

2. **Isomer Distributions. Haloanisoles.**—The bromo- and chloroanisole isomer distributions were obtained by glpc analysis (glpc column 1 at 168°, and 8, respectively). Because of interfering products in the anisole-boron trichloride-peroxide experiment, glpc column 1 at 145° was used. Known mixtures of the various isomeric haloanisoles were prepared. A plot was made

of the peak area ratio *vs.* the concentration ratio, and the data from the various product mixtures were compared with this plot.

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## Synthesis and Properties of *p*-Polyphenyl Derivatives<sup>1</sup>

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Various derivatives of *p*-polyphenyl were prepared by chlorination (antimony pentachloride or chlorine-aluminum chloride), bromination (bromine-aluminum bromide), sulfonation (sulfuric acid), nitration (mixed acid or nitronium tetrafluoroborate), and reduction (lithium-ethylenediamine). Attempts were made to isomerize the polymer with promoted Lewis acid catalysts. Nitro-*p*-polyphenyl was converted to its amino counterpart on treatment with hydrazine-diethylene glycol or tin-hydrochloric acid. According to thermogravimetric analysis, stability of the derivatives fell in the order: chlorinated > (*p*-polyphenyl) > brominated > "isomerized" > amino > nitro. Except for the nitrated *p*-polyphenyl, none of the products exhibited appreciable solubility in boiling *o*-dichlorobenzene.

The aromatic nucleus has been shown to function as a monomer in polymerizations yielding homopolymer. For example, benzene was converted to *p*-polyphenyl in Lewis acid catalyst-oxidant systems such as, ferric chloride,<sup>2</sup> molybdenum pentachloride,<sup>3</sup> or aluminum chloride-cupric chloride.<sup>4,5</sup> As a result, appreciable quantities of this polymer can now be readily obtained by a simple procedure from inexpensive starting materials.<sup>5,6</sup>

Our principal objective in the present study was to investigate the chemical behavior of *p*-polyphenyl. More specifically, we wished to prepare a variety of derivatives and ascertain their properties. Several closely related studies have been reported involving sulfonation,<sup>7,8</sup> subsequent caustic fusion,<sup>8</sup> and finally, cross-linking of the phenolic derivative with formaldehyde.<sup>8</sup> Wherever possible in the discussion, the chemical character of *p*-polyphenyl will be compared with that of the individual, lower benzhomologs described in the prior literature.

### Results and Discussion

**Halogenation.**—Various conditions were effective for halogenation of *p*-polyphenyl. With excess antimony pentachloride at 70–115°, about 50% chlorination was achieved. Almost complete replacement of hydrogen was attained upon reaction with chlorine gas in stannic chloride with aluminum chloride as catalyst. Strong absorption maxima in the infrared spectra of the chlorinated derivatives were present at 1330 and 735 cm<sup>-1</sup>. Carbon-chlorine stretching is known<sup>9</sup> to produce bands in the 750–700-cm<sup>-1</sup> region. In addition, a weaker band was situated at 1065 cm<sup>-1</sup>. Varying degrees of halogenation were observed during preparation

of *p*-polyphenyl in Lewis acid catalyst-oxidant systems.<sup>2–5,10,11</sup> In addition, antimony pentachloride was employed in another study for introduction of chlorine (one halogen per one to six rings).<sup>12</sup> Chlorination of biphenyl has received considerable attention since before the turn of the century. The literature on monohalogenation has been summarized.<sup>13,14</sup> Complete replacement<sup>15,16</sup> can be accomplished with chlorine gas and a Lewis acid catalyst or with antimony pentachloride.

In the presence of aluminum bromide, substitution in the polymer by bromine occurred with ease to yield a product which contained an average of about three halogen atoms per monomer unit. The infrared spectrum in the 625–4000-cm<sup>-1</sup> region was quite simple, exhibiting bands of appreciable strength only at 1020, 1305, and 1330 (sh) cm<sup>-1</sup>. In the presence of a Friedel-Crafts catalyst, polybromination of biphenyl can be effected with formation of octa- and decabromobiphenyls.<sup>17</sup>

**Sulfonation.**—Treatment of *p*-polyphenyl with concentrated sulfuric acid at 264° for 20 hr produced sulfonation of about 60% of the aromatic units. The indicated absorption frequencies were noted in the infrared spectrum: 765, 820–880, 1000–1070, 1170, 1300, 1375, 1600, 1710, 3050, and 3500 cm<sup>-1</sup>. It is conceivable that the product contains some water of hydration.

Marvel and co-workers<sup>7,8</sup> found that sulfonation could be realized with chlorosulfonic acid, fuming sulfuric acid, or concentrated sulfuric acid. Depending on time and temperature, their extent of reaction varied from one sulfur per ring to one for each six rings.

(1) Paper XI, Polymerization of Aromatic Nuclei, taken in part from the undergraduate thesis of V. J. M., 1964.  
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 (14) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishing Co., New York, N. Y., 1965.  
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 (17) H. Hahn, German Patent 1,136,683 (1962); *Chem. Abstr.*, **59**, 1530 (1963).

Infrared analysis revealed characteristic absorption bands at 3500, 1320, and 1040  $\text{cm}^{-1}$ . It is highly significant that, at the higher degrees of substitution, the polymers were soluble in acetone-water or ethanol-water. The observed solubility, coupled with earlier evidence,<sup>2-4</sup> convincingly refutes the contention<sup>18</sup> that *p*-polyphenyl formed from benzene is probably highly cross-linked. Since even the very low molecular weight *p*-polyphenyls, *e.g.*, *p*-sexiphenyl, show marked solvent resistance, the property of insolubility cannot be used as a criterion of cross-linking with this polymer class.

Attention should be directed to the studies of Van Allan<sup>19</sup> on reaction of lower members in the *p*-polyphenyl series with oleum or chlorosulfonic acid. In addition to sulfonation in the open *para* positions of *p*-terphenyl and *p*-quaterphenyl, dibenzothiophene-5,5-dioxide structures were formed. Therefore, it is reasonable to surmise that sulfonated polyphenyl may contain some sulfone bridging units of this type.

**Nitration.**—*p*-Polyphenyl underwent nitration by mixed acid under quite mild conditions. Introduction of essentially one nitro group per nucleus was indicated by the increase in weight. Since the nitro group is deactivating, distribution of the substituents is most likely quite uniform. In the infrared spectrum strong absorption bands characteristic of nitroaromatics<sup>9</sup> were situated at 1340 and 1520  $\text{cm}^{-1}$ . The peaks at 830 and 900  $\text{cm}^{-1}$  are indicative of 1,2,4 substitution.<sup>9</sup> Analysis revealed the presence of a small amount of sulfur, probably as part of sulfonic acid groups, in addition to the expected elements. The nitrogen value, 9.75% was in rather good agreement with theory, 10.4%, based on weight increase and taking into account the sulfonic acid functionalities. Furthermore, the C/N atomic ratio of 6.5 corresponded reasonably well to the theoretical value of 6.

Nitration of the polymer also proceeded smoothly with nitronium tetrafluoroborate in sulfolane. The results in relation to yield and nature of the product, *e.g.*, infrared spectrum, were very similar to those described for the mixed acid system. In this case no sulfur was present in the nitro-*p*-polyphenyl. The high degree of specificity associated with nitration is illustrated by the lack of appreciable attack when fuming nitric acid in acetic anhydride was used.

Biphenyl has been nitrated with nitric acid under a variety of conditions, in water, acetic acid, acetic anhydride, and sulfuric acid.<sup>13,14</sup> *p*-Terphenyl was investigated to a lesser extent.<sup>13,14</sup> In many of these cases the *ortho/para* ratio was reported to be quite high. There may well be some correlation between the *ortho/para* ratio in biphenyl and ease of the corresponding reaction with the polymer (essentially all positions hindered).

**Amino-*p*-polyphenyl.**—The reagent of choice for reduction of the nitrated polymer consisted of hydrazine hydrate in diethylene glycol. From weight loss incurred during reaction, 94–101% conversion of nitro to amino groups was indicated. In the infrared spectrum the most pronounced absorption was evident at 805, 1390, 1470, and 1600 with a minor band at 3380  $\text{cm}^{-1}$ . Reference to the literature<sup>9</sup> reveals that the

NH<sub>2</sub> internal deformation mode occurs at 1590–1650 and the external one in the 650–900- $\text{cm}^{-1}$  region. All of the principal maxima characteristic of the precursor were absent with the exception of that at 1520  $\text{cm}^{-1}$  which had so diminished in intensity as to become a shoulder. Elemental analysis furnished the value of 15.0% for nitrogen in comparison with the theoretical figure of 15.4%. Oxygen was also found to be present to the extent of about 7%. This observation can be rationalized in several possible ways: incomplete reduction (nitro or azoxy groups), and the incorporation of various functionalities (sulfonic acid, carboxy, or quinone) in side reactions during nitration.

Several other reducing systems were also found to be effective, namely, tin-hydrochloric acid and stannous chloride-hydrochloric acid. The infrared spectra of the products were very similar to that of the material obtained with hydrazine. However, these alternative routes were examined less thoroughly since the product was somewhat soluble in acid solution. Unsatisfactory results were observed from the indicated combinations: iron powder-sulfuric acid, iron powder-hydrochloric acid, hydrazine hydrate-ethanol,<sup>20</sup> and hydrazine hydrate-diethylene glycol-potassium hydroxide.<sup>21</sup>

**Reduction.**—On treatment of *p*-polyphenyl with excess lithium metal in ethylene diamine, a reduced product was obtained which possessed a C/H atomic ratio (0.69) very near to the theoretical value of 0.60 for the completely saturated derivative. This is equivalent to an average of nine hydrogens per ring. Under less severe conditions and with other systems (lithium-methylamine, sodium-*t*-butyl alcohol, and calcium-ammonia), higher C/H ratios were observed. The reduced product possessed strong new bands in the infrared spectrum at 2915 and 2860 (CH<sub>2</sub> stretching frequencies)<sup>9</sup> and at 1445  $\text{cm}^{-1}$  (CH<sub>2</sub> deformations).<sup>9</sup> There was broad, weak absorption at 990  $\text{cm}^{-1}$  which is characteristic of the cyclohexane structure,<sup>9</sup> and also at 895  $\text{cm}^{-1}$ . Furthermore, the bands normally present in *p*-polyphenyl were absent or drastically diminished in intensity. However, even with the almost completely saturated products the principal *para* peak, though greatly reduced in intensity, remained unshifted at 805  $\text{cm}^{-1}$ . Thus one can conclude that the reduction does not occur in a random manner, since the position of the main absorption in *p*-polyphenyls changes with alteration in chain length.<sup>4,12</sup> There is the possibility that some olefinic residues may be present. The reduced polymer demonstrated unexpectedly low solubility, possibly due to the occurrence of some cross-linking during reaction.

Aromatic hydrocarbons are known to undergo complete reduction with lithium in low molecular weight amines.<sup>2, 23</sup> For example, benzene yielded cyclohexane, and bicyclohexyl was obtained from biphenyl.<sup>22</sup> Drastic conditions must be used, otherwise, monoolefins comprise the principal products.<sup>22</sup>

**Attempted Isomerization.**—Studies were carried out with the aim of isomerizing *p*-polyphenyl by appro-

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appropriate exposure to Lewis acid catalysts. We observed that rather severe conditions were required to appreciably alter the structure of the polymer, e.g., treatment with molten aluminum bromide above 140°, or with an aluminum chloride–sodium chloride melt at 200–220° for 3 hr with water or hydrogen chloride cocatalyst. Appearance of absorption bands at 790 and 870 cm<sup>-1</sup> suggested the presence of *m*-phenylene linkages.<sup>9</sup> New absorption maxima were also located at 1700 and 1580 cm<sup>-1</sup>. Alternatively some of the observed changes might well result from nuclear coupling arising from a Scholl reaction.<sup>24</sup> Direct cross-linking could conceivably lead to polynuclear structures. The coupling hypothesis is consistent with several lines of evidence, namely a change in color<sup>2</sup> from brown to black, and an increase in the C/(H + Cl) ratio<sup>2</sup> from 1.49 to 1.6–1.8.

Associated with the transformation is a decrease in strength of the *para* band at 805 cm<sup>-1</sup>. A question arises concerning the significance of the enhanced absorption in the 755-cm<sup>-1</sup> region, since a monosubstitution peak also occurs in this vicinity. However, it is unlikely that an increase in end groups by chain cleavage is responsible since there is only very weak absorbance at 700 cm<sup>-1</sup> which is the approximate position regarded as specific for monosubstitution.<sup>9</sup>

Recently, Wynberg and Wolf<sup>25</sup> showed that, in the presence of promoted aluminum chloride, diphenyl-1,1'-<sup>14</sup>C undergoes random distribution of the <sup>14</sup>C. On this basis, they expressed doubt concerning the validity of our *p*-polyphenyl structural assignment. The present isomerization studies, coupled with ample previous evidence,<sup>2-4</sup> strongly support the contention that the benzene polymer possesses essentially an all-*para* configuration. It should be pointed out that interchain forces of appreciable magnitude must be overcome in the conversion of a *para* unit to the *meta* form in *p*-polyphenyl. Because of the energy barriers to isomerization associated with the long-chain structure, the greater reluctance to rearrangement *vis-a-vis* the lower members is quite understandable. Furthermore, the high insolubility of the polymer may be an important contributing factor. In other related work, rearrangement<sup>26,27</sup> of the terphenyls with promoted aluminum chloride resulted in an equilibrium mixture<sup>28</sup> of *m*- (63%) and *p*-terphenyl (37%). The mechanistic aspects of this type of rearrangement have been discussed by previous investigators.<sup>25,29,30</sup>

**Attempted Reactions.**—Attempts to acylate or alkylate *p*-polyphenyl met uniformly with failure. Reagents which were investigated under Friedel-Crafts conditions included acetyl chloride, ethyl bromide, isopropyl bromide, *t*-butyl chloride, and 2,4-dichlorobenzyl chloride. In addition, no substitution was detected with the indicated reagents: mercuric oxide–perchloric acid, mercuric acetate–acetic acid, and phosphorus trichloride–aluminum chloride.

**Thermal Stability and Solubility of *p*-Polyphenyl Derivatives.**—The outstanding resistance of aromatic polymers to thermal degradation is well known. Previous studies<sup>2</sup> have shown that *p*-polyphenyl does not deteriorate appreciably in air at temperatures below 525°. Thermogravimetry was used to obtain data on the thermal stability in air for the various derivatives. The results, reported as the temperature corresponding to 90% weight retention, are summarized in Table I.

TABLE I  
SOLUBILITY AND THERMAL STABILITY OF  
*p*-POLYPHENYL DERIVATIVES

<i>p</i> -Polyphenyl derivative	—Source— Table entry	3	Solubility in <i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> , %	TGA, temp, 90% wt retention, °C
Chlorinated ( <i>p</i> -Polyphenyl)	I <i>a</i>	...	6 0.6	605 570
Chlorinated	I	1	...	550
Brominated	<i>a</i>	...	8	525
"Isomerized"	VI	7	12	510
Amino	IV	3	8 <sup>b</sup>	445
Nitro	II	4	20–30 <sup>c</sup>	380

<sup>a</sup> See Experimental Section. <sup>b</sup> 8% soluble in boiling methanol–hydrochloric acid (50:50). <sup>c</sup> 18% soluble in boiling methanol; some decomposition may be taking place in *o*-dichlorobenzene.

With the exception of nitro-*p*-polyphenyl, the polymers were relatively resistant to breakdown. The order of stability is chlorinated > (*p*-polyphenyl) > brominated > "isomerized" > amino > nitro. Under an inert atmosphere, serious degradation of *p*-polyphenyl occurred only when temperatures in the vicinity of 700° were attained.<sup>31</sup> In thermogravimetry<sup>31</sup> under nitrogen, the benzene polymer was found superior to polyphenyl prepared by other methods, namely *via* poly-1,3-cyclohexadiene or the Wurtz reaction on *m*-dibromobenzene.

Except for the nitrated *p*-polyphenyl, none of the derivatives exhibited appreciable solubility in boiling *o*-dichlorobenzene. The amino-*p*-polyphenyl dissolved only to a limited extent in methanol–hydrochloric acid.

### Experimental Section<sup>32</sup>

**Instrumental Analyses.**—The infrared spectra were obtained by the potassium bromide pellet technique with a Beckman IR-8 spectrophotometer. A Standard automatic thermo recording balance was used for the thermogravimetric analyses ( $\Delta T$ , 6°/min).<sup>33</sup>

***p*-Polyphenyl.**—The standard procedure<sup>4,5</sup> was followed: C<sub>6</sub>H<sub>6</sub>/AlCl<sub>3</sub>/CuCl<sub>2</sub> = 8/2/1 (*M*) at 31–32° for 2 hr. Elemental analysis gave 91.45% carbon, 5.08% hydrogen, and 1.67% chlorine; C/(H + Cl) = 1.49 (atomic ratio).

**Chlorination. 1. With Chlorine–Aluminum Chloride.**—Chlorine gas was passed with stirring during 2.5 hr at 50–70° into a mixture of the polymer (5 g), aluminum chloride (13.4 g), and stannic chloride (100 ml). An exothermic reaction was noted. The product, after purification by triturating with concentrated

(31) Mr. R. Farmer, private communication, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, Attn. ASRCN-12.

(32) Oxygen analyses were carried out by Geller Laboratories, Charleston, W. Va. Except as indicated, others were performed by Drs. Weiler and Strauss, Oxford, England, or Galbraith Laboratories, Knoxville, Tenn. We are grateful to F & M Scientific Corp. for analysis of nitro-*p*-polyphenyl with the Model 185 analyzer. In general, the total of the elemental analyses fell a few per cent short of 100%. Since the polymers cannot be purified by standard techniques, small amounts of impurities, e.g., inorganic materials, may be present. Also, in some cases minor quantities of extraneous functionalities of unknown nature may constitute part of the structure.

(33) We wish to thank Mr. Gregory J. Kubas for analysis of the brominated polymer.

(24) A. T. Balaban and C. D. Nenitzescu, "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 23.

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hydrochloric acid, washing with water, and drying under vacuum at 110–120°, was obtained as a brown powder, darker than polyphenyl, wt 13.6 g. The calculated C/(H + Cl) atomic ratio was 1.55.

*Anal.* Found: C, 35.0; H, 0.13; Cl, 62.2.

2. **With Antimony Pentachloride.**—Antimony pentachloride (0.4 mole) was used as the chlorinating agent for *p*-polyphenyl (5.3 g) during 5 hr at 70° with agitation. The work-up is described in the preceding section, wt 11.2 g; the calculated C/(H + Cl), atomic ratio was 1.56.

*Anal.* Found: C, 42.2; H, 0.7; Cl, 54.7.

**Bromination.**—Bromine (20 ml, 0.39 mole) was added at room temperature to a well-stirred mixture of *p*-polyphenyl (5 g), anhydrous aluminum bromide (13 g), and stannic chloride (100 ml) during about 1 hr. After 2 hr at 50–55°, the reaction mixture was cooled and worked up as in the case of chlorination. This derivative was in the form of a brown powder, wt 20.1 g, darker than polyphenyl. A value of 1.48 was calculated for the C/(H + Br) atomic ratio.

*Anal.* Found: C, 23.3; H, 0.43; Br, 70.1.

**Sulfonation.**—The procedure of Marvel and co-workers<sup>7,8</sup> was used. A mixture of *p*-polyphenyl (0.07 mole) and concentrated sulfuric acid (2.48 moles) was stirred under nitrogen at 264° for 20 hr. After addition of the mixture to ice, the liquid was decanted. The filtered solid was washed with 25 ml of water and then dried at 120°, wt 5.7 g of dark solid.

*Anal.* Found: C, 50.3; H, 2.9; S, 16.0.

**Nitration.** 1. **With Mixed Acid.**—A mixture of nitric acid (22.7 ml, *d*, 1.42) and concentrated sulfuric acid (58 ml) was added with stirring during 1 hr at 5–10° to a mixture of *p*-polyphenyl (5.3 g), concentrated sulfuric acid (100 ml), and water (20 ml). The reaction mixture was then maintained at 5–10° for 2.5 hr and 41° for 4 hr. Modifications of this procedure were occasionally made. The contents were then stirred with ice and filtered. After the dark solid was washed to neutrality with distilled water, drying was effected at 120° under vacuum, wt 8.5–9 g (100–106% of theory for one nitro per ring).

*Anal.* Found: C, 54.0; H, 2.28; N, 9.75; O, 32.66; S, 0.81.

In contrast to the parent hydrocarbon, the dark brown product burned readily in a flame.

2. **With Nitronium Tetrafluoroborate.**<sup>34</sup>—To the *p*-polyphenyl (1.6 g) suspended in 50 ml of sulfolane, 125 ml of 0.5 *M* nitronium tetrafluoroborate (0.0625 mole) in sulfolane was added dropwise. After being heated for 1 hr at 70–75°, the reaction mixture was poured over ice. The resulting product was worked up as described in the preceding section, wt 2.73 g (107% of theory for one nitro per ring).

**Reduction of Nitro-*p*-polyphenyl.** 1. **With Hydrazine-Diethylene Glycol.**—A mixture of nitro-*p*-polyphenyl (4.27 g), hydrazine (11.2 g), water (2 g), and diethylene glycol (106 g) was heated at 115–211° with stirring for 48 hr. In another ex-

periment reduction was carried out for 11 hr at 92–238°. The reaction mixture was then cooled, diluted with water, and filtered. After repeated washing with water, the polymer (dark brown) was dried at 100–110° under vacuum, wt 3.15 g (101%).

*Anal.* Found: C, 70.52; H, 4.76; N, 15.0; O, 7.36.

2. **With Tin and Hydrochloric Acid.**—Granulated<sup>35</sup> (20 mesh) tin (0.15 mole) was added to a mixture of nitrated *p*-polyphenyl (8.6 g) and concentrated hydrochloric acid (200 ml) at the reflux temperature. More tin (0.3 mole) was introduced in portions during an additional 3 hr at reflux. After filtration, the solid was exposed to boiling caustic solution, filtered, washed with water, and dried under vacuum at 50°, wt 6.2 g (104%).

**Reduction of *p*-Polyphenyl with Lithium in Ethylenediamine.**—Lithium (1.4 moles total) was added slowly during 2–3 hr on each of three successive days (2 days at 30–35°, 1 day at 50–55°) to a stirred mixture of *p*-polyphenyl (4 g) and ethylenediamine (2.1 moles) under nitrogen. After reaction was complete, anhydrous ammonium chloride was added, followed by careful mixing with ice–hydrochloric acid. The product was washed with water and dried at 110° under vacuum, wt 4.25 g, light gray color. The calculated C/(H + Cl) atomic ratio was 0.69.

*Anal.* Found: C, 85.42; H, 10.26; Cl, 0.78.

**Attempted Isomerization.**—A mixture of *p*-polyphenyl (4 g), aluminum bromide (0.5 mole), and water (0.18 g) was blanketed with nitrogen and then stirred for 2 hr at 210–220° while hydrogen bromide was introduced. Work-up of the cooled mixture involved treatment with cold dilute hydrochloric acid, steam distillation, and then the standard triturations. The product was a dark purple brown; C/(H + Cl + Br) = 1.72 and C/(H + Br + O) = 1.6 assuming the presence of dibenzofuran structures (calculated atomic ratios).

*Anal.* Found: C, 89.85; H, 4.31; Cl, 1.0; Br, 0.5; O, 2.6.

The indicated results were obtained from a similar reaction at 140–160° for 4 hr; C/(H + Cl + Br) = 1.78 and C/(H + Cl + Br + O) = 1.58 assuming the presence of dibenzofuran structures (calculated atomic ratios).

*Anal.* Found: C, 88.06; H, 4.06; Br, 0.3; Cl, 1.5; O, 4.1.

Little or no change in the polymer was noted under the indicated conditions: aluminum chloride or bromide in benzene with water or hydrogen halide cocatalyst at 72–77° for 12 hr; aluminum chloride–antimony trichloride with water–hydrogen chloride cocatalyst at 200–220° for 4 hr.

**Solubility.**—After exposure of the polymer (0.5 g) to boiling *o*-dichlorobenzene (50 ml) for 4 hr, the mixture was filtered hot. The solubility data are recorded in Table I. In all cases, when this procedure was repeated on the insoluble fraction less than 2% went into solution. In three control runs involving *p*-polyphenyl and water, 0.9–1.8% of the polymer was lost during handling.

**Acknowledgment.**—We gratefully acknowledge support provided by the National Science Foundation.

(34) Prepared according to procedure c of S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961).

(35) Mossy tin appeared to be less effective.