen, *J. Am. Chem. Soc.*, **55**, 4531 (1933).