Polymerization of Benzene to *p*-Polyphenyl by Ferric Chloride[1]

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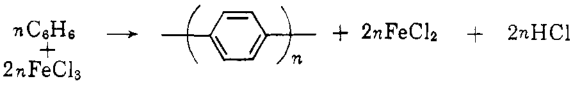
p-Polyphenyl containing a small amount of chlorine was prepared from benzene under mild conditions by treatment with ferric chloride. The polymer was identified by elemental analyses, infrared spectrum, X-ray diffraction pattern, pyrolysis products, and oxidative degradation. A minor amount of structural irregularity was indicated by the pyrolysis studies. The benzene–ferric chloride reaction also yielded a very small quantity of low molecular weight product composed mainly of chlorobenzene and 4,4′-dichlorobiphenyl. The oxidative cationic mechanism for the polymerization is supported by the finding that ferric chloride easily converts 1,4-cyclohexadiene to benzene. The initially formed *p*-polyphenyl is readily transformed during reaction to a polymer possessing a darker color and a higher C/(H + Cl) atomic ratio.

Recently it was shown that the aromatic nucleus can function as a monomer in polymerizations leading to homopolymers.[2] For example, benzene was transformed in a simple, one-step procedure to *p*-polyphenyl by treatment with either aluminum chloride–cupric chloride[2,3] or molybdenum pentachloride.[4] Except for the synthesis of impure *p*-polyphenyl from poly-1,3-cyclohexadiene,[5] previous attempts to prepare a highly homogeneous polyphenyl by classical methods have been unsuccessful. The pertinent literature has been summarized recently.[3,4]

We have found that when benzene is allowed to react with a 1:1 molar ratio of ferric chloride–water for very short periods at about 70°, *p*-polyphenyl which contains a small amount of chlorine is formed (Table I). Since hydrogen chloride and ferrous chloride are also generated, the reaction apparently proceeds as indicated.



The structure of the rust-colored product was derived primarily from elemental analyses, infrared spectrum, X-ray diffraction pattern, pyrolysis products, and oxidative degradation. The polymer possessed a C/(H + Cl) atomic ratio of 1.51, in good agreement with the limiting theoretical value of 1.5 for polyphenyl.

TABLE I

POLYMERS FROM BENZENE-FERRIC CHLORIDE-WATER

			Polymer				
H_2O/-$FeCl_3$, molar ratio	Time, min.	Temp., °C.	Yield, g.	% C	% H	% Cl	C/-(H + Cl), atomic ratio
1.0	0.5	70 ± 2	3.9	88.38	4.69	6.00	1.51
1.0[a]	120	70 ± 8	8.1	84.23	3.43	11.35	1.87
0.2[b]	120	80 ± 2	4.2	82.74	2.42	13.50	2.46

[a] See the standard procedure. [b] Ref. 11.

In the infrared spectrum, a strong band occurred at 807 cm.$^{-1}$ characteristic of *para*-substitution. Other absorption maxima were situated at 1001 cm.$^{-1}$ (*para*) and 1481 cm.$^{-1}$ (C=C skeletel in-plane vibrations). In addition, diffuse bands were detected at 767, 1095, and 1400 cm.$^{-1}$.

The X-ray diffraction pattern, which established the crystallinity of the polymer, gave *d*-spacings of 4.48, 3.82, 3.16, 7.96, and 2.07 Å., *in decreasing order of intensity.* These *d*-spacings correspond closely to the values reported for *p*-quaterphenyl: 4.49, 3.83, 2.04, 3.14, and 1.76 Å., in decreasing order of intensity.[4] The most intense *d*-spacing of 4.48 Å. corresponds to the distance of 4.5 Å. reported to be the length of a phenyl unit.[5,6] The X-ray data provide support for the thesis that the rings are essentially co-planar (as in the lower *p*-polyphenyls[6]) and that the structure is predominantly *para*.[5]

Pyrolysis of the polymer *in vacuo* at 750–800° gave a sublimate in addition to residual material resembling carbon black. The sublimed product contained biphenyl, low molecular weight *p*-polyphenyls including terphenyl, quaterphenyl, and quinquephenyl, in addition to uncharacterized higher molecular weight substances. Identification was accomplished by comparison of the melting points and the infrared and ultraviolet spectra with those of the authentic materials. Gas chromatographic analysis of the unpurified terphenyl revealed the presence of 10–15% of *m*-terphenyl. The *meta* isomer might arise from rearrangement[7,8] during pyrolysis, or from a small amount of irregular structure in the polymer, such as *meta*-linkages, polyphenyl branches or cross links. The occurrence of a minor amount of *p*-chlorobiphenyl in the sublimate provides information concerning the terminal structure of the chains.

Chromic acid oxidation of the polymer yielded terephthalic acid, 4,4′-biphenyldicarboxylic acid, *p*-chlorobenzoic acid, and unidentified acidic products. The dicarboxylic acids were characterized in the form of their dimethyl esters. It is reasonable to conclude that the terephthalic acid is derived from *p*-terphenyl units in the polymer chain, the 4,4′-biphenyldicarboxylic acid from *p*-quaterphenyl units, and the *p*-chlorobenzoic acid from end-group structures. The absence of isomeric benzenedicarboxylic acids was established by gas chromatographic and infrared analysis of the unpurified dimethyl terephthalate.

Attention was also given to the low molecular weight products formed in the reaction. The benzene

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[1] Paper IV in the series, Polymerization of Aromatic Nuclei; from the forthcoming Ph.D. thesis of F. W. Koch.

[2] P. Kovacic and A. Kyriakis, *Tetrahedron Letters*, 467 (1962).

[3] P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).

[4] P. Kovacic and R. M. Lange, *J. Org. Chem.*, **28**, 968 (1963).

[5] C. S. Marvel and G. E. Hartzell, *J. Am. Chem. Soc.*, **81**, 448 (1959).

[6] L. W. Pickett, *Proc. Royal Soc.* (London), **142A**, 333 (1933); *J. Am. Chem. Soc.*, **58**, 2299 (1936).

[7] E. H. Smith, Polyphenyls: Literature Search, U. S. Atomic Energy Commission, ER-8098, 1956.

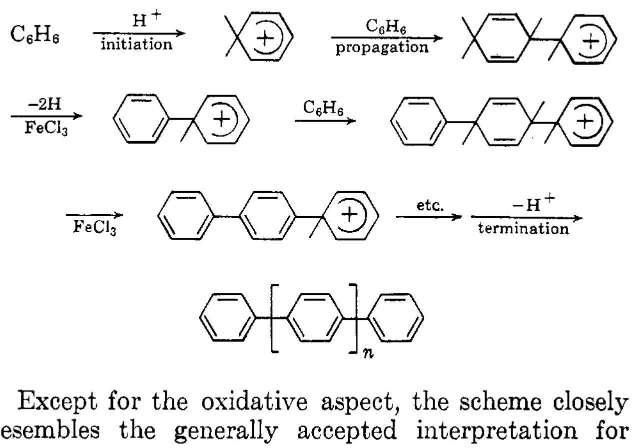
[8] L. Silverman, *et al.*, NAA-SR-1203, North American Aviation, Inc., 1955.

filtrate from the reaction mixture contained very small amounts of a gross mixture. In addition to chlorobenzene which was the major component, 4,4′-dichlorobiphenyl was isolated by gas chromatography, and its identity revealed by comparison with authentic material. The biphenyl derivative can be considered to represent the dimer stage of the polymerization. Since ferric chloride readily chlorinates aromatic compounds, the presence of the chlorine substituents is understandable.[9] Solvent extraction studies demonstrated the essential absence of low molecular weight extractable material in the polymer. Unfortunately, the high insolubility of the product prevents molecular weight determination by colligative or light scattering techniques. However, the position of the principal *para*-band and the absence of fine structure in the infrared spectrum indicate that the molecular weight is higher than that of the *p*-polyphenyl synthesized from poly-1,3-cyclohexadiene.[3,5]

The extreme insolubility and good thermal stability of the polymer are characteristic of *p*-polyphenyl.[3,5] After one-half hour in air at 450°, there was a weight loss of only 16%. In summary of the data relevant to the polymer configuration, the infrared and X-ray diffraction studies, pyrolysis products, and oxidative degradation point to a predominantly *para*-structure. However, thermal degradation also indicates a minor amount of irregularity, presumably branching or cross-linking. On the basis of the experimental evidence, one may conclude that the polymer obtained with ferric chloride is very similar to the *p*-polyphenyl synthesized by the cupric chloride–aluminum chloride[2,3] or the molybdenum pentachloride method.[4]

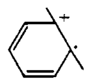
The concept of oxidative cationic polymerization provides a plausible interpretation of the reaction.

$$\mathrm{FeCl_3 + H_2O \rightleftharpoons H_2O \cdots > FeCl_3 \rightleftharpoons H^+FeCl_3(OH)^-}$$



Except for the oxidative aspect, the scheme closely resembles the generally accepted interpretation for olefin polymerization catalyzed by Lewis acids.[10] The necessity of a Brönsted acid cocatalyst in order for polymerization to occur has been demonstrated previously.[11] Presumably, ferric chloride functions both as the catalyst and oxidant. In order to test the hypothesis that cyclohexadiene units are converted to aromatic structures during the reaction, the dehydrogenation of 1,4-cyclohexadiene by ferric chloride was investigated. Reaction was found to occur readily with formation of benzene. The chlorine content of the polymer might arise from nuclear chlorination by ferric chloride or from chain termination by chloride.

Alternative hypotheses should also be considered. For example, one-electron reduction of ferric chloride could conceivably provide a radical–carbonium ion[12] (I) as the initiating species.



I

Unless the polymerization conditions are carefully controlled, a product is obtained possessing a darker color and a C/(H + Cl) atomic ratio greater than 1.5. Higher temperatures and increased reaction times favor the subsequent transformation which presumably involves the conversion of *p*-polyphenyl to a polymer containing polynuclear structures (Table I). The increase in the atomic ratio is accompanied by a corresponding rise in chlorine content. The close similarity of the infrared spectra for the polymers of varying C/(H + Cl) atomic ratio supports the contention that chlorinated polynuclear structures are present in the high ratio polymers. It is significant that the brown-black product is more susceptible to oxidative thermal degradation than is *p*-polyphenyl (Table II). The presence of polynuclear structures would be expected to darken the color and make the polymer more susceptible to oxidative and substitutive attack. Since the *p*-polyphenyl obtained with ferric chloride is darker in color and undergoes oxidative thermal degradation more readily than the product from aluminum chloride–cupric chloride,[3] it very likely contains a minor amount of polynuclear structure. The possible presence of trace amounts of metal catalyst complicates rationalization of the data on oxidative thermal stability.

Table II

Thermal and Oxidative Stability of Benzene Polymers

Temp., °C.	Wt. loss, % Polyphenyl[a]	 Chlorinated *p*-polyphenyl[b]	 Polynuclear polymer[c]
350	0.49	0.35	2.08
400	0.99	0.94	4.88
450	16.15	2.70	56.89
500	55.50	15.55	95.59
550	97.0	73.0	...
600	100	99.9	...

[a] C, 88.38%; H, 4.69%; Cl, 6.00%; C/(H + Cl), atomic ratio 1.51. [b] C, 72.40%; H, 3.54%; Cl, 23.60%; C/(H + Cl), atomic ratio 1.47. [c] C, 75.05%; H, 1.96%; Cl, 20.15%; C/(H + Cl), atomic ratio 2.45; from C_6H_6 (2 moles)–$FeCl_3$ (1 mole) at reflux for 28 hr.

Several interpretations come to mind relative to the subsequent transformation: (1) the direct linking of individual *p*-polyphenyl chains, and (2) a reaction of the polymer with benzene–ferric chloride leading to polynuclear structures. Item 1 appears unlikely since attempts to cross link *p*-polyphenyl by treatment with ferric chloride in liquid media were unsuccessful. Although there was a drastic rise in chlorine content due to chlorination by ferric chloride, the C/(H + Cl) ratio did not increase (Table III).

(9) P. Kovacic, C. Wu, and R. W. Stewart, *J. Am. Chem. Soc.*, **82**, 1917 (1960); P. Kovacic and N. O. Brace, *ibid.*, **76**, 5491 (1954).

(10) See ref. 3 for leading references.

(11) P. Kovacic and C. Wu, *J. Polymer Sci.*, **47**, 45 (1960).

(12) W. Aalbersberg, J. Gaaf, and E. L. Mackor, *J. Chem. Soc.*, 905 (1961).

TABLE III

p-POLYPHENYL–FERRIC CHLORIDE

Solvent	G.	*p*-Polyphenyl, C/H atomic ratio	$H_2O/FeCl_3$, molar	Time, hr.	Polymer product Yield, g.	% C	H	Cl	C/(H + Cl), atomic ratio
n-C_8H_{18}	114	1.42	0	9	6.3	79.31	4.88	9.86	1.28
n-C_8H_{18}	114	1.42	0.5	9	4.8	73.29	3.74	18.55	1.43
o-$C_6H_4Cl_2$	147	1.50	0.5	6	4.8	72.40	3.54	23.60	1.45
o-$C_6H_4Cl_2$	147	1.50	0	9	4.8	79.19	4.00	15.59	1.48
H_3PO_4 (85%) + P_2O_5	115 + 27.4	1.53	. . .	9	4.9	85.02	4.89	7.60	1.40
$SnCl_4$	260	1.53	0	14	5.4	75.10	4.00	18.69	1.38

Furthermore, there is positive evidence in support of the second interpretation. *p*-Polyphenyl was allowed to react with benzene and ferric chloride under conditions whereby benzene undergoes only a minute amount of polymerization (Tables IV and V). A significant increase both in weight and C/(H + Cl) ratio resulted.

TABLE IV

p-POLYPHENYL–BENZENE–FERRIC CHLORIDE REACTION

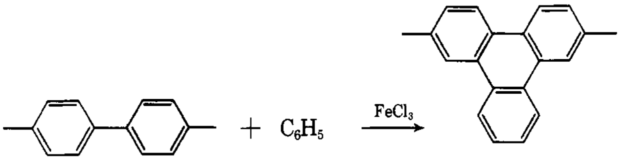
Time, hr.	Product Yield, g.	% C	H	Cl	C/-(H + Cl), atomic ratio
2	5.9	84.05	3.58	11.58	1.79
4	6.1	84.30	3.92	10.62	1.66

TABLE V

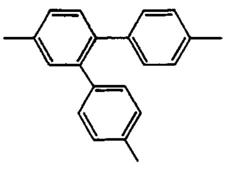
BENZENE–FERRIC CHLORIDE REACTION

Time, hr.	Product Yield, g.	% C	H	Cl	C/-(H + Cl), atomic ratio
2	0.14	85.08	3.89	8.78	1.72
4	0.20	78.74	2.92	11.74	2.02

The polynuclear synthesis may take place as illustrated.



Alternatively, protonation of the polymer could well produce sites capable of initiating polymerization.



II

The *o*-terphenyl units might then be converted subsequently to polynuclear regions by intramolecular dehydrogenation. The initially formed fused ring system could conceivably facilitate further reaction. The problem of polynuclear formation is undergoing further investigation.

Experimental[13]

Materials.—The following reagent grade chemicals were used: benzene, thiophene free, Mallinckrodt Chemical Works, dried over sodium and distilled; anhydrous ferric chloride, sublimed powder, Matheson Coleman and Bell, or Fisher Scientific Co.; biphenyl, *o*-, *m*-, and *p*-terphenyl, 4-chlorobiphenyl, terephthalic acid, and *p*-chlorobenzoic acid, Eastman Kodak Co.; *p*-quaterphenyl, K and K; 4,4′-biphenyldicarboxylic acid, Aldrich Chemical Co.; 4,4′-dichlorobiphenyl, Matheson Coleman and Bell; *n*-octane, 99 mole %, Phillips Petroleum Co., dried over sodium and distilled; *o*-dichlorobenzene, distilled from lithium hydride.

Apparatus.—Beckman DK-2 ultraviolet spectrophotometer (chloroform or cyclohexane); Beckman IR-7 or Perkin-Elmer Model 237 infrared spectrophotometer (carbon disulfide or 0.25–0.5% in potassium bromide); F and M Model 500 gas chromatograph, 6 ft., 20% silicone rubber on Chromosorb W, or 12 ft., 15% silicone rubber on Chromosorb W, or 20 ft., 15% silicone grease on Chromosorb W; X-ray diffraction apparatus, copper Kα radiation (λ 1.539 Å.).

***p*-Polyphenyl from Benzene–Ferric Chloride. 1. General Procedure.**—Water (1 mole) was added dropwise with stirring under nitrogen at 10–25° to a mixture of benzene (2 moles) and ferric chloride (1 mole). The reaction mixture was heated during 20 min. to 70 ± 3°; whereupon hydrogen chloride was rapidly evolved and the contents darkened. After 30 sec., the mixture was quickly cooled and filtered. The residue was washed with benzene and then triturated repeatedly with boiling concentrated hydrochloric acid until the filtrate was colorless. After the polymer was treated with hot 2 *M* sodium hydroxide, the acid triturations were repeated. The red-brown solid was washed thoroughly with distilled water, and dried at 140–150° for 2 hr. Precautions were taken to avoid contamination.

2. **Low Molecular Weight Products.**—The initial benzene filtrate from four reactions was washed with 3 *N* hydrochloric acid until the aqueous layer was colorless and then with water until the washings were neutral to litmus. After distillation of benzene from the dried organic layer, fractionation with an "Ace Minilab Apparatus" gave chlorobenzene, b.p. 125–131°, 3.5 g. The viscous liquid, 0.5 g., which remained was examined by gas chromatography and found to consist of a gross mixture. The major component, isolated by gas chromatography, was 4,4′-dichlorobiphenyl, m.p. 140–144°.[14] The infrared and ultraviolet spectra were essentially identical with those of the authentic material, m.p. 145–146°.

3. **Analysis for Ferrous Chloride.**—A mixture of benzene (2 moles), ferric chloride (1 mole), and water (1 mole) was allowed to react for 30 min. (see the general procedure). After filtration under nitrogen, the residue was stirred with 300 ml. of 3 *N* hydrochloric acid and filtered. The solid was subsequently heated with about 400 ml. of 6 *N* hydrochloric acid, and filtered. The original organic filtrate was extracted with two 50-ml. portions of 3 *N* hydrochloric acid. Dilution of the combined aqueous extracts to a volume of 1 l. was effected. Aliquots were titrated potentiometrically with 0.1 *N* ceric ammonium nitrate standardized with ferrous sulfate (Beckman pH meter, saturated calomel reference, and platinum indicator electrode). Ferrous ion was found to be present in the combined extract to the extent of 0.33 mole.

Characterization of *p*-Polyphenyl. 1. X-Ray Diffraction Pattern.—*d*-Spacing of 4.48, 3.82, 3.16, 7.96, and 2.07 Å in decreasing order of intensity, were obtained.[15]

2. **Infrared Spectrum.**—Absorption maxima were present at 767 (broad), 807, 1003, 1095, 1400 (broad), and 1481 cm.$^{-1}$. The infrared spectrum of the polymer possessing a high C/(H

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[13] Melting points and boiling points are uncorrected. Elemental analyses were performed by Drs. Weiler and Strauss, Oxford, England.

[14] We wish to thank C. E. Stephan for the isolation and characterization of this compound.

[15] We are grateful to R. M. Lange for obtaining these data and to C. S. Smith for the use of the X-ray equipment.

+ 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 ($\lambda_{max}^{CHCl_3}$ 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 ($\lambda_{max}^{CHCl_3}$ 299 mμ) were identical with those of authentic *p*-quaterphenyl. *p*-Quinquephenyl was characterized by the infrared and ultraviolet spectra ($\lambda_{max}^{CHCl_3}$ 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]

$$\mathrm{ArN_2^{\oplus}} \xrightarrow{\mathrm{RS^{\ominus}}} \mathrm{ArSR} + \mathrm{N_2}$$
$$\qquad \xrightarrow{\mathrm{Ar'S^{\ominus}}} \mathrm{Ar'SN{=}NAr}$$

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.

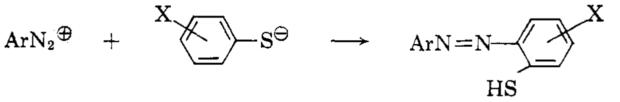
$$\underset{\substack{\mathrm{I} \\ (p\text{- and } m\text{-})}}{2n\ {}^{\ominus}\mathrm{SC_6H_4N_2}^{\oplus}} \longrightarrow \underset{\mathrm{II}}{-\!\!(\mathrm{SC_6H_4SN{=}NC_6H_4})\!\!-_n} + n\mathrm{N_2}$$

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°.

$$\underset{p\text{-II}}{-\!(\mathrm{SC_6H_4})\!-\!(\mathrm{SN_2C_6H_4})\!-} \xrightarrow{250^\circ} \underset{p\text{-III}}{-\!(\mathrm{SC_6H_4})\!-_5\!(\mathrm{SN_2C_6H_4})\!-} + \mathrm{N_2}$$

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.